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molybdenum for the manufacture of special tool steels. It is available in a number of oxide forms as well as the d⁺⁻⁻ⁱⁱⁱⁱⁱde. Molybdic acid is used in a number of chemical ap⁺, ,ations and in make-up of glazes for ceramics.

Molybdenum has not been considered as a serious pollutant, but it is a biologically active metal. It may be an important element insofar as protection of the ecosystem is concerned because of its role in algal physiology. Certain species of algae can concentrate molybdenum by a factor up to 15 (Lackey 1959).[210] Bioassay tests in fresh water on the fathead minnow gave a 96-hour LC50 for molybdic anhydride (MoO_3) of 70 mg/l in soft water and 370 mg/l in hard water. Although molybdenum is essential for the growth of the alga *Scenedesmus*, the threshold concentration for a deleterious effect is 54 mg/l. Molybdenum concentration factors for marine species have been reported as: 8 in benthic algae; 26 in zooplankton; 60 in soft parts of molluscs; 10 in crustacean muscles; and 10 in fish muscle (Lowman et al. 1971).[221]

Recommendation

The panel recommends that the concentration of molybdenum in sea water not exceed 0.05 of the 96-hour LC50 at any time for the most sensitive species in sea water, and that the 24-hour average not exceed 0.02 of the 96-hour LC50.

Nickel

᠁el does not occur naturally in elemental form. It is present as a constituent in many ores, minerals and soils, particularly in serpentine-rock-derived soils.

Nickel is comparatively inert and is used in corrosion-resistant materials, long-lived batteries, electrical contacts, spark plugs, and electrodes. Nickel is used as a catalyst in hydrogenation of oils and other organic substances. Its salts are used for dyes in ceramic, fabric, and ink manufacturing. Nickel may enter waters from mine wastes, electroplating plants, and from atmospheric emissions.

Nickel ions are toxic, particularly to plant life, and may exhibit synergism when present with other metallic ions. Nickel salts in combination with a cyanide salt form moderately toxic cyanide complexes which, as nickel sulfate combined with sodium cyanide, gave a 48-hour LC50 of 2.5 mg/l and a 96-hour LC50 of 0.95 mg/l as CN^-, using fathead minnows (*Pimephales promelas*) at 20 C (Doudoroff 1956).[148] Alkaline conditions reduced toxicity of a nickel cyanide complex considerably, with concentrations below 100 mg/l showing no apparent toxic effect on fish.

Nickel salts can substantially inhibit the biochemical oxidation of sewage (Malaney et al. 1959).[223] In fresh waters, nickel has been reported to be less toxic to fish and river crabs than zinc, copper, and iron (Podubsky and Stedronsky 1948).[248] However, other investigators found ni᠁ to be more toxic to fish than iron and manganese (Doudoroff and Katz 1953).[150]

Ellis (1937)[156] reported that nickelous chloride from electroplating wastes did not kill goldfish (*Carassius auratus*) at 10 mg/l during a 200-hour exposure in very soft water. Wood (1964)[304] reported that 12 mg/l of nickel ion kill fish in 1 day and 0.8 mg/l kill fish in 10 days. Doudoroff and Katz (1953)[150] reported survival of stickleback (*Gesterosteus aculeatus*) for 1 week in 1 mg/l of nickel as $Ni(NO_3)_2$.

The lethal limit of nickel to sticklebacks has been reported as 0.8 mg/l (Murdock 1953)[254] and 1.0 mg/l (Jones 1939).[198] The median lethal concentration of nickel chloride ($NiCl_2,6H_2O$) was reported as 4.8 mg l for guppies (*Becilia reticulata*) (Shaw and Lowrance 1956).[262] Goldfish (*Carassius auratus*) were killed by nickel chloride at 4.5 mg/l as nickel in 200 hours (Rudolfs et al. 1953).[256] Tarzwell and Henderson (1960)[278] reported 96-hour LC50's for fathead minnows (*Pimephales promelas*) as 4.0 mg/l in soft water and 24 mg/l in hard water, expressed as $NiCl_2,6H_2O$. Anderson (1948)[112] reported a threshold concentration of nickel chloride for immobilization of *Daphnia* in Lake Erie water at 25 C to be less than 0.7 mg/l in 64 hours of exposure. Bringmann and Kuhn (1959a,[131] 1959b[132]) reported nickel chloride threshold concentrations as nickel of 1.5 mg/l for *Scenedesmus*, 0.1 mg/l for *Escherichia coli*, and 0.05 mg/l for *Microregma*.

Nickel is present in sea water at 5 to 7 µg/l, in marine plants at up to 3 mg/l, and in marine animals at about 0.4 mg/l.

Marine toxicity data for nickel are limited. The top minnow *Fundulus* was found to survive in concentrations of 100 mg/l Nickel from the chloride in salt water, although the same species was killed by 8.1 mg/l of the salt (3.7 mg/l Ni) in tap water (Thomas cited by Doudoroff and Katz 1953).[150] Long-term studies on oysters (Haydu *unpublished data*)[314] showed substantial mortality at a nickel concentration of 0.12 mg/l. Calabrese et al. (*unpublished data*)[310] found 1.54 mg/l of nickel to be the LC50 for eggs of the oyster (*Crassostrea virginica*).

Recommendation

It is recommended that an application factor of 0.02 be applied to 96-hour LC50 data on the most sensitive marine species to be protected. Although limited data are available on the marine environment, it is suggested that concentrations of nickel in excess of 0.1 mg/l would pose a hazard to marine organisms, and 0.002 mg/l should pose minimal risk.

Phosphorus

Phosphorus as phosphate is one of the major nutrients required for algal nutrition. In this form it is not normally toxic to aquatic organisms or to man. Phosphate in large quantities in natural waters, particularly in fresh waters, can lead to nuisance algal growths and to eutrophication. This is particularly true if there is a sufficient amount of nitrate or other nitrogen compounds to supplement the

phosphate. Thus, there is a need for control of phosphate input into marine waters. See Sewage and Nutrients, p. 275, for a discussion of the effects of phosphate as a nutrient.

Phosphorus in the elemental form is particularly toxic and subject to bioaccumulation in much the same way as mercury (Ackman et al. 1970,[104] Fletcher 1971[162]). Isom (1960) [188] reported an LC50 of 0.105 mg/l at 48 hours and 0.025 mg/l at 163 hours for bluegill sunfish (*Lepomis macrochirus*) exposed to yellow phosphorus in distilled water at 26 C and pH 7.

Phosphorus poisoning of fish occurred on the coast of Newfoundland in 1969 and demonstrated what can happen when the form of an element entering the sea is unknown or at least not properly recognized (Idler 1969,[185] Jangaard 1970,[191] Mann and Sprague 1970[224]). The elemental phosphorus was released in colloidal form and remained in suspension (Addison and Ackman 1970).[105] After the release of phosphorus was initiated, red herrings began to appear. The red discoloration was caused by haemolysis, typical of phosphorus poisoning in herring (*Clupea harengus*), and elemental phosphorus was found in herring, among other fishes, collected 15 miles away (Idler 1969,[185] Jangaard 1970[191]).

Fish will concentrate phosphorus from water containing as little as one μg/l (Idler 1969).[185] In one set of experiments, a cod swimming in water containing one μg/l elemental phosphorus for 18 hours was sacrificed and the tissues analyzed. The white muscle contained about 50 μg/kg, the brown, fat tissue about 150 μg/kg, and the liver 25,000 μg/l (Idler 1969,[185] Jangaard 1970[191]). The experimental findings showed that phosphorus is quite stable in the fish tissues. Fish with concentrated phosphorus in their tissues could swim for considerable distances before succumbing. In addition to the red surface discoloration in herring, other diagnostic features of phosphorus poisoning included green discoloration of the liver and a breakdown of the epithelial lining of the lamellae of the gill (Idler 1969).[185]

A school of herring came into the harbor one and one-half months after the phosphorus plant had been closed down. These herring spawned on the wharf and rocks near the effluent pipe, and many of them turned red and died. A few days later, "red" herring were caught at the mouth of the harbor on their way out. The herring picked up phosphorus from the bottom sediments which contained high concentrations near the effluent pipeline (Ackman et al. 1970).[104] Subsequently, this area was dredged by suction pipeline, and the mud was pumped to settling and treatment ponds. No further instances of red herring were reported after the dredging operation, and the water was comparatively free of elemental phosphorus (Addison et al. 1971).[106]

Reports of red cod caught in the Placentia Bay area were investigated, and it was found that no phosphorus was present in the cod tissues. Surveys of various fishing areas in Newfoundland established that red cod are no more prevalent in Placentia Bay than in other areas. In laboratory studies, cod exposed to elemental phosphorus have not shown the red discoloration observed in herring and salmonids. However, cod do concentrate phosphorus in muscle tissue as well as in the liver and can eventually succumb to phosphorus poisoning (Dyer et al. 1970).[154]

It was demonstrated by field investigations and laboratory experiments (Ackman et al. 1970,[104] Fletcher et al. 1970,[163] Li et al. 1970,[216] Zitko et al. 1970,[309] Fletcher 1971[162]) that elemental phosphorus accounted for the fish mortalities in Placentia Bay. This is not to say that other pollutants, such as fluorides, cyanides, and ammonia, were not present (Idler 1969).[185]

The conclusion was reached by the scientists working on the problem that elemental phosphorus in concentrations so low that they would be barely within the limits of detection are capable of being concentrated by fish. Further work is needed on the effects of very low concentrations of phosphorus on fish over extended periods. Discharge of elemental phosphorus into the sea is not recommended.

Recommendation

It is recommended that an application factor of 0.01 be applied to marine 96-hour LC50 data for the appropriate organisms most sensitive to elemental phosphorus. On the basis of data available at this time it is suggested that concentrations of elemental phosphorus equal to or exceeding 1 μg/l constitute a hazard to the marine environment

Selenium

Selenium has been regarded as one of the dangerous chemicals reaching the aquatic environment. Selenium occurs naturally in certain pasture areas. Toxicity of selenium is sometimes counteracted by the addition of arsenic which acts as an antagonist. Selenium occurs in nature chiefly in combination with heavy metals. It exists in several forms including amorphous, colloidal, crystalline, and grey. Each physical state has different characteristics, soluble in one form, but insoluble in another. The crystalline and grey forms conduct electricity, and the conductivity is increased by light. This property makes the element suitable for photoelectric cells and other photometry uses. Selenium is also used in the manufacture of ruby glass, in wireless telegraphy and photography, in vulcanizing rubber, in insecticidal preparations, and in flameproofing electric cables. The amorphous form is used as a catalyst in determination of nitrogen and for dehydrogenation of organic compounds.

Ellis (1937)[156] showed that goldfish (*Carassius auratus*) could survive for 98 to 144 hours in soft water of pH ranging from 6.4 to 7.3 at 10 mg/l sodium selenite. Other data (ORSANCO 1950)[243] showed that 2.0 mg/l of selenium administered as sodium selenite was toxic in 8 days, affec appetite and equilibrium, and lethal in 18 to 46 d

More work is required to test for effects of selenium compounds under different conditions. Daphnia exhibited a threshold effect at 2.5 mg/l of selenium in a 48-hour exposure at 23 C (Bringmann and Kuhn 1959a).[131] Barnhart 1958)[118] reported that mortalities of fish stocked in a Colorado reservoir were caused by selenium leached from bottom deposits, passed through the food chain, and accumulated to lethal concentrations by the fish in their liver.

Recommendation

In view of the possibility that selenium may be passed through the food chain and accumulated in fish, it is recommended that an application factor of 0.01 be applied to marine 96-hour LC50 data for the appropriate organisms most sensitive to selenium. On the basis of data available at this time, it is suggested that concentrations of selenium equal to or exceeding 0.01 mg/l constitute a hazard in the marine environment, and levels less than 0.005 mg/l present minimal risk of deleterious effects.

Silver

Silver is one of the more commercially important metals; 4,938 tons were consumed in the U.S. during 1968, excluding that used for monetary purposes (U.S. Department of the Interior, Bureau of Mines 1969).[289] It is the best known conductor of heat and electricity. Although not oxidized by air, silver is readily affected by hydrogen sulfide to form the black silver sulfide.

Silver has many uses. In addition to making currency, it is used for photographic purposes, for various chemical purposes, and also in jewelry making and in silverplating of cutlery.

Silver is toxic to aquatic animals. Concentrations of 400 ug/l killed 90 per cent of test barnacles (*Balanus balanoides*) in 48 hours (Clarke 1947).[140] Concentrations of silver nitrate from 10 to 100 μg/l caused abnormal or inhibited development of eggs of *Paracentrotus* and concentrations of 2 μg/l of silver nitrate delayed development and caused deformation of the resulting plutei (Soyer 1963).[266] Adverse effects occurred at concentrations below 0.25 μg/l of silver nitrate, and several days were required to eliminate adverse effects by placing organisms in clean water (Soyer 1963).[266] Silver nitrate effects on development of *Arbacia* have been reported at approximately 0.5 μg/l (Soyer 1963,[266] Wilber 1969[299]). In combination with silver, copper acts additively on the development of *Paracentrotus* eggs (Soyer 1963).[266] On a comparative basis on studies on Echinoderm eggs (Soyer 1963),[266] silver has been found to be about 80 times as toxic as zinc, 20 times as toxic as copper, and 10 times as toxic as mercury.

Calabrese et al. (*unpublished manuscript*)[310] noted an LC50 of 5 mg/l silver for eggs of the American oyster (*Crassostrea virginica*). Jones (1948)[200] reported that the lethal concentration limit of silver, applied as silver nitrate, for sticklebacks (*Gasterosteus aculeatus*) at 15 to 18 C was 0.003 mg/l, which was confirmed approximately by Anderson (1948),[112] who found 0.0048 mg/l to be the toxic threshold for sticklebacks. Jackim et al. (1970)[190] reported adverse effects on the liver enzymes of the killifish *Fundulus heteroclitus* at 0.04 mg/l of silver.

The sublethal responses to silver compounds may be great, in view of the effects on developing eggs; and further research should be conducted on effects of sublethal concentrations of silver compounds by themselves and in combination with other chemicals. The disruption of normal embryology or of nutrition could be of much greater importance than direct mortality in the perpetuation of the species.

Concentrations of silver cannot exceed that permitted by the low solubility product of silver chloride. However, silver complexes may be present, and their effects are unknown.

Recommendation

It is recommended that the concentrations of silver in marine waters not exceed 0.05 of the 96-hour LC50 for the appropriate species most sensitive to silver. On the basis of data available at this time, it is suggested that concentrations of silver equal to or exceeding 5 μg/l constitute a hazard to the marine environment, and levels less than 1 μg/l present minimal risk of deleterious effects.

Sulfides

Sulfides in the form of hydrogen sulfide have the odor of rotten eggs and are quite toxic. Hydrogen sulfide is soluble in water to the extent of 4000 mg/l at 20 C and 1 atmosphere. Sulfides are produced as a by-product in tanneries, chemical plants, and petroleum refineries, and are used in pulp mills, chemical precipitation, and in chemical production. Hydrogen sulfide is produced in natural decomposition processes and in anaerobic digestion of sewage and industrial wastes. Sulfate in sea water is reduced to sulfide in the absence of oxygen. In the presence of certain sulfur-utilizing bacteria, sulfides can be oxidized to colloidal sulfur. At the normal pH and oxidation-reduction potential of aerated sea water, sulfides quickly oxidize to sulfates.

Hydrogen sulfide dissociates into its constituent ions in two equilibrium stages, which are dependent on pH (McKee and Wolf 1963).[226]

The toxicity of sulfides to fish increases as the pH is lowered because of the HS^- or H_2S molecule (Southgate 1948).[265] Inorganic sulfides are fatal to sensitive species such as trout at concentrations of 0.05 to 1.0 mg/l, even in neutral and somewhat alkaline solutions (Doudoroff 1957).[149] Hydrogen sulfide generated from bottom deposits was reported to be lethal to oysters (de Oliveira 1924).[145]

Bioassays with species of Pacific salmon (*Oncorhynchus*

tshawytscha, O. kisutch) and sea-run trout (*Salmo clarkii clarkii*) showed toxicity of hydrogen sulfide at 1.0 mg/l and survival without injury at 0.3 mg/l (Van Horn et al. 1949,[291] Dimick 1952,[147] Haydu et al. 1952,[179] Murdock 1953,[234] Van Horn 1959[290]). Holland et al. (1960)[182] reported that 1 mg/l of sulfide caused loss of equilibrium in 2 hours, first kills in 3 hours, and 100 per cent mortality in 72 hours with Pacific salmon.

Hydrogen sulfide in bottom sediments can affect the maintenance of benthic invertebrate populations (Thiede et al. 1969).[280] The eggs and juvenile stages of most aquatic organisms appear to be more sensitive to sulfides than do the adults. Adelman and Smith (1970)[107] noted that hydrogen sulfide concentrations of 0.063 and 0.020 mg/l killed northern pike (*Esox lucius*) eggs and fry, respectively; and at 0.018 and 0.006 mg/l, respectively, reduced survival, increased anatomical malformations, or decreased length were reported.

Recommendation

It is recommended that an application factor of 0.1 be applied to marine 96-hour LC50 for the appropriate organisms most sensitive to sulfide. On the basis of data available at this time, it is suggested that concentrations of sulfide equal to or exceeding 0.01 mg/l constitute a hazard in the marine environment, and levels less than 0.005 mg/l present minimal risk of deleterious effects, with the pH maintained within a range of 6.5 to 8.5.

Thallium

Thallium salts are used as poison for rats and other rodents and are cumulative poisons. They are also used for dyes, pigments in fireworks, optical glass, and as a depilatory.

Thallium forms alloys with other metals and readily amalgamates with mercury. It is used in a wide variety of compounds. Nehring (1963)[238] reported that thallium ions were toxic to fishes and aquatic invertebrates. The response of fishes to thallium poisoning is similar to that of man, an elevation in blood pressure. In both the fish and invertebrates, thallium appears to act as a neuro-poison (Wilber 1969).[299]

Adverse effects of thallium nitrate have been reported for rainbow trout (*Salmo gairdneri*) at levels of 10 to 15 mg/l; for perch (*Perca fluviatilis*) at levels of 60 mg/l; for roach (*Rutilus rutilis*) at levels of 40 to 60 mg/l; for water flea (*Daphnia* sp.) at levels of 2 to 4 mg/l; and for *Gammarus* sp. at levels of 4 mg/l. The damage was shown within three days for the various aquatic organisms tested. Damage also resulted if the fish were exposed to much lower concentrations for longer periods of time (Wilber 1969).[299]

Recommendation

Because of a chronic effect of long-term exposure of fish to thallium, tests should be conducted for at least 20 days on sensitive species. Techniques should measure circulatory disturbances (blood pressure) and other sublethal effects in order to determine harmful concentrations. The concentration in sea water should not exceed 0.05 of this concentration. On the basis of data available at this time, it is suggested that concentrations of thallium equal to or exceeding 0.1 mg/l constitute a hazard in the marine environment, and levels less than 0.05 mg/l present minimal risk of deleterious effects.

Uranium

Uranium is present in wastes from uranium mines and nuclear fuel processing plants, and the uranyl ion may naturally occur in drainage waters from uranium-bearing ore deposits. Small amounts may also arise from its use in tracer work, chemical processes, photography, painting and glazing porcelain, coloring glass, and in the hard steel of high tensile strength used for gun barrels.

Many of the salts of uranium are soluble in water, and it is present at about 3 μg/l in sea water. A significant proportion of the uranium in sea water is in the form of stable complexes with anionic constituents. It has been estimated that uranium has a residence time of 3×10^6 years in the oceans (Goldberg et al. 1971),[172] a span that makes it one of the elements with the slowest turnover time. Uranium is stabilized by hydrolysis which tends to protect it against chemical and physical interaction and thus vents its removal from sea water. The salts are considered to be 4 times as germicidal as phenol to aquatic organisms.

Natural uranium (U-238) is concentrated from water by the algae *Ochromonas* by a factor of 330 in 48 hours (Morgan 1961).[232] Using River Havel water, Bringmann and Kuhn (1959a,[131] 1959b[132]) determined the threshold effect of uranyl nitrate, expressed as uranium, at 28 mg/l on a protozoan (*Microregma*), 1.7 to 2.2 mg/l on *Escherichia Coli*, 22 mg/l on the alga *Scenedesmus*, and 13 mg/l on *Daphnia*. Tarzwell and Henderson (1956)[277] found the sulfate, nitrate, and acetate salts of uranium considerably more toxic to fathead minnows (*Pimephales promelas*) on 96-hour exposure in soft water than in hard water, the 96-hr LC50 for uranyl sulfate being 2.8 mg/l in soft water and 135 mg/l in hard water.

The sparse data for uranium toxicity in sea water suggest that uranyl salts are less toxic to marine organisms than to freshwater organisms. Yeasts in the Black Sea were found to be more active than the bacteria in taking up uranium (Pshenin 1960).[251] Studies by Koenuma (1956)[205] showed that the formation of the fertilization membrane of *Urechis* eggs was inhibited by 250 mg/l of uranyl nitrate in sea water, and that this concentration led to polyspermy.

Recommendation

It is recommended that an application factor 0.01 be applied to marine 96-hour LC50 data

he appropriate organisms most sensitive to uranium. On the basis of data available at this ir '+ is suggested that concentrations of uranium ·il :o or exceeding 0.5 mg/l constitute a hazard .i the marine environment, and levels less than .1 mg/l present minimal risk of deleterious effects.

Vanadium

Vanadium occurs in various minerals, such as chileite nd vanadinite. It is used in the manufacture of vanadium .eei. Vanadates were used at one time to a small extent or medicinal purposes. Vanadium has been concentrated iy certain marine organisms during the formation of oil-icaring strata in geological time. Consequently, vanadium nters the atmosphere through the combustion of fossil uels, particularly oil. In addition, eighteen compounds ot anadium are used widely in commercial processes (Council in Environmental Quality 1971).[144]

Recommendation

It is recommended that the concentration of vanadium in sea water not exceed 0.05 of the 96-hour LC50 for the most sensitive species.

Zinc

Most of the available information on zinc toxicity is for freshwater organisms, and for this reason the reader is refe d to the discussion of zinc in Section III, p. 182.

Recommendation

Because of the bioaccumulation of zinc through the food web, with high concentrations occurring particularly in the invertebrates, it is recommended that an application factor of 0.01 be applied to marine 96-hour LC50 data for the appropriate organisms most sensitive to zinc. On the basis of data available at this time, it is suggested that concentrations of zinc equal to or exceeding 0.1 mg/l constitute a hazard in the marine environment, and levels less than 0.02 mg/l present minimal risk of deleterious effects.

It should be noted that there is a synergistic effect when zinc is present with other heavy metals, e.g., Cu and Cd, in which case the application factor may have to be lowered by an order of magnitude (LaRoche 1972).[211]

OIL IN THE MARINE ENVIRONMENT

Oil is becoming one of the most widespread contaminants of the ocean. Blumer (1969)[319] has estimated that between ' and 10 million metric tons of oil may be entering the oceans from all sources. Most of this influx takes place in co regions, but oil slicks and tar balls have also been obse .ed on the high seas (Horn et al. 1970,[334] Morris

1971[343]). Collections of tar balls were made by towing a neuston net which skims the surface, and the investigators found that the tar balls were more abundant than the normal sargassum weed in the open Atlantic, and that their nets quickly became so coated with tar and oil that they were unusable. Thus, oil pollution of the sea has become a global problem of great, even though as yet inadequately assessed, significance to the fisheries of the world.

Sources of Oil Pollution

Although accidental oil spills are spectacular events and attract the most public attention, they constitute only about 10 per cent of the total amount of oil entering the marine environment. The other 90 per cent originates from the normal operation of oil-carrying tankers, other ships, offshore production, refinery operations, and the disposal of oil-waste materials (Table IV-4).

Two sources of oil contamination of the sea not listed in Table IV-4 are the seepage of oil from underwater oil reservoirs through natural causes and the transport of oil in the atmosphere from which it precipitates to the surface of the sea. Natural seepage is probably small compared to the direct input to the ocean (Blumer 1972);[320] but the atmospheric transport, which includes hydrocarbons that have evaporated or been emitted by engines after incomplete combustion, may be greater than the direct input.

Some of these sources of oil pollution can be controlled more rigorously than others, but without application of adequate controls wherever possible the amount of petroleum hydrocarbons entering the sea will increase. Our technology is based upon an expanding use of petroleum; and the production of oil from submarine reservoirs and the use of the sea to transport oil will both increase. It is estimated that the world production of crude oil in 1969 was nearly 2 billion tons; on this basis total losses to the sea are somewhat over 0.1 per cent of world production.

TABLE IV-4—*Estimated Direct Petroleum Hydrocarbon Losses to the Marine Environment (Airborne Hydrocarbons Deposited on the Sea Surface are Not Included)* (Millions of tons)

	1969	1975 (estimate)[a]		1980 (estimate)	
		Min	Max	Min	Max
1. Tankers	.530	.056	.805	.075	1.062
2. Other ships	.500	.705	.705	.940	.940
3. Offshore production	.100	.160	.320	.230	.460
4. Refinery operations	.300	.200	.450	.440	.650
5. Oil wastes	.550	.825	.825	1.200	1.200
6. Accidental spills	.200	.300	.300	.440	.400
TOTAL	2.180	2.246	3.405	3.325	4.752
Total Crude Oil Production	1820	2700		4000	

[a] The minimum estimates assume full use of known technology; the maximums assume continuation of present practices.
Revelle et al. 1972[245].

Some losses in the exploitation, transportation, and use of a natural resource are inevitable; but if this loss ratio cannot be radically improved, the oil pollution of the ocean will increase as our utilization increases.

Biological Effects of Petroleum Hydrocarbons

Description of Oil Pollution Oil is a mixture of many compounds, and there are conflicting views concerning its toxicity to marine organisms. Crude oils may contain thousands of compounds, and will differ markedly in their composition and in such physical properties as specific gravity, viscosity, and boiling-point distribution. The hydrocarbons in oil cover a wide range of molecular weights from 16 (methane) to over 20,000. Structurally, they include aliphatic compounds with straight and branched chains, olefins, and the aromatic ring compounds. Crude oils differ mainly in the relative concentrations of the individual members of these series of compounds. The various refinery processes to which oil is subjected are designed to isolate specific parts of the broad spectrum of crude oil compounds, but the refined products themselves remain complex mixtures of many types of hydrocarbons.

In spite of the many differences among them, crude oils and their refined products all contain compounds that are toxic to species of marine organisms. When released to the marine environment, these compounds react differently. Some are soluble in the water; others evaporate from the sea surface, form extensive oil slicks, or settle to the bottom if sand becomes incorporated in the oil globule. More complete understanding of toxicity and the ecological effects of oil spills will require studies of the effects of individual components, or at least of classes of components, of the complex mixture that made up the original oil. The recent development of gas chromatography has made it possible to isolate and identify various fractions of oil and to follow their entry into the marine system and their transfer from organism to organism.

An oil slick on the sea surface can be visually detected by iridescence or color, the first trace of which is formed when 100 gallons of oil spread over 1 square mile (146 liters/km[2]) (American Petroleum Institute 1949).[317] The average thickness of such a film is 0.145 microns. Under ideal laboratory conditions, a film 0.038 microns thick can be detected visually (American Petroleum Institute 1963).[318] For remote sensing purposes, oil films with a thickness of 100 microns can be detected using dual polarized radiometers, 1 micron using radar imagery, and 0.1 microns using multispectral imagery in the UV region (Catoe and Orthlieb 1971).[323] A summary of remote sensing capabilities is presented in Table IV-5. Because remote sensing is less effective than the eye in detecting surface oil, any concentration of oil detectable by remote means currently available will exceed the recommendations given below.

The death of marine birds from oiling is one of the earliest and most obvious effects of oil slicks on the sea surface.

Thousands of seabirds of all varieties are often involved in a large spill. Even when the birds are cleaned, they frequently die because the toxic oil is ingested in preenir their feathers. Dead oiled birds are often found along t, coast when no known major oil spill has occurred, and the cause of death remains unknown.

When an oil spill occurs near shore or an oil slick is brought to the intertidal zone and beaches, extensive mortality of marine organisms occurs. When the Tampico Maru ran aground off Baja California in 1957, about 60,000 barrels of spilled diesel fuel caused widespread death among lobsters, abalones, sea urchins, starfish, mussels, clams, and hosts of smaller forms (North 1967).[344] A beneficial side effect of this accident was also noted by North. When the sea urchins that grazed on the economically important kelp beds of the area were killed in massive numbers by the oil spill, huge canopies of kelp returned within a few months (see p. 237). The oil spills from the wreck of the tanker Torrey Canyon and the Santa Barbara oil well blowout both involved crude oil, and in both cases oil reached the beaches in variable amounts some time after release. The oil may thus have been diluted and modified by evaporation or sinking before it reached the beach. In the Santa Barbara spill many birds died, and entire plant and animal communities in the intertidal zone were killed by a layer of encrusting oil often 1 or 2 centimeters thick (Holmes 1967).[333] At locations where the oil film was not so obvious, intertidal organisms were not severely damaged (Foster et al. 1970).[327] In the case of the Tor Canyon, the deleterious effects have been attributed more to the detergents and dispersants used to control the oil than to the oil itself (Smith 1968).[347]

A relatively small oil spill in West Falmouth, Massachusetts, occurred within a few miles of the Woods Hole Oceanographic Institution in September 1969. An oil barge, the Florida, was driven onto the Buzzards Bay Shore where it released between 650 and 700 tons of No. 2 fuel oil into the coastal waters. Studies of the biological and chemical effects of this spill are continuing, more than two years after the event (Blumer 1969,[319] Hampson and Sanders 1969,[331] Blumer et al. 1970,[322] Blumer and Sass 1972[321]). Massive destruction of a wide range of fish, shellfish, worms, crabs, other crustaceans, and invertebrates occurred in the region immediately after the accident. Bottom-living fish and lobsters were killed and washed ashore. Dredge samples taken in 10 feet of water soon after the spill showed that 95 per cent of the animals recovered were dead and the others moribund. Much of the evidence of this immediate toxicity disappeared within a few days, either because of the breaking up of the soft parts of the organism, burial in the sediments, or dispersal by water currents. Careful chemical and biological analyses reveal, however, that not only has the damaged area been slow to recover but the extent of the damage has been expan/ with time. A year and a half after the spill, identifi.

TABLE IV-5—Summary of Remote Sensor Characteristics For Oil Detection

ngth	Detection mechanism	Performance summary	Possible sensor configuration					Comments
			Type	Resolution	Weight	Volume	Swath width	
traviolet ($\leq 0.4 \mu m$).	Reflectance differential (Oil/ Water contrast) Fluorescence	Reflective signature a. Repeatable positive response from thin slicks ($\sim$.1 micron). b. Variable response from thicker slicks dependent upon oil type, water quality and illumination conditions. c. Atmospheric haze limitations major. d. Signal limitations prevent night-time detection. Fluorescence signature 1. Artificial Excitation (narrow-band) a. Spectral character strongly correlated to oil thickness. b. Intensity strongly correlated to oil type (API) and oil thickness, weakly correlated to temperature. c. Decay characteristics moderately to strongly correlated to oil type, uncorrelated to oil thickness. d. All characteristics independent of ambient illumination conditions. 2. Solar excitation (broad-band) a. Spectral character moderately to weakly correlated to oil type and thickness. b. Intensity strongly correlated to oil type, oil thickness and ambient illumination conditions. c. Decay characteristics not detectable. d. Signal limitations prevent operation except under strong solar illumination.	UV Vidicon UV Scanner Pulsed Laser	500 lines/frame (high scene illumination) 100–200 lines/frame (low scene illumination) 2 mr 1 mr	33 lbs. 90 lbs. 150 lbs.	2 cu. ft. 3.5 cu. ft. 4 cu. ft.	40° FOV (727 ft @ 10 K) 2.7 mi @ 10 K 10 ft. @ 10 K	Developed equipment available for UV vidicon and/or scanner. Integrates well with CRT display. Line scanner may require data buffer for high resolution, real time display, or film processor Effective against thin and thick slicks under solar, or artificial illumination. Active laser system sensitivity limitations hinder use in detection or mapping mode. Identification capability very good, with moderate to good thickness determination.
.ble 7 μm).	Reflectance Differential (0.1/ Water Contrast)	Reflective Signature a. Variable response from all slicks dependent upon thickness, oil type, water quality and illumination conditions b. Signal limitations prevent moonless nighttime detection. c. False alarm problem significant. d. Atmospheric haze limitation major. e. Maximum contrast between oil and water occurs at (.38 to .45μm) and (.6 to .68μm). f. Minimum contrast between oil and water occurs at (.45 to .58μm). g. Best contrast achieved with overcast sky.	Aerial Cameras RC-8 500-EL KA-62 Vidicon	2 ft.@ 10 K 3.5 ft.@ 10 K ″ ″ 500 lines/frame	190 lbs. 16 lbs. 61.5 lbs. 33 lbs.	11.76 cu. ft. .4 cu. ft. 5.24 cu. ft. 2 cu. ft.	74° FOV 3.5 mi. @ 10 K 40° FOV with zoom lens 7270 ft. at 10 K	Aerial cameras real time display not possible. Sensitivity limitations prevent night-time operations. Compensation for atmospheric haze difficult. UV photography great potential for detecting oil. Color is good; however, sunlight gives false response. Panchromatic, IR and color photography and TV give good results only when oil is thick and ropy. Vidicon useful for real-time detection and mapping at various wave lengths, giving option for good detection with negligible false alarms for day operation and fair-to-good detection with low false alarms for night operation. Display characteristics optimum for surveillance.
frared Near Infrared (0.6 to 0.1 μm) Far Infrared (8 to 14 μ	Reflectance Differential (0.1/ Water Contrast) Thermal Emission Differential	Reflective Signature a. Repeatable positive response from all slicks under all conditions. b. Moonless night-time detection capability. c. False alarm problems negligible. d. Atmospheric haze limitation moderate.	Line Scanner Framing Scanner	2 mr 4 mr	90 lbs. 220 lbs	4.0 cu. ft. 3.5 cu. ft.	2.7 mi @ 10 K 25° FOV	Line scanner oil-slick response variable but essentially predictable, but may have some false alarm problems.

TABLE IV-5—Summary of Remote Sensor Characteristics For Oil Detection—Continued

Wave length	Detection mechanism	Performance summary	Possible sensor configuration					Comments
			Type	Resolution	Weight	Volume	Swath width	
		Thermal Signature a. Variable response dependent grossly upon oil type and dependent significantly upon thickness and solar heating. Variability predictable to significant degree (slicks > 10 μm) b. Day/night detection independent of illumination conditions. c. False alarm problem slight. d. Atmospheric haze limitations moderate to slight.						Day/night detection under VFR conditions. Real time display capabilities good but limited to "single-look" display generation. Developed equipment available.
Microwave...........	Emissive Differential (Oil/ Water Contrast) Wave Structure Modification	**Emissive Signature** a. Emissivity of petroleum products is significantly higher than that of a calm sea surface. b. Crude oil pollutants have decreasing dielectric constants (increasing emissivity) with increasing API gravity. c. Microwave signature of oil film inversely proportional to sensor wave length. d. The horizontal polarized microwave signature of oil is twice the vertically polarized signature of an oil slick on a flat water surface. e. Detection improves with decreasing sensor wave lengths and becomes poorer as the sea state increases. f. Atmospheric cloud limitations moderate to slight. g. Can effectively detect slicks less than 0.1 mm at viewing. h. Dual frequency microwave techniques show great promise in measuring oil slick thickness.	Line Scanning Imager	1.4°	68 lbs.	3 cu. ft.	2.7 mi @ 10 K	Clouds that are raining between sensor and slick as well as very high sea states hamper performance. Technology for equipment development available. Real time display consists of facsimile and/or CRT.
Radar...............	Wave Structure Modification Scattering Cross-section Differential	**Reflective Signature** a. Oil film on surface of water suppresses capillary which results in a significant difference in energy back scattered from contaminated surface and that scattered from surrounding clean water (from oil slicks very little energy back scattered by three orders of magnitude). b. Vertical polarization capable of detecting and mapping oil slick less than 1 micron. c. Atmospheric cloud limitations slight.	Forward Scanning (35 GH₂) Synthetic Aperature (3.3 GH₂)	100×100 ft.² 100×100 ft.²	~600 lbs. ~1500 lbs	10 cu. ft. 17 cu. ft.	38 mi @ 12 K 150 mi @ 36 K	Technology exists for equipment development of forward scanning and synthetic aperature radar. Real time display possible for forward scanning radar via facsimile and/or CRT; synthetic aperature radar requires optical processing.

fractions of the source oil were found in organisms that still survived on the perimeter of the area. Hydrocarbons ingested by marine organisms may pass through the wall of the gut and become part of the lipid pool (Blumer et al. 1970).[322] When dissolved within the fatty tissues of the organisms, even relatively unstable hydrocarbons are preserved. They are protected from bacterial attack and can be transferred from food organism to predators and possibly to man.

The catastrophic ecological effects of the oil spills of the Tampico Maru, and the Florida appear to be more severe than those reported from other oil spills such as the Torrey Canyon and the Santa Barbara blowout. The Tampico Maru and the Florida accidents both released refined oils (in one case diesel oil and in the other, No. 2 fuel oil) and both occurred closer to shore than either the Torrey Canyon or the Santa Barbara accidents which released crude oil. The differences in the character of the oil and the proximity to shore may account for the more dramatic effects of the first two accidents, but it is clear that any release of oil in the marine environment carries a threat of destruction and constitutes a danger to world fisheries. •

Persistence of Oil in the Ocean As mentioned above, oil can be ingested by marine organisms and incorporated in their lipid pool. Hydrocarbons in the sea are also degraded by marine microorganisms. Very little is known as yet about the rate of this degradation, but known that no single microbial species will degrade

vhole crude oil. Bacteria are highly specific, and several species will probably be necessary to decompose the numer-ous types of hydrocarbons in a crude oil. In the process of .e. osition, intermediate products will be formed and different species of bacteria and other microorganisms may be required to attack these decomposition products (ZoBell 969).[348]

The oxygen requirement of microbial oil decomposition is severe. The complete oxidation of one gallon of crude oil requires all the dissolved oxygen in 320,000 gallons of air-saturated sea water (ZoBell 1969).[348] It is clear that oxi-dation might be slow in an area where previous pollution has depleted the oxygen content. Even when decomposition of oil proceeds rapidly, the depletion of the oxygen content of the water by the microorganisms degrading the oil may have secondary deleterious ecological effects. Unfortunately, the most readily attacked fraction of crude oil is the least toxic, i.e., the normal paraffins. The more toxic aromatic hydrocarbons, especially, the carcinogenic polynuclear aro-matics, are not rapidly degraded.

That our coastal waters are not devoid of marine life, after decades of contamination with oil, indicates that the sea is capable of recovery from this pollution. However, increasing stress is being placed on the estuarine and coastal environment because of more frequent oil pollution inci-dents near shore; and once the recovery capacity of an environment is exceeded, deterioration may be rapid and catastrophic. It is not known how much oil pollution the sea can accept and recover from, or whether the present addition approaches the limit of the natural system.

It appears that the oceans have recovered from the oil spilled during the six years of the second World War, though some unexplained recent oil slicks have been at-tributed to the slow corrosion of ships sunk during that conflict. It has been estimated (SCEP)[345] that during the war, the United States lost 98 vessels with a total oil ca-pacity of about 1 million tons, and that another 3 million tons of oil were lost through the sinking of ships of other combatants during the same period. These losses were large in the context of the 1940's, but the total for that period was only about twice the annual direct influx to the ocean at the present time. Although no extensive dele-terious effects of these sinkings and oil releases on the fisheries catch of the world have been found, it must be emphasized again that when a pollutant is increasing yearly in magnitude past history is not a reliable source of pre-diction of future effects.

The Toxicity of Oil There is a dearth of dependable observations on the toxicity of oil to marine organisms. It is difficult to evaluate the toxicity of this complex mixture of compounds which is not miscible with sea water. A variety of techniques have been used which are not intercom-parable. In some experiments, oil is floated on the water in the test container, and the concentration given is derived from the total quantity of oil and the total quantity of

water. This is clearly not the concentration to which the organism has been exposed. In other experiments, extracts of oil with hot water or with various solvents have been added to the test jar without identification of the oil fraction being tested. In still other cases, care has been taken to produce a fine emulsion of oil in sea water more representa-tive of the actual concentration to which the test organism is exposed. Considering the differences in the meaning of "concentration" in these tests and the variation in sensi-tivity of the test organisms, it is not surprising that the ranges of toxicity that can be found in the literature vary by several orders of magnitude.

Studies of the biological effects of oil have been reviewed by Clark (1971).[325] Mironov (1971)[342] carried out toxicity studies by comparable techniques using a variety of marine organisms. In testing eleven species of phytoplankton, he found that cell division was delayed or inhibited by concen-trations of crude oil (unspecified type) ranging from 0.01 to 1000 ppm. He also showed that some copepods were sensitive to a 1 ppm suspension of fresh or weathered crude oil and of diesel oil. Freegarde et al. (1970)[328] found that the larvae of *Balanus balanoides* and adult *Calanus* copepods maintained in a suspension of crude oil ingest, without apparent harm, droplets of oil that later appear in the feces. Mironov (1967)[341] found 100 per cent mortality of developing flounder spawn at concentrations of three types of oil ranging from 1 to 100 ppm and an increased abnor-mality of development at longer periods of time in concen-trations as low as 0.01 ppm. In contrast other experimenters have found that concentrations of several per cent are necessary to kill adult fish in a period of a few days (Chip-man and Galtsoff 1949,[324] Griffith 1970[329]).

The evidence is clearer that a combination of oil and detergents is more toxic than oil alone. This was first definitely established in studies of the Torrey Canyon spill (Smith 1968),[347] and the toxicity of the various detergents used in this operation is discussed by Corner et al. (1968).[326] The four detergents tested were all more toxic than Kuwait crude oil, and all showed signs of toxicity between 2 and 10 ppm. The solvents used with these detergents were also highly toxic but tended to lose their toxicity over time through evaporation. A bioassay test carried out by the Michigan Department of Natural Resources (1969)[338] re-vealed that the least toxic detergent mixed with oil could be a hundred times as concentrated (1800 ppm) as the most toxic (14 ppm) and cause the same toxic effect. La Roche et al. (1970)[337] defined bioassay procedures for oil and oil dispersant toxicity evaluation using fish, *Fundulus heteroclitus*, and the sandworm, *Nereis virens* (Table IV–6).

The mortality of seabirds as a result of oil pollution is direct and immediate, and in a major oil spill, is measured in the thousands. The diving birds which spend most of their life at sea are most prone to death from oil pollution, but any bird that feeds from the sea or settles on it is vul-nerable. In oil-matted plumage air is replaced by water

TABLE IV-6—Determinations (Summarized) of Acute Toxicities of 10 Chemical Dispersants Alone and in Combination with Crude Oil to Sandworm (Nereis virens) and Mummichog (Fundulus heteroclitus) in Laboratory Bioassay Tests

Substance	98 hour LC50 (ml/l)	
	Nereis	Fundulus
Crude oil A		16.5
Crude oil B	6.1	6.2
Oil and dispersants[a]	.055-.781	.157-1
Dispersants	.007-7.10	.008-2

[a] Ranges of values for 10 dispersants mixed 1 part dispersant to 10 parts of oil by volume. LaRoche et al. 1970[347].

causing loss of both insulation and buoyancy, and oil ingested during preening can have toxic effects.

Hartung and Hunt (1966)[332] fed oils directly to birds by stomach tube and later analyzed the pathological and physiological effects through autopsies. The lethal dose for three types of oil ranged from 1 ml to 4 ml per kilogram (ml/kg) when the birds were kept outdoors under environmental stress. The experimenters concluded that a duck could typically acquire a coating of 7 grams of oil and would be expected to preen approximately 50 per cent of the polluting oil from its feathers within the first few days. Enough of this could easily be ingested to meet the lethal dosage of 1 to 4 ml/kg. Thus, birds that do not die promptly from exposure to cold or by drowning as a result of oil pollution may succumb later from the effects of ingestion.

Corrective Measures

The only effective measure for control of oil pollution in the marine environment is prevention of all spills and releases. The time-lag involved in corrective methods means that some damage will inevitably occur before the corrective measures take effect. Furthermore, the soluble parts of the oil already in the water will not be removed by any of the present methods of post-spill cleanup.

Control measures have been introduced that appreciably reduce excessive oil pollution from normal tanker operations (see Table IV-4). The load on top (LOT) process concentrates waste oil that is ultimately discharged with the new cargo (IMCO 1965a,[335] 1965b[336]). This procedure recovers somewhat more than 98 per cent of oil that would otherwise be released to the sea. It has been estimated (Revelle et al. 1972)[345] that 80 per cent of the world fleet uses these control measures today, and if they continue to do so faithfully these ships will contribute only 3.0×10^4 tons of the total tonnage of oil loss. In contrast, the 20 per cent of the fleet not using these control measures contributes 5×10^6 tons. If these control measures were not in use by a major fraction of the tanker fleet, the contamination of the sea from this source would be about five times greater than it is today.

Among the earliest methods for the cleanup of spilled oil was to pick up or bury the material that came ashore while disregarding the oil that remained at sea. It was found that the use of straw to absorb the oil made this cleanup procedure easier, and in the cleanup of the Arrow oil spill (Ministry of Transport, Canada 1970),[340] peat moss was found to be an effective absorbent for Bunker C oil. Recent studies promise mechanical means for handling and cleaning sand contaminated with oil by use of earth moving equipment, fluid-bed, and froth flotation techniques (Gumtz and Meloy 1971,[330] Mikolaj and Curran 1971,[339] Sartor and Foget 1971).[346]

The use of detergents to treat oil slicks is essentially cosmetic. It removes the obvious evidence of oil and for that reason appeals to the polluter. However, after treatment with detergent, the oil is dispersed in the form of fine droplets and becomes even more available to the biota of the sea than it would be if it were left in the form of a surface film. Because of the finer degree of dispersion, the soluble toxic fractions dissolve more rapidly and reach higher concentrations in sea water than would result from natural dispersal. The droplets themselves may be ingested by filter-feeding organisms and thus become an integral part of the marine food chain. Some of the oil may pass through the gut in the feces of these organisms, but Blumer et al. (1970)[322] have shown that it can pass through the gut wall and be incorporated in the organism's lipid pool. It can thus be transferred from organism to organism and, potentially, into the food that man takes from the ocean for his use.

Sinking of oil has been achieved by scattering talc chalk on the oil causing it to agglutinate into globules of greater density than sea water. Such sunken oil tends to kill bottom fauna before even the motile bottom dwellers have time to move away. The sessile forms of commercial importance, such as clams, oysters and scallops, cannot escape, and other motile organisms such as lobsters (*Homarus americanus*) may actually be attracted in the direction of the spill where exposure will contaminate or kill them. Little is known about the rate of degradation of oil in bottom sediments, but it is known that some fractions will persist for over two years (Blumer 1969,[319] Blumer and Sass 1972[321]). Chipman and Galtsoff (1949)[324] showed that the toxicity of oil is not diminished by adsorption on carbonized sand which can be used as a sinking agent.

Efforts were made to burn the oil in both the Torrey Canyon and the Wafra, which was wrecked off the coast of South Africa in 1971. When oxidation is complete, oil is converted to carbon dioxide and water and removed as a pollutant. Burning oil within a tanker, however, is difficult; and it has not been successful even when oxidants are added. Volatile fractions may burn off quickly, but most of the oil resists combustion. Incomplete combustion is therefore not only more common, but the smoke and volatile oils themselves become atmospheric pollutants many of which ultimately return to the sea through precipitation and accu

ation on the water surface. Oil can be burned on the surface
of the sea by using wicks or small glass beads to which the
oil clings thus removing itself from the quenching effects of
h[...]er. The use of "seabeads" was successful in burning
'un[...]' C oil on the beach and moderately successful in
burning a slick in two to three foot seas in the cleanup
following the wreck of the Arrow (Ministry of Transport,
Canada 1970).[340] However, during burning, the elevated
temperature of the oil increases the solubility in water of
the most toxic components, and this can cause greater
biological damage than if the oil is left unburned.

Mechanical containment and removal of oil appear to
be ideal from the point of view of avoiding long-term bio-
logical damage, but however promptly such measures are
taken, some of the soluble components of the oil will enter
the water and it will not be possible to remove them. A
variety of mechanisms for containing oil have been pro-
posed, such as booms with skirts extending into the water.
Various surface skimmers to collect oil and pump it into a
standby tanker have been conceived. Unfortunately, most
wrecks occur during less than ideal weather conditions
which makes delivery and deployment of mechanical de-
vices difficult. Floating booms are ineffective in a rough sea,
because even if they remain properly deployed, oil can be
carried over the top of them by wind and splashing waves
or under them by currents. In protected waters, however,
recovery can be quite effective, and among the methods of
oil removal used today, booms are one of the most effective
[...] [...]tions for their use are favorable.

[...]. [...]obiological degradation is the ultimate fate of all oil
left in the sea, but as was mentioned previously, the oxygen
requirement for this is severe. There is also the problem of
providing other nutrients, such as nitrogen and phosphorus,
for the degrading bacteria. Nevertheless, this process is a
natural" one, and research into increasing the rate of
bacteriological degradation without undesirable side effects
is to be encouraged.

Although an ultimate solution to the cleanup of oil spills
is desperately needed, prevention of spills remains the most
effective measure. When wrecks occur, every effort should
be made to offload the oil before it enters the marine en-
vironment. Oil spills that occur in harbors during transfer
of oil to a refinery or of refined oil to a tanker should be
more easily controlled. Portable booms could confine any
oil released and make possible recovery of most harbor
spillage. Available technology is adequate to prevent most
accidental spills from offshore well drilling or operations.
It is necessary to require that such technology be faithfully
employed.

Recommendations

No oil or petroleum products should be dis-
charged into estuarine or coastal waters that:

can be detected as a visible film, sheen, or
discoloration of the surface, or by odor;

- can cause tainting of fish or edible inverte-
brates or damage to the biota;
- can form an oil deposit on the shores or
bottom of the receiving body of water.

In this context, discharge of oil is meant to include
accidental releases that could have been prevented
by technically feasible controls.

Accidental releases of oil to the marine environ-
ment should be reclaimed or treated as expe-
ditiously as possible using procedures at least
equivalent to those provided in The National Con-
tingency Plan of 1970. The following recommen-
dations should be followed to minimize damage
to the marine biota.

- Oil on the sea surface should be contained
by booms and recovered by the use of surface
skimmers or similar techniques.
- In the event of a tanker wreck, the oil re-
maining in the hulk should be off-loaded.
- Oil on beaches should be mechanically re-
moved using straw, peat moss, other highly
absorbent material, or other appropriate
techniques that will produce minimal dele-
terious effects on the biota.
- Failing recovery of oil from the sea surface
or from a wrecked tanker, efforts should be
made to burn it in place, provided the con-
tamination is at a safe distance from shore
facilities. If successful, this will minimize
damage to the marine biota.
- Dispersants should be used only when neces-
sary and should be of minimal potential
toxicity to avoid even greater hazard to the
environment.
- Sinking of oil is not recommended.

All vessels using U.S. port facilities for the pur-
pose of transporting oil or petroleum products
should be required to demonstrate that effective
procedures or devices, at least equivalent to the
"Load on Top" procedure, are used to minimize
oil releases associated with tank cleaning.

In order to protect marine wildlife:

- recommendations listed above should be fol-
lowed;
- a monitoring program should follow long-
term trends in petroleum tar accumulation
in selected areas of the oceans;
- no oil exploration or drilling should be per-
mitted within existing or proposed sanctu-
aries, parks, reserves or other protected areas,
or in their contiguous waters, in a manner
which may deleteriously affect their biota;

- **oil exploration or drilling should not be conducted in a manner which may deleteriously affect species subject to interstate or international agreements.**

TOXIC ORGANICS

The toxic organics constitute a considerable variety of chemical compounds, almost all of which are synthetic. The total production of synthetic organic chemicals in the U.S. in 1968 was 120,000 million pounds, a 15 per cent increase over 1967; 135,000 million pounds were produced in 1969, a 12 per cent increase over 1968 (United States Tariff Commission 1970).[377] This figure, in the order of 5×10^{13} grams, may be compared with the total productivity of the sea, which is in the order of 2×10^{16} grams of carbon incorporated into phytoplankton per year (Ryther 1969).[373] When considered in a global and future context, the production of synthetic chemicals by man cannot be considered an insignificant fraction of nature's productivity.

The majority of the synthetic organic chemicals, including those considered toxic, are readily degradable to elementary materials which reenter the chemical cycles in the biosphere. These pose no long-term hazard if applied or released into the environment in quantities sufficiently small to meet the recommendations for mixing zones (see p. 231).

The chemicals of most concern are the more stable compounds that enter the environment, whether they are introduced incidentally as waste materials or deliberately through their use. The toxicity, chemical stability, and resistance to biological degradation of such chemicals are factors that must be considered in assessing their potential effects on ecosystems. Moreover, because of the partitioning of nonpolar compounds among the components of marine ecosystems, relatively high concentrations of these, including halogenated hydrocarbons, are frequently found in organisms.

Only recently it was discovered that polychlorinated biphenyls (PCB), a class of chlorinated hydrocarbons used in a variety of industrial applications, were widespread contaminants in marine ecosystems (Duke et al.).[354a] Concentrations up to or higher than 1000 ppm in the body fat of estuarine birds have been recorded in both Europe and North America (Risebrough et al. 1968,[371] Jensen et al. 1969[360]). Moreover, both DDT and PCB have been found in organisms from depths of 3200 meters in the open North Atlantic Ocean (Harvey et al. 1972).[359]

The discovery of a man-made contaminant such as PCB, unknown in the environment a few years ago, in such unexpectedly high concentrations in marine organisms raises several questions. Are the concentrations of these compounds still increasing in the marine environment and at what rate, and what are the long-term effects upon the marine communities? Is it possible that other pollutants,

undetected by the methodologies that measure the chlorinated hydrocarbons, are present in comparable amounts?

Criteria employed in the past to protect freshwater ecosystems were based on data now seen to be inadequate a on an approach that looked at pollutant concentrations in waste water effluents rather than in the receiving system. Evidently it is necessary to attempt to relate the amounts of input into the ecosystem to the levels in the various components of the ecosystem, including indicator organisms. The concentrations of a persistent pollutant in an indicator organism are considered the best way of following accumulation trends in an aqueous ecosystem that serves as a sink for the pollutant, once the capacity of the ecosystem to absorb the pollutant has been determined. If the concentrations in the indicator organisms exceed those considered safe for the ecosystem, input should then be reduced, restricted, or eliminated until environmental levels are acceptable on the basis of established criteria. Inputs of persistent pollutants into the marine environment, however, are in many cases indirect and not immediately controllable, e.g. river runoffs, atmospheric fallout, and dumping by foreign and domestic ships. The sources of the chemicals in atmospheric fallout may be located anywhere in the world.

Different recommendations must therefore be developed to protect the marine environment from increasing amounts and varieties of organic pollutants that might be anticipated over the next century. The same recommendations may be applied to estuaries, but these must also be protected from a variety of chemicals that are less persistent and pose long-term hazard, but that may, because of toxic effect upon organisms, cause unacceptable amounts of damage. These include many of the pesticides, components of sewage, biological wastes from slaughter houses, and other organic wastes from industry.

Acute toxicity values and subacute effects of pesticides on marine life are listed in Appendix III–Table 6, and in Table IV–7, p. 265. Table IV–7 is a summary of the "most sensitive" organisms taken from Appendix III–Table 6 and includes a list of chemicals that are considered to have potential environmental importance in estuarine or marine ecosystems. The list includes many of the pesticides that are readily degradable in the environment but because of their high toxicity are potentially dangerous to estuarine ecosystems. The list, which should be revised as new data become available, proposes a minimum number of such chemicals. Appendix III–Table 6 includes the following information relative to the potential importance of each material as coastal and marine contaminants. (a) Production figures, which are taken from the 1969 Tariff Commission reports, are listed in the second column. The production figures provide a useful clue to the compounds that are of potential importance as marine pollutants. The order of the chemicals generally follows that of the Tariff Commission reports and is not intended to be a ranking in order of importance. (b) The third column of the table indic.

TABLE IV-7—Presence and Toxicity of Organic Chemicals in the Marine System

Chemical (1)	U.S. production pounds, gal./yr (2)	Presence in sea water or marine organisms (3)	Trophic accumulation (4)	Most sensitive organisms tested (5)	Formulation (6)	Conc. (ppb active ingredient in water) (7)	Method of assessment (8)	Test procedure (9)	Reference (10)
STICIDES, Total	1.1×10⁹ lb	...	...	...					
ngicides									
Fungicides, total	1.4×10⁸	...	...	...					
Pentachlorophenol	4.6×10⁷	Expected	Unknown	Insufficient data for marine organisms					
2,4,5-Trichlorophenol	Not available (1969) 2.8×10⁷ (1968)	Unknown	Unknown	Crassostrea virginica American oyster	....	600	TLM	48 hr static lab bioassay	Davis and Hidu 1969[354]
Nabam (Ethylene bis[dithio-carbamic acid], disodium salt)	1.9×10⁶	Unlikely	Unlikely	Dunaliella tertiolecta	....	100	.270. O. D. expt/O.D. control	10 day growth test	Ukeles 1962[376]
Hexachlorobenzene	Not available	Expected	Detected in birds (Vos et al., 1968)[378] Koeman and Genderen, 1970)[363]	Insufficient data for marine organisms					
rbicides									
Herbicides, total	3.9×10⁸	...	...	...					
Amitrole (3-amino-1,2,4-triazole)	Not available	Unlikely	Unlikely	Insufficient data					
Chloramben (3-amino-2,5-dichlorobenzoic acid, sodium salt)	Not available	Unlikely	Unlikely	Chlorococcum sp Phaeodactylum tricornutum	Methyl ester	2.5×10³	50% decrease in growth	Growth measured as ABS. (525 mu) after 10 days	Walsh 1972[379]
Picloram (4-amino-3,5,6-trichloropicolinic acid) (Tordon[R])	Not available	Unlikely	Unlikely	Isochrysis galbana	....	1×10⁵	50% decrease in O₂ evolution*	....	Walsh 1972[379]
					....	5×10⁴	50% decrease in growth	Measured as ABS. (525 mu) after 10 dys	Walsh 1972[379]
Simazine [2-chloro-4,6-bis-(ethylamino)-s-triazine]	Not available	Unlikely	Unlikely	Isochrysis galbana	Technical acid	500	50% decrease in growth	Measured as ABS. (525 mu) after 10 days	Walsh 1972[379]
				Phaeodactylum tricornutum	Technical aid	500	50% decrease in growth	Measured as ABS. (525 mu) after 10 days	Walsh 1972[379]
trazine hloro-4-ethyl-ai propyl-amino-s-b.	Not available	Unlikely	Unlikely	Chlorococcum sp., Chlamydomonas sp., Monochrysis lutheri	Technical acid	100	50% decrease in growth	Measured as ABS. (525 mu) after 10 days	Walsh 1972[379]
				Isochrysis galbana	Technical acid	100	50% decrease in O₂ evolution*	....	Walsh 1972[379]
				Phaeodactylum tricornutum	Technical acid	100	50% decrease in O₂ evolution*	....	Walsh 1972[379]
Monuron [3-(p-chloro-phenyl)-1,1-dimethylurea]	Not available	Unlikely	Unlikely	Protococcus sp.	....	20	.00 OPT. DEN. expt/opt DEN control	10 day growth test	Ukeles 1962[376]
				Dunaliella tertiolecta	....	20	.00 OPT. DEN. expt/opt DEN control	10 day growth test	Walsh 1972[379]
				Phaeodactylum tricornutum	....	20	.00 OPT. DEN. expt/opt DEN control	10 day growth test	Ukeles 1962[376]
Diuron [3-(3,4,-dichloro-phenyl)-1,1-dimethylurea]	Not available	Unlikely	Unlikely	Protococcus	....	0.02	.52 OPT. DEN. expt/opt DEN control	10 day growth test	Ukeles 1962[376]
				Monochrysis lutheri	....	0.02	.00 OPT. DEN. expt/opt DEN control	10 day growth test	Ukeles 1962[376]
Maleic hydrazide [1,2-di-hydropyridazine-3,6-dione]	2.8×10⁶ lb.	Unlikely	Unlikely	Insufficient data					
Fenuron [1,1-dimethyl-3-phenylurea]	Not available	Unlikely	Unlikely	Chlorococcum sp.	Technical acid	750	50% decrease in growth	10 day growth test	Walsh 1972[379]
				Isochrysis galbana	Technical acid	750	50% decrease in growth	10 day growth test	Walsh 1972[379]
				Monochrysis lutheri	....	290	.67 OPT. DEN. expt/opt DEN control	10 day growth test	Ukeles 1962[376]
Ametryne [2-ethylamino-4-isopropylamino-6-methyl-mercapto-s-triazine]	Not available	Unlikely	Unlikely	Chlorococcum sp.	Technical acid	10	50% decrease in growth	Measured as ABS. (525 mu) after 10 days	Walsh 1972[379]
				Isochrysis galbana	Technical acid	10	50% decrease in O₂ evolution*	....	Walsh 1972[379]
				Monochrysis lutheri Phaeodactylum tricornutum	Technical acid	10	50% decrease in O₂ evolution*	....	Walsh 1972[379]

*/O. as measured by Gilson differential respirometer on 4 ml of culture in log phase. Length of test 90 minutes.

TABLE IV-7—Presence and Toxicity of Organic Chemicals in the Marine System—Continued

Chemical (1)	U.S. production pounds, gal./yr (2)	Presence in sea water or marine organisms (3)	Trophic accumulation (4)	Most sensitive organisms tested (5)	Formulation (6)	Conc. (ppb active ingredient in water) (7)	Method of assessment (8)	Test procedure (9)	Reference (10)
Herbicides, cont.									
Endothal [7-oxabicyclo-(2.2.1) heptane-2,3-di-carboxylic acid, disodium salt]	Not available	Unlikely	Unlikely	Mercenaria mercenaria Hard clam	....	1.25×10^4	TLM	12 day static lab bioassay	Davis and Hidu 1969[354]
MCPA [4-chloro-2-methyl-phenoxyacetic acid]	Not available	Unlikely	Unlikely	Crassostrea virginica American oyster	....	1.56×10^4	TLM	48 hr static lab bioassay	Davis and Hidu 1969[354]
2,4-D & derivatives.........	1.0×10^8 lb	Unknown	Unknown	Crassostrea virginica American oyster Dunaliella tertiolecta	Ester	740	TLM	14 day static lab bioassay	Davis and Hidu 1969[354]
2,4,5-T & derivatives [2,4,5-trichlorophenoxy-acetic acid]	2.8×10^7 lb	Unknown	Unknown	Isochrysis galbana	Technical acid	5×10^4	50% decrease in O_2 evolution*	....	Walsh 1972[379]
				Phaeodactylum tri-cornutum	Technical acid	5×10^4	50% decrease in growth	Measured as ABS. (525 mu) after 10 days	Walsh 1972[379]
Silvex [2-(2,4,5-trichloro-phenoxy)propionic acid]	1.6×10^6	Unlikely	Unlikely	Crassostrea virginica American oyster Dunaliella tertiolecta	....	710	TLM	14 day static lab bioassay	Davis and Hidu 1969[354]
Diquat [6,7-Dihydrodipyrido (1,2-a:2',1'-c)pyrazidi-linium dibromide]	Not available	Unlikely	Unlikely	Chlorococcum sp.	Dibromide	5×10^6	50% decrease in O_2 evolution*	....	Walsh 1972[379]
				Dunaliella tertiolecta	Dibromide	5×10^6	50% decrease in O_2 evolution*	....	Walsh 1972[379]
				Isochrysis galbana	Dibromide	1.5×10^6	50% decrease in growth	Measured as ABS. (525 mu) after 10 days	Walsh 1972[379]
				Phaeodactylum tri-cornutum	Dibromide	5×10^6	50% decrease in O_2 evolution*	....	Walsh 1972[379]
Paraquat [1,1'-dimethyl-4,4'-dipyridilium dichloride]	Not available	Unlikely	Unlikely	Dunaliella tertiolecta	Dichloride	$^{.4}6$	50% decrease in O_2 evolution*	....	Walsh 1972[379]
				Isochrysis galbana	Dichloride	5×10^5	50% decrease in growth	Measured as ABS. (525 mu) after 10 days	Walsh 1972[379]
Trifluralin[α,α,α-Trifluoro-2,6-dirtino-N,N-dipropyl-p-toluidine]	Not available	Unlikely	Unlikely	Chlorococcum sp.	Technical acid	2.5×10^3	50% decrease in growth	Measured as ABS. (525 mu) after 10 days	Walsh 1972[379]
				Isochrysis galbana	Technical acid	2.5×10^3	50% decrease in growth	Measured as ABS. (525 mu) after 10 days	Walsh 1972[379]
				Phaeodactylum tri-cornutum	Technical acid	2.5×10^3	50% decrease in growth	Measured as ABS. (525 mu) after 10 days	Walsh 1972[379]
Cacodylic acid [Hydroxydi-methyl arsine oxide]	Not available	Unlikely	Unlikely	Insufficient data					
Insecticides									
Insecticides, total (includes rodenticides)	5.7×10^8 lb								
Heptachlor [Heptachloro-tetrahydro-endo-methano-indene] (includes hepta-chlor epoxide)	Not available	Oysters (Bugg et al. 1967)[350]	Bald Eagles (Krantz et al. 1970)[365]	Thalassoma bifasciatum Bluehead	100%	0.8	LC-50	96 hr static lab bioassay	Eisler 1970b[357]
Endrin [Hexachloro-epoxy-octahydro-endo-endo-di-methanonaphthalene]	Not available	Oysters (Bugg et al. 1967,[350] Casper, 1967,[352] Rowe et al. 1971)[372]	Brown Pelican (Schreiber and Risebrough 1972,[374] Rise-brough et al. 1968)[371]	Mugil cephalus Striped mullet Menidia menidia Atlantic silverside	100% 100%	0.3 0.05	LC-50 LC-50	96 hr static lab bioassay 96 hr static lab bioassay	Eisler 1970b[357] Eisler 1970b[357]
Dieldrin [Hexachloro-epoxy-octahydro-endo-exo-dimethanonaphthalene]	Not available	Oysters (Bugg et al. 1967,[350] Casper, 1967,[352] Rowe et al. 1971)[372]	Bald eagles (Krantz et al. 1970)[365] Grey Whale, Sperm Whale (Wolman and Wilson 1970)[380] Brown Pelican (Schreiber and Risebrough 1972)[374]	Anguilla rostrata American eel	100%	0.9	LC-50	96 hr static lab bioassay	Eisler 1970b[357]
Aldrin [Hexacflloro-hexa-hydro-endo-exo-dimeth-anonaphthalene]	Not available	Oysters (Bugg et al. 1967)[350]	Unlikely, converts to dieldrin (Korschgen 1970)[364]	Palaemon macrodactylus Korean shrimp	Technical	0.74 (0.51–1.08)	TL-50	96 hr static lab bioassay	Earnest (unpub-lished)[362]
Chlordane [Octochloro-hexahydro-methanoin-dene]	Not available	Oysters (Bugg et al. 1967)[350]	Expected	Palaemon macrodactylus Korean shrimp	100%	18 (10–39)	TL-50	96 hr static lab bioassay	Earnest (unpub-lished)[362]

* /O_2 evolution measured by Gilson differential respirometer on 4 ml of culture in log phase. Length of test 90 minutes.

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TABLE IV-7—*Presence and Toxicity of Organic Chemicals in the Marine System*—Continued

Chemical (1)	U.S. production pounds, gal./yr (2)	Presence in sea water or marine organisms (3)	Trophic accumulation (4)	Most sensitive organisms tested (5)	Formulation (6)	Conc. (ppb active ingredient in water) (7)	Method of assessment (8)	Test procedure (9)	Reference (10)
Insecticides, cont.									
Strobane[R] (polychlorinated terpenes)	Not available	Expected	Expected	Insufficient data for marine species					
Toxaphene [Chlorinated camphene]	Not available	Bay mussel (Modin, 1969);[367] Oysters (Bugg et al. 1967)[360]	Expected	Gasterosteus aculeatus threespine stickle-back	100%	7.8	TLM	96 hr static lab bioassay	Katz 1961[362]
DDT compounds.........	1.2×10⁸ lb.	Jensen et al. 1969,[360] Risebrough et al. 1968[371]							
p,p'-DDT [1,1,1-Trichloro-2,2-bis(p-chlorophenyl) ethane	...	(References cited above)		Penaeus duorarum Pink shrimp	Technical 77%	0.12 0.17 (0.09–0.32)	TL-50 TL-50	28 day bioassay 96 hr intermittent flow lab bioassay	Nimmo et al. 1970[369] Earnest (unpublished)[382]
p,p'-DDD(p,p'-TDE) [1,1-Dichloro-2,2-bis (p-chlorophenyl)ethane	...			Palaemon macrodactylus	99%	2.5 (1.6–4.0)	TL-50	96 hr intermittent flow lab bioassay	Earnest (unpublished)[382]
p,p'-DDE [1,1-Dichloro-2,2-bis(p-chlorophenyl) ethylene	....	(References cited above)		Falco peregrinus Peregrine Falcon	....	....	Eggshell thinning	DDE in eggs highly correlated with shell thinning	Cade et al. 1970[361]
Mirex [Dodecachloro-octahydro-1,3,4-methano-2H-cyclobuta[cd]pentalene]	Not available	Expected	Expected	Penaeus duorarum Pink shrimp	Technical	1.0	100% paralysis/death in 11 days	Flowing water bioassay	Lowe et al. 1971[366]
Benzene hexachloride [Hexachlorocyclohexane]	Not available	Southern hemisphere sea birds (Tatton and Ruzicka 1967)[376]		Penaeus setiferus White shrimp	8.1%	2.8	TLM	24 hr static lab bioassay	Chin and Allen 1958[353]
Lindane [gamma-hexachlorocyclohexane]	Not available	Oysters (Bugg et al. 1967,[360] Casper 1967)[352]	Expected Sand shrimp	Crangon septemspinosa Sand shrimp	100%	5	LC-50	96 hr static lab bioassay	Eisler 1969[355]
				Pagurus longicarpus Hermit crab	100%	5	LC-50	96 hr static lab bioassay	Eisler 1969[355]
Endosulfan [Hexachlorohexahydro-methanobenzo-dioxathiepin-3-o· ·hiodan[R])	Not available	Bay mussel (Koeman and Genderen 1970)[363]	Sandwich Tern, Common Eider (Koeman and Genderen 1970)[363]	Palaemon macrodactylus Korean shrimp	96%	3.4 (1.8–6.5)	TL-50	96 hr intermittent flow lab bioassay	Earnest (unpublished)[382]
Met... ...or (1,1,1-Trichloro-2,2,bis(p-methoxy-phenyl)ethane]	Not available	Oysters (Bugg et al. 1967)[360]	Unlikely	Palaemon macrodactylus	89.5%	0.44 (0.21–0.93)	TL-50	96 hr static lab bioassay	Earnest (unpublished)[382]
Carbaryl (Sevin) [1-naphthyl-N-methylcarbamate]	Not available	Unlikely	Unlikely	Palaemon macrodactylus	100%	7.0 (1.5–28)	TL-50	96 hr intermittent flow lab bioassay	Earnest (unpublished)[382]
				Cancer magister Dungeness crab	80%	6	Prevention of hatching and molting	24 hr static lab bioassay	Buchanan et al. 1970[349]
Coumaphos (Co-ral) [O,O-Diethyl-O-(3-chloro-4-methyl-2-oxo-2H-1-benzopyran-7-yl)-phosphorothioate]	Not available	Unlikely	Unlikely	Crassostrea virginica American oyster	....	110	TLM	48 hr static lab bioassay	Davis and Hidu 1969[354]
Diazinon [O,O-Diethyl-O-(2-isopropyl-4-methyl-6-pyrimidinyl)phosphorothioate]	Not available	Unlikely	Unlikely	Insufficient data					
Parathion [O,O-Diethyl-O-p-nitrophenyl-phosphorothioate]	Not available	Unlikely	Unlikely	Cyprinodon variegatus Sheepshead minnow	....	10	Acetylcholinesterase activity in control vs. expt groups. Control=1.36; Expt.=0.120	72 hr static exposure	Coppage (unpublished)[381]
Dursban [O,O Diethyl-O-3,5,6-trichloro-2-pyridyl-phosphorothioate]	Not available	Unlikely	Unlikely	Palaemon macrodactylus Korean shrimp	....	0.01 (0.002–0.046)	TL-50	96 hr intermittent flow bioassay	Earnest (unpublished)[382]
Fenthion [O,O-Dimethyl-O-(4-methylthio-m-tolyl)phosphorothioate] (Baytex)	Not available	Unlikely	Unlikely	Palaemon macrodactylus	....	3.0 (1.5–60)	TL-50	96 hr intermittent flow bioassay	Earnest (unpublished)[382]
Methyl parathion [O,O,-Dimethyl-O-p-nitrophenyl-phosphorothioate]	5.1×10⁷ lb	Unlikely	Unlikely	Crangon septemspinosa Sand shrimp	100%	2	LC-50	96 hr static lab bioassay	Eisler 1969[355]
Guthion [O,O-Dimethyl-S-(4-oxo-1,2,3-benzotriazino-3-methyl)phosphorodithioate]	Not available	Unlikely	Unlikely	Gasterosteus aculeatus threespine stickle-back	93%	4.8	TLM	96 hr static lab bioassay	Katz 1961[362]
Dioxathion (Delnav) [2,3-p-n-S,S-bis(O,O-phosphorodithioate]	Not available	Unlikely	Unlikely	Crangon septemspinosa Sand shrimp	100%	38	LC-50	96 hr static lab bioassay	Eisler 1969[355]
				Fundulus heteroclitus Mummichog	100%	6	LC-50	96 hr static lab bioassay	Eisler 1970a[356]
				Menidia menidia Atlantic silverside	100%	6	LC-50	96 hr static lab bioassay	Eisler 1970b[357]

TABLE IV-7—Presence and Toxicity of Organic Chemicals in the Marine System—Continued

Chemical (1)	U.S. production pounds, gal./yr (2)	Presence in sea water or marine organisms (3)	Trophic accumulation (4)	Most sensitive organisms tested (5)	Formulation (6)	Conc. (ppb active ingredient in water) (7)	Method of assessment (8)	Test procedure (9)	Reference (10)
Insecticides, cont.									
Phosdrin [1-methoxycarbonyl-1-propen-2-yl-dimethylphosphate]	Not available	Unlikely	Unlikely	Crangon sepemspinosa Sand shrimp	100%	11	LC-50	96 hr static lab bioassay	Eisler 1969[255]
Malathion [S-(1,2-dicarbethoxyethyl)-O,O-dimethyldithiophosphate]	Not available	Unlikely	Unlikely	Thalasomma bifasciatum Bluehead	100%	27	LC-50	96 hr static lab bioassay	Eisler 1970b[257]
Phosphamidon [2-Chloro-N,N-diethyl-3-hydroxy-crotonamide dimethyl phosphate]	Not available	Unlikely	Unlikely	Insufficient data					
Phorate [O,O Diethyl-S-([Ethylthio]methyl)-phosphorodithioate]	Not available	Unlikely	Unlikely	Cyprinodon variegatus Sheepshead minnow	....	5	Acetylcholinesterase activity** in control vs expt. groups. Control=1.36; Expt.=0.086	72 hr static exposure	Coppage (unpublished)[261]
DDVP [O,O-Dimethyl-O-(2,2-dichlorovinyl)phosphate]	Not available	Unlikely	Unlikely	Crangon septemspinosa Sand shrimp	....	4	LC-50	96 hr static lab bioassay	Eisler 1969[266]
Trichlorfon [O,O-Dimethyl-1-hydroxy-2,2,2-trichloro-ethylphosphonate] (Dipterex)	Not available	Unlikely	Unlikely	Crassostrea virginica American oyster	....	1,000	TLM	48 hr static lab bioassay	Davis and Hidu 1969[264]
TEPP [Tetraethyl pyrophosphate]	Not available	Unlikely	Unlikely	Crassostrea virginica	....	>1×10⁴	TLM	14 day static lab bioassay	Davis and Hidu 1969[264]
Related products									
DBCP [1,2-Dibromo-3-chloropropane] (Nemagon ᴿ)	8.6×10⁶ lb	Unknown	Unknown	Mercenaria mercenaria Hard clam	....	780	TLM	12 day static lab bioassay	Davis and Hidu 1969[264]
Methyl bromide	2.0×10⁷ lb	Unknown	Unknown	Insufficient data					
TAR AND TAR CRUDES									
Benzene	1.2×10⁹ gal.	Unknown	Unknown	Insufficient data					
Toluene	7.6×10⁸ gal.	Unknown	Unknown	Insufficient data					
Xylene	3.8×10⁸ gal.	Unknown	Unknown	Insufficient data					
Naphthalene	8.5×10⁸ gal.	Unknown	Unknown	Insufficient data					
PLASTICIZERS									
Phthalic anhydride esters, total	8.8×10⁸ lb.	Expected	Unknown	Insufficient data					
Adipid acid esters, total	6.6×10⁷	Unknown	Unknown	Insufficient data					
SURFACE-ACTIVE AGENTS									
Dodecylbenzenesulfonates, total	5.7×10⁸ lb. (1968)	Unknown	Unlikely	Insufficient data					
Ligninsulfonates, total	4.4×10⁹ lb.	Unknown	Unknown	Insufficient data					
Nitrilotriacetic acid	Not available	Unknown	Unlikely	Cyclotella nana	Monohydrated sodium salt	5×10³	38% growth as compared to controls	72 hr static lab bioassay	Erickson et al. 1950[362]
				Homarus americanus American lobster	Monohydrated sodium salt	1×10⁵	100% mortality	7 day static lab bioassay	NMWQL 1970[356]
HALOGENATED HYDROCARBONS									
Carbon tetrachloride	7.6×10⁸ lb (1968)	Unknown	Unlikely	Insufficient data					
Dichlorodifluoromethane	3.3×10⁸ (1968)	Unknown	Unlikely	Insufficient data					
Ethylene dichloride	4.8×10⁸ (1968)	Expected	Unlikely	Insufficient data					
Aliphatic chlorinated hydrocarbon wastes of vinyl chloride production	3×10⁷ lb (estimated as 1% of vinyl chloride production)	Surface waters and marine organisms of North Atlantic and North Sea (Jensen et al. 1970)[361]	Unknown	Gadus morrhua Cod	67% 1,1,2-trichloroethane, 20% 1,2-di-ethane	10,000	LC-50	10 hr lab bioassay	Jensen et al. 1970[361]
Polychlorinated biphenyl	Not available	Jensen et al. 1969[360], Risebrough et al. 1968[371]	....	Penaeus duorarum Pink shrimp	Aroclor 1254	0.94	51% mortality	15 day chronic exposure in flowing seawater	Nimmo et al. 1971[370]
Polychlorinated terphenyl	Not available	Expected	Expected	Insufficient data					
Brominated biphenyls	Not available	Unknown	Expected	Insufficient data					
CYCLIC INTERMEDIATES									
Monochlorobenzene	6.0×10⁸ lb	Expected	Unlikely	Insufficient data					
Phenol	1.7×10⁹ lb	Expected	Unlikely	Mercenaria mercenaria Hard Clam	....	5.3×10⁴	TLM	48 hr static lab bioassay	Davis and Hidu 1969[264]
MISCELLANEOUS CHEMICALS									
Tetraethyl lead	4.8×10⁸	Unlikely	Unlikely	Insufficient data					

** ACh hydrolysed/hr/mg brain.

whether or not the compound has been detected in sea water or in marine organisms. Compounds which have been detected are of greater immediate concern than those w   have not. Frequently, because of their low solubility in   .cr, some of the non-polar compounds which are biologically accumulated can be detected in an organism but not in the water itself. (c) The fourth column, trophic accumulation, indicates whether the compound has been shown to pass through the food web from prey species to predator. Compounds that are so accumulated are of greater concern than compounds of comparable toxicity which are not. Finally, the species thought to be most sensitive to the compound are indicated in the final columns with reference to original studies in the scientific literature. These data are useful as a guide only and are not sufficient in themselves for definitive evaluation of the environmental significance of each compound.

The report, "The Effects of Chemicals on Aquatic Life, vol. 3, Environmental Protection Agency, Water Quality Office, 1971," has been useful as a guide to the available toxicity data of industrial chemicals on marine organisms. Appendix III–Table 6 is a compendium of data on toxicity of pesticides to marine organisms. These sources are incomplete and should be continually revised.

Bases for Recommendations

1. In order to provide an adequate level of protection for commercially important marine species and for species cr 'ered important in the maintenance of stability of the e\ cem, an application factor of one one-hundredth (0.01) is used when pesticides or organic wastes that are not trophically accumulated in food webs are applied or released in estuarine or marine environments. This factor is arbitrary and was derived from data available on marine and freshwater organisms. (See Section III, p. 121.) It assumes that a concentration of one one-hundredth (0.01) of that causing harm to the most sensitive species to be protected will not damage this species or the ecosystem. Future studies may show that the application factor must be decreased or increased in magnitude.

2. The application factor may also be used for the compounds that are trophically accumulated in food webs in order to protect fish and invertebrates to which these compounds are toxic. It cannot be used, however, to protect fish-eating birds and mammals which may trophically accumulate these compounds from their prey species, in part because sublethal effects such as eggshell thinning and hormone imbalance may adversely affect reproductive capacity and therefore the long term survival of populations. Levels that would protect fish-eating birds and mammals against the effects of compounds that are trophically accumulated from prey species are given in the discussion of Marine Wildlife (see pp. 224–228).

The recommendations below apply to all organics of b   roved and potential toxicity.

Recommendations

In general, marine life with the exception of fish-eating birds and mammals should be protected where the maximum concentration of the chemical in the water does not exceed one one-hundredth (0.01) of the LC50 values listed in Column 7, Table IV–7, pp. 265–268. If new data indicate that an ecosystem can adequately degrade a particular pollutant, a higher application factor for this pollutant may be used.

In order to maintain the integrity of the ecosystem to the fullest possible extent, it is essential to consider effects on all non-target organisms when applying pesticides to estuarine habitats in order to control one or more of the noxious species. For those occasions when chemicals must be used, the following guidelines are offered:

- a compound which is the most specific for the intended purpose should be preferred over a compound that has broad spectrum effects;
- a compound of low persistence should be used in preference to a compound of greater persistence;
- a compound of lower toxicity to non-target organisms should be used in preference to one of higher toxicity;
- water samples to be analyzed should include all suspended particulate and solid material: residues associated with these should therefore be considered as present in the water;
- when a derivative such as p,p'-DDE or 1-napthol is measured with or instead of the parent compound, the toxicity of the derivative should be considered separately: if the toxicity of a derivative such as an ionic species of a pesticide is considered equivalent to that of the original parent compound, concentrations should be expressed as equivalents of the parent compound.

It is recommended that the chemicals listed in Table IV–7 and all chemicals subsequently added to this list be considered as toxic organic compounds potentially harmful to the marine environment. It is emphasized that the data in Table IV–7 are not sufficient in themselves for final evaluation of the environmental significance of each compound.

OXYGEN

An extensive review and discussion of the present information on biological responses to variations in dissolved oxygen has been published recently by Doudoroff and

Shumway (1970).[383] This review has been used in developing oxygen recommendations by both the Freshwater and Marine Panels in their reports. On the basis of this large body of information, recommendations for "levels of protection" for freshwater fish populations have been developed. Estuarine and marine organisms have not been studied as extensively, and the present information is inadequate for satisfactory analysis of the response of communities to temporal and spatial variations in dissolved oxygen concentrations.

The generalizations presented by the Freshwater Panel appear to be valid, with qualifications, for estuarine and marine situations.

1 A reduction in dissolved oxygen concentration reduces the rate of oxygen uptake by aquatic plants and animals. However, as noted by Doudoroff and Shumway, the observed response of many organisms under laboratory conditions measured in such terms as growth rate, swimming speed, or hatching weight, shows fractional or percentage reductions that approximately correlate with the logarithm of the deviation of the dissolved oxygen concentration from equilibrium with the atmosphere, under conditions of *constant* dissolved oxygen concentrations. Thus, reduction in the dissolved oxygen concentration by 1 mg/l from the saturation value has much less effect than reduction by 1 mg/l from the 50 per cent of saturation value.

2 The non-threshold character of these responses means that some risk of effect on the aquatic populations is associated with any reduction in the dissolved oxygen concentrations. As noted above, the risk of damage increases as dissolved oxygen concentrations decrease from saturation values. Selection of risk acceptance is a social and economic evaluation involving other uses of any particular environment that must precede recommendations derived using the risk acceptance and the pertinent scientific information.

3 Consideration of the effects of dissolved oxygen concentrations on aquatic life must include the responses of developing eggs and larvae, as well as the maturing and adult individuals. Species that have limited spawning areas should be identified and the biological risk of decreased oxygen concentrations evaluated accordingly.

For estuaries and coastal waters, consideration must be given to the distribution of dissolved oxygen with depth, since even under natural conditions low oxygen concentrations may be found in the deeper waters. Special consideration should be given to estuary type, topography, currents, and seasonal development of pycnoclines.

Many estuaries and coastal regions are highly productive, and the characteristic pattern with photosynthesis in the upper-water layer or adjacent marshes leads to large population densities in the upper layers and loss of oxygen to the atmosphere from the supersaturated surface waters or the marsh plants. Subsequent decomposition of these organisms and their wastes in the deeper waters leads to oxygen depletion. Several deeper coastal plain estuaries and fjords show

oxygen depletion from this sequence. Addition of mineral and organic plant nutrients to such regions may intensify the production and subsequent decomposition processes. The effects of particular additions will depend on the wa depths and rate of vertical mixing, and it is necessary ᵥ construct an oxygen balance model for each case. Sewage treatment that consists of partial or nearly complete mineralization of the organic materials may still produce a discharge that will damage the aquatic system, i.e., an amount of organic matter nearly equal in oxygen demand to the original sewage is produced in the environment. The principal effect of many "secondary" treatment systems is the trading of an intense local effect near the outfall for a more widespread effect at greater distances. One of the major considerations in defining water quality recommendations for nutrients in any estuarine or coastal region should be the risk associated with oxygen depletions from increased production. Deliberate moderate additions of nutrients to increase the yield of some fishery should also give due regard to this secondary effect.

Recommendation

Each proposed change in the dissolved oxygen concentration in estuaries and coastal waters should be reviewed for risk of damage to aquatic life. The limited laboratory data and field observations on marine organisms suggest that easily observed effects, which are in many cases deleterious, occur with dissolved oxygen concentrati of 4 to 5 mg/l as daily minimum values for peri ᵤ of several days. As a guideline, therefore, reduction of the dissolved oxygen concentration to values below 4 mg/l can be expected to change the kinds and abundances of the aquatic organisms in the affected volume of water and area of bottom. Particular attention should be directed toward identifying species with restricted spawning and nursery areas and conservatism should be used in applying guidelines to these areas. (See the expanded discussion in Section III, pp. 131–135.)

RADIOACTIVE MATERIALS IN THE AQUATIC ENVIRONMENT

This section considers radioactivity in all surface waters inhabited by plants and animals including fresh, estuarine, and marine waters of the U.S. The subject matter pertains primarily to the impact of environmental radioactivity on aquatic organisms, although it also contains some discussion of human radiation exposure from aquatic food chains. A recent report by the National Academy of Sciences (1971)[397] presented a review of radioactivity in the marine environment, and that review has been used extensively in ᵗʰᵉ preparation of this report.

Characteristics and Sources of Radioactivity

Radiation is the energy emitted spontaneously in the p. , of decay of unstable atoms of radioisotopes. This energy can exist either in the form of electromagnetic rays or subatomic particles and cannot be detected by man's senses. Radiation can be detected, however, by means of electronic instruments, and quantities present at very low levels in the environment can be measured with remarkable accuracy. Radioactivity which occurs naturally in the environment originates from primordial radioisotopes and their decay products (daughters) and from reactions between cosmic rays from outer space and elements in the atmosphere or in the earth. Some of the more abundant primordial radioisotopes in terms of their radioactivity are potassium (^{40}K), palladium (^{234}Pd), rubidium (^{87}Rb), uranium (^{238}U) and thorium (^{237}T), the first accounting for 90 per cent of the natural radiation in the oceans. While beryllium (^{7}Be) is the most abundant radioisotope produced by cosmic rays, carbon (^{14}C) and hydrogen (^{3}H) (tritium) are biologically the most interesting. The presence of natural radioactivity was unknown until 1896 when Becquerel discovered uranium. Until the development of the atomic bomb during World War II, virtually all of the radioactivity on earth came from natural sources.

The first man-made radioisotopes were not released into the environment in any significant amounts until the atomic bomb was tested and used in war even though the uranium 2.° om was first split (fissioned) by neutron bombardment . in 1938. While the release of radioisotopes was drastically reduced with the halting of nuclear weapons testing in the atmosphere by signatories of the test ban treaty, radioactive wastes continue to be released from nuclear powered ships and submarines, nuclear power plants, nuclear fuel reprocessing plants, and to a lesser extent from laboratories and hospitals. Two methods have been used in handling radioactive wastes. High levels have been concentrated and held in special storage tanks, while low levels of radioactive wastes in small volumes have been diluted and dispersed in the aquatic environment—particularly in the oceans. Some manmade radioisotopes, such as strontium 90 and cesium 137, are the debris of split atoms and are called fission products. Other radioisotopes, such as zinc 65 and cobalt 60, are activation products, produced when stray neutrons from the fission process strike the atoms of stable elements.

Cycling of Radioactive Materials The physical, chemical, and physiological behavior of radioisotopes is essentially identical with that of the stable isotopes of the same element—at least until disintegration occurs. It should be pointed out, however, that in some instances the physical and chemical states of a radioisotope introduced into the aquatic environment may vary from that of the stable element in water. At the time of disintegration, the decaying at change into different types of atoms of the same ele-

ment or into atoms of a different element. If the behavior of a particular element in an ecosystem is known, the behavior of the radioisotopes of that element can be predicted. The reverse also is true, and radioisotopes can serve as excellent tracers in following the movement of elements through complex environmental systems. Radioactive wastes in the aquatic environment may be cycled through water, sediment, and the biota. Each radioisotope tends to take a characteristic route and has its own rate of movement through various temporary reservoirs. The route taken by tritium is different from that of other radioisotopes. Tritium becomes incorporated in the water molecule and cannot be removed by present waste treatment practices. It is not concentrated appreciably by either biota or sediments.

When radioactive materials enter surface waters they are diluted and dispersed by the same forces that mix and distribute other soluble or suspended materials (National Academy of Sciences 1957).[393] The dominant forces are mechanical dilution that mixes radioisotopes in the waste stream as it leaves an outfall structure; advection and turbulent diffusion that mix materials in the receiving waters; and major transport currents that move masses of water over relatively long distances. On the other hand, precipitation and sedimentation tend to restrict the area of dispersion. When first introduced into fresh or marine water, a substantial part of the materials present in radioactive wastes becomes associated with solids that settle to the bottom, and many of the radioisotopes are bound chemically to the sediments. The sediments may also be moved geographically by currents. Even though in some instances sediments remove large quantities of radioisotopes from the water, and thus prevent their immediate uptake by the biota, this sediment-associated radioactivity may later leach back to the water and again become available for uptake by the biota.

Plants and animals, to be of any significance in the passage of radioisotopes through a food web in the aquatic environment, must accumulate the radioisotope, retain it, be eaten by another organism, and be digested. Radioisotopes may be passed through several trophic levels of a food web, and concentrations can either increase or decrease from one trophic level to the next, depending upon the radioisotope and the particular prey-predator organisms. This variation among trophic levels occurs because different organisms within the same trophic level have different levels of concentration and different retention times, which depend upon their metabolism or capacity to concentrate a given radioisotope. The concentration of a radioisotope by an organism is usually discussed in terms of a concentration factor: the ratio of the concentration of the radioisotope in the organism to that in its source, that is, the amount in water or food. Radioisotopes with short half-lives are less likely to be highly concentrated in the higher trophic levels of the food chain because of the time required to move from the water to plants, to herbivores, and eventually to carni-

vores. Organisms that concentrate radioisotopes to a high level and retain them for long periods of time have been referred to as "biological indicators for radioactivity." These organisms are of value in showing the presence of radioactive materials even though the concentrations in the water may be less than detectable limits.

Exposure Pathways

The radiation emitted by radioisotopes that are present in aquatic ecosystems can irradiate the organisms in many different ways. In order to evaluate the total radiation dose received by the aquatic organisms, and thus the risk of their being injured, all sources of exposure must be considered. These sources include both natural and man-made radiation, both external and internal.

Major Sources of External Radiation   1 Radioisotopes in the surrounding water that tend to remain in solution, or at least suspended in the water, become associated more readily with aquatic organisms than the radioisotopes that settle out.

2   Radioisotopes present on or fixed to sediments are significant to aquatic life, particularly to benthic organisms in the vicinity of existing major atomic energy plants.

3   Radioisotopes attached to the outer surfaces of organisms are of greater significance to micro-organisms, which have a larger surface-to-volume ratios, than shellfish or fish.

4   Cosmic-rays are of relatively minor importance to aquatic life that lives a few feet or more below the water surface, because of the shielding afforded by the water.

Major Sources of Internal Radiation   1 Radioisotopes in the gastrointestinal tract frequently are not assimilated, but during their residence in the tract expose nearby internal organs to radiation.

2   Assimilated radioisotopes are absorbed from water through the integument or from food and water through the walls of the gastrointestinal tract, metabolized, and are incorporated into tissues where they remain for varying periods of time. Aquatic plants, including algae absorb radioactive materials from the ambient water and from the interstitial water within the sediments.

It is difficult to measure the amount of radiation absorbed by aquatic organisms in the environment because they are simultaneously irradiated by radioisotopes within their body, on the surface of their body, in other organisms, in the water, and in sediments. Exposure thus depends on an organism's position in relation to the sediments and to other organisms, and to movement of some species in and out of the contaminated area.

Biological Effects of Ionizing Radiation

Ionizing radiation absorbed by plant and animal tissue may cause damage at the cellular and molecular levels. The degree of radiation damage to an organism depends upon the source (external or internal), the type (electromagnetic

or particulate), the dose rate (intensity per unit of time), and the total dose. Possible effects to the individual organism may include death, inhibition or stimulation of growth physiological damage, changes in behavioral patterns, developmental abnormalities, and shortening of life span. In addition, the extent of biological damage from radiation can be modified by environmental stresses such as changes in temperature and salinity. Under certain conditions, irradiation can cause gross pathological changes which are easily observed, or more subtle changes which are difficult or impossible to detect. In addition to somatic changes which affect the individual, genetic changes also may occur which may affect the offspring for many generations. At one time, it was widely believed that there was a threshold radiation dose below which damage did not occur, but now the consensus of most radiobiologists is that any increase over background radiation will have some biological effect. While the non-existence of a threshold dose is difficult to prove, most radiation biologists agree that even background levels of radiation from primordial radioisotopes and cosmic rays have resulted in some genetic changes over the ages. These radiation-induced changes usually constitute less than 1 per cent of all spontaneously occurring mutations (Asimov and Dobzhansky 1966).[384]

The amount of radiation absorbed by an organism can be expressed in various ways. The rad (radiation absorbed dose) is the unit used to measure the absorbed dose of radiation and refers to the absorption of 100 ergs of energy per gram of irradiated material. Because a rad of alpha or n tron radiation produces greater biological damage than a rad of gamma radiation, another unit called the rem (roentgen equivalent man) also is used. To obtain the rem, or dose equivalent, the number of rads absorbed by the tissue is multiplied by the quality factor and other necessary modifying factors to compensate for the effects of different types of radiation. The acute doses of radiation required to produce somatic damage to many species of aquatic organisms have been established within broad limits (National Academy of Sciences 1971).[367] Some bacteria and algae can tolerate doses of many thousands of rads, but the mean lethal dose (LD_{50}—30 days) for fish is in the range of several hundred to a few thousand rads. Eggs and early developmental stages are more sensitive than are adults. By comparison, the mean lethal dose for humans is about 300 rads.

The acute mean lethal dose has little value in placing restrictions on the amounts of radioactive material present in aquatic environments. Much more meaningful is the highest level of chronic exposure that results in no demonstrable damage to aquatic populations. A vast amount of research on dose-effect relationships for warm-blooded animals has led to the recommendations on human radiation exposure. People who work with radiation may receive no more than 5 rem in any one year. The recommended limit for the general public is 0.5 rem in one year for individuals bi restricted to only 0.17 rem per year as an average for po,

tions. The lower level permitted for populations is to re-
uce the possibility of genetic changes becoming established.
 compared with the experimental data available for
warm blooded animals, only a meager amount of informa-
tion is available on chronic dose-effect relationships for
aquatic forms. The preponderance of available data indi-
cates, however, that no effects are discernible on either indi-
vidual aquatic organisms or on populations of organisms at
dose rates as high as several rads per week. In populations of
wild species, genetic damage may be removed by natural
selection and somatically weakened individuals are prob-
ably eaten by predators. Consequently, aquatic organisms
adversely affected by radiation are not readily recognized
in the field.

The natural populations of fish that have probably sus-
tained the greatest exposure to man-made radioactive ma-
terials are those near major atomic energy installations, for
example, in the Columbia River near Hanford; in White
Oak Creek and White Oak Lake, near Oak Ridge; and in
the Irish Sea near Windscale, England. Small fish which
received chronic irradiation of about 10.9 rads per day from
radioisotopes in the sediments of White Oak Creek produced
larger broods but with a higher incidence of abnormal em-
ryos (Blaylock and Mitchell 1969).[385] Chironomid larvae
living in the bottom sediments and receiving about five
rads per week had an increased frequency of chromosomal
aberrations but the abundance of the worms was not af-
fected. The stocks of plaice in the vicinity of the Windscale
outfall have been unaffected by annual dose rates of about
0 rads per year—primarily from the bottom sediments
(Ministry of Agriculture, Fisheries and Food 1967).[392]
Columbia River salmon spawning in the vicinity of the
Hanford outfalls have been unaffected by doses in the range
of 100 to 200 millirads per week (Watson and Templeton
in press).[402] These observations on chronic exposure of
aquatic organisms provide a subjective assessment of radia-
tion sensitivities in natural populations but are not suffi-
ciently definitive to form the basis for the development of
water quality recommendations.

Restrictions on Radioactive Materials

The amounts of radioactive materials present in water
must be restricted in order to assure that populations of or-
ganisms are not damaged by ionizing radiation and also to
limit the amount of radioactive material reaching man via
aquatic food chains. Permissible rates of intake of the vari-
ous radioisotopes by man have been calculated so that the
resulting annual dose is no greater than the recommended
limit. Therefore, when the rate of consumption of aquatic
organisms is determined, e.g., pounds of fish or shellfish per
year, maximum concentrations of radionuclides permissible
in the edible parts of the organisms can be computed. These
maximum concentrations are well below the concentrations
which have produced detectable effects on natural aquatic
populations. It is probable that the aquatic environment

will be protected by the restrictions currently imposed on
the basis of human health.

The regulations which serve to protect man from radia-
tion exposure are the result of years of intensive studies on
the biological effects of radiation. Vast amounts of informa-
tion have been considered by the International Commission
on Radiological Protection (ICRP) (1960,[389] 1964,[390]
1965[391]), the National Council on Radiation Protection and
Measurements (NCRP) (1959,[398] 1971[399]), and the U.S.
Federal Radiation Council (FRC) (1960,[387] 1961[388]), in
developing recommendations on the maximum doses of
radiation that people may be allowed to receive under
various circumstances or that may occur in water. The
Drinking Water Standards (U.S. Department of Health,
Education and Welfare, Public Health Service 1962[400]) and
the Code of Federal Regulations (1967)[386] are responsive to
the recommendations of the FRC, ICRP, and NCRP, and
provide appropriate protection against unacceptable radia-
tion dose levels to people where drinking water is the only
significant source of exposure above natural background.
Where fish or other fresh or marine products that have
accumulated radioactive materials are used as food by hu-
mans, the concentrations of the radiosiotopes in the water
must be further restricted to ensure that the total intake of
radioisotopes from all sources will not exceed the recom-
mended levels.

Conclusions

Previous attempts to restrict radioactive discharges to
marine environments have resulted in recommended maxi-
mum permissible concentrations in sea water (National
Academy of Sciences 1959a,[394] 1959b,[395] 1962,[396] 1971[397]).
These recommendations are most useful as a first approxi-
mation in predicting safe rates of discharge of radioactive
wastes, but their applicability as water quality recommenda-
tions is limited and they are not intended for general use in
fresh or estuarine waters where the concentrations of a great
variety of chemical elements vary widely.

Three approaches to the control of levels of radioactivity
in the aquatic environment have been used: (1) controlling
the release of radioactivity based upon the specific activity
approach—the ratio of the amount of radioactive isotope
present to the total amount of the element (microcuries per
milligram) (National Academy of Sciences 1962),[396] (2)
relating the effects of radiation upon aquatic organisms
caused by a given concentration of a radioisotope or com-
binations of radioisotopes in the water, and (3) restricting
concentrations of radioisotopes to those permitted in water
and food for human consumption.

Since concentrations of stable elements vary from one
body of water to another, and with time, and since adequate
data are not available to relate effects of radiation upon
aquatic organisms to specific levels of radioactivity in the
water, restrictions contained in the Code of Federal Regu-

lations (1967)[386] on liquid effluents are considered adequate to safeguard aquatic organisms.

Because it is not practical to generalize on the extent to which many of the important radioisotopes will be concentrated by aquatic organisms, nor on the extent to which they will be used for food by people, no attempt is made here to specify maximum permissible concentrations (MPC) for water in reference to uptake by the organisms. Rather, each case requires a separate evaluation that takes into account the peculiar features of the region. Such an evaluation should be approved by an agency of the State or Federal Government in each instance of radioactivity contamination in the environment. In each particular instance of proposed contamination, there must be a determination of the organisms present, the extent to which these organisms concentrate the ratioisotopes, and the extent to which man uses the organisms as food. The rates of release of radioisotopes must be based on this information.

Recommendation

Aquatic organisms concentrate radioisotopes to various degrees in their tissues. The concentration in sea water should be low enough so that the concentration in any aquatic species will not exceed Radiation Protection Guides of the U.S. Federal Radiation Council (1961)[401] for organisms harvested for use as human food. This recommendation is based upon the assumption that radiation levels which are acceptable as human food will not injure the aquatic organisms including wildlife.

SEWAGE AND NUTRIENTS

Magnitude of the Problem

The discharge of municipal sewage is a major factor affecting the water quality of receiving systems. Because the amount of municipal waste produced is directly related to the human population, the unit emission rates together with information on the number of people using a system provide an accurate estimate of the load that is imposed on a particular estuary or section of coastal water.

The effect of sewage discharges on water quality varies widely and depends on (1) its composition and content of toxic materials, (2) the type and degree of treatment prior to discharge, (3) the amount released, (4) the hydrodynamics of the receiving waters, and (5) the response of the ecosystem. Increasing human population and affluence have resulted in increasing amounts of domestic and industrial wastes. However, because the kind and degree of treatment often can be improved, it should be possible to cope with this pollution problem and to maintain or improve the quality of the marine environment.

In most cases the discharge of sewage effluent is intentional and the source of sewage and sewage treatment products entering marine ecosystems can be described more

TABLE IV-8—Average Sewage Emissions for a Densely Populated Area

Constituent	Mass emission rate (tons/day)[a]	Unit emission rate (lb/capita/d)
Dissolved solids	3,600	1.03
Suspended solids	565	0.162
BOD	560	0.160
Total nitrogen (N)	165	0.047
Phosphate (P₀₄)	100	0.029

[a] For 700 mgd of sewage; population of 7 million.
NAS-NRC Committee on Oceanography 1970[417].

accurately than the sources of other pollutants entering the ecosystem. The volume of discharges and certain aspects of their composition, specifically, the amount of organic matter and the inorganic nutrients, can be monitored continuously by existing automated methods. Average values for some important constituents and their emission rates in a densely populated coastal area are given in Table IV-8.

Runoff from agriculture areas is an important factor in the nutrient enrichment of freshwater systems, but it is less important to marine systems because relatively fewer farms are concentrated on estuaries and coasts. Nevertheless, agricultural practices should be considered. Pesticides, fertilizers and animal wastes may be carried by rivers into estuaries. Runoff from duck farms was involved in a study on excessive nutrient enrichment by Ryther (1954).[423] Commoner (1970)[404] has emphasized that in the Unit￢ States during the last twenty-five years the amount of trogen used in agriculture has increased fourteenfold while the amount of nitrogen released via sewage has increased only seventy per cent.

In addition to degradable organic materials derived from fecal and food wastes, municipal sewage also contains a wide variety of "exotic" or synthetic materials that are nondegradable or degrade slowly and only under special conditions (e.g., petroleum residues, dissolved metals, detergents, dyes, solvents, and plasticizers). Some of these adversely affect the biota of receiving waters, and many interfere with the biological degradation of organic matter either in the treatment plant or in the environment. Because waste treatment technology currently in use is designed to treat the fecal and food materials derived from organic wastes, an operational definition of municipal sewage "exotics" is all those materials not derived from fecal or food sources. If the exotic materials accumulate in the receiving ecosystem, the capacity for recycling of the degradable organic materials may be reduced.

Oxygen Depletion

Efficient biological degradation of organic materials requires dissolved oxygen, and overload of sewage in receiving waters can result in oxygen depletion and secondary ef￢ such as objectionable odors, plant and animal die-off,

generally decreased rates of biological degradation. Such effects can also be created by excessive algal growth and subsequent die-off.

most widely used method for estimating the organic pollution load of a waste is the 5 day Biochemical Oxygen Demand Test (BOD_5). Discussions of the test (Fair et al. 1968,[407] Standard Methods 1971[403]) and its limitations (Wilhm and Dorris 1968[426]) are available. Among the important limitations of the BOD_5 are: it does not indicate the presence of organics which are not degraded under the prescribed conditions; it assumes that no toxic or inhibitory materials will affect microbial activity; and it does not measure the nitrogeneous oxygen demand of the organic waste. The chemical oxygen demand (COD) is an alternate procedure for determining the amount of oxidizable material in a water sample. However, it does not indicate the nature of biological oxygen consumption in a given time, and it does not distinguish between inorganically and organically oxidizable materials. Both BOD_5 and COD measurements must be recognized as being only partial descriptions of the sewage load of a receiving water. While BOD_5 and COD measurements are useful for evaluating treatment systems, these two measurements do not adequately assess the environmental impact of a given sewage load (Wilhm and Dorris 1968).[426]

Excessive Nutrient Enrichment

Marine plants, like those on land and in fresh water, require fertilizing elements essential for their growth and reproduction. These essential elements are natural constituents of municipal sewage and the amount that can be added to the marine environment without deleterious effect is determined by the stimulated growth of aquatic plants. Even if the major share of the organic material is removed from the sewage in treatment plants, the growth of normal marine plants can increase if the fertilizing elements present in sewage are added to the environment. Sewage treatment plants are designed to remove the organic material and the suspended solids and to decrease the bacterial population by disinfection. In most cases, this is done by processes that release or "mineralize" the plant nutrients which then stimulate the growth of algae in the receiving waters. In only a few cases have efforts been made to remove these fertilizers from the effluent to prevent or reduce the excessive growth of plants in the aquatic environment.

In the marine environment, growth of phytoplankton is commonly limited by the availability of essential nutrients, the most important of which are phosphorus and nitrogen in available forms. In some cases, shortages of silicate can inhibit the growth of the diatoms and encourage growth of other species. In certain limited areas, other elements such as iron and manganese have been reported as limiting growth of algae, and the presence or absence of other growth stimulating substances, such as vitamin B_{12}, can influence both the amount and the character of plant species

capable of growing. It should be noted that in the marine environment, several elements essential for plant growth such as potassium, magnesium, and sulfur, are present in great excess.

Organic material produced by natural phytoplankton populations produces an oxygen demand when the material is consumed or decomposed. Oxygen is produced by the process of photosynthesis, but this production occurs only near the surface during daylight when the amount of light penetrating the water is adequate. Due to the sedimentation of dead organic particulate material, decomposition usually takes place in the deep waters where photosynthetically produced oxygen is not available.

The amount of organic material which can be produced by marine phytoplankton as a result of the addition of fertilizing elements is dependent upon the composition of the organic material. Redfield et al. (1963)[420] give the following ratios as characteristic of living populations in the sea and of the changes which occur in amounts of various elements left in water as a result of algal growth

Δ0:	ΔC:	ΔN :	ΔP =
276:	106:	16 :	1 by atoms or
138:	40:	7¼:	1 by weight

In addition to the readily available forms of phosphorus and nitrogen (dissolved orthophosphate, ammonia, nitrite, and nitrate), organic forms of phosphorus and nitrogen may be made available by bacterial decomposition. Some dissolved organic nitrogen compounds are also available for direct assimilation.

It should be emphasized that these ratios are not constant in the rigorous sense of the stoichiometric ratios in chemistry. The plant cells can both enjoy a "luxury" consumption of each element (Lund 1950)[414] or survive nutritional deficiencies (Ketchum 1939,[410] Ketchum et al. 1949[411]). In terms of the total production of organic material these variations are important only when concentrations of the elements are unusually low. It has been shown, for example, in New England coastal waters that nitrogen is almost completely removed from the sea water when there is still a considerable amount of phosphorus available in the system. Under these circumstances the plants will continue to assimilate phosphorus, even though total production of organic matter is limited by the nitrogen deficiency (Ketchum et al. 1958,[412] Ryther and Dunstan 1971[423]).

The amount of oxygen dissolved in sea water at equilibrium with the atmosphere is determined by salinity and temperature. Nutrient elements added to the marine environment should be limited so that oxygen content of the water is not decreased below the criteria given in the discussion of Dissolved Oxygen in this Section. In many polluted estuaries, the amount of fertilizing elements added in municipal sewage is sufficient to produce enough organic material to completely exhaust the oxygen supply during decomposition. The oxygen content of sea water and of

fresh water at equilibrium with the atmosphere is presented for different temperatures in Table IV-9. For the purposes of this table, a sea water of 30 parts per thousand (%o) salinity has been used, which is characteristic of the near-shore coastal waters. The salinity effect on concentration of oxygen at saturation is minor compared to effects of temperature in the normal ranges found in coastal waters.

From the ratios of elements given above and the saturation values for oxygen, one can derive the effect of nutrient enrichment of marine waters. For example, from an addition of phosphorus and available nitrogen to final concentrations of 50 and 362.5 micrograms per liter respectively in the receiving water, enough organic material could be produced to remove 6.9 milligrams per liter of oxygen from the water. Data in Table IV-9 indicate that sea water with a salinity of 30 %o and a temperature of 25 C will contain, at saturation, 6.8 milligrams of oxygen per liter. This concentration of nutrients would thus permit the system to become anoxic and would violate the requirement that oxygen not be changed beyond levels expressed in the section on Dissolved Oxygen. Fresh water would contain 8.1 mg/l of oxygen at saturation at 25 C, so that the same amount of nutrient addition would remove 84 per cent of the available oxygen.

The example used might be considered to set an upper limit on the amount of these nutrients added to water. The actual situation is, of course, much more complicated. It is clear from the data in Table IV-9 that summer conditions place the most stringent restrictions on nutrient additions to the aquatic environment. Furthermore, the normal content of nutrients in the natural environment has to be considered. If these were already high, the amount of nutrients that could be added would have to be reduced. As mentioned above, the ratio of elements present in the natural environment would also be important. Nitrogen is frequently the element in minimum supply relative to the requirement of the phytoplankton, and addition of excess phosphorus under these circumstances has less influence than addition of nitrogen. Differences in the ratios of nitrogen to phosphorus may also modify the type of species present. Ryther (1954),[422] for example, found that unusually low nitrogen to phosphorus ratios in Moriches Bay and Great South Bay on Long Island, New York, encourage the growth of micro-

scopic forms of *Nannochloris atomus* at the expense of the diatoms normally inhabiting this estuary.

Many forms of blue-green algae are capable of fixing nitrogen from the gaseous nitrogen dissolved in sea wat̄ Nitrogen deficiencies could be replenished by this mecḥ nism so that decrease in phosphorus content without concomitant decrease in nitrogen content might still lead to overenrichment, as well as shift the dominant phytoplankton population.

Oxygen content of upper water layers can be increased by exchanges with the atmosphere. This process is proportional to the partial pressure of oxygen in the two systems so that the more oxygen deficient the water becomes, the more rapid is the rate of replacement of oxygen in the water by atmospheric oxygen. Finally, mixing and dilution of the contaminated water with adjacent bodies of water could make additional oxygen available. All of these variables must be considered in order to determine acceptable levels at which nutrients present in sewage can be added to an aquatic environment. In fact, many polluted estuaries already contain excessive amounts of these fertilizing elements as a result of pollution by municipal sewage.

The effects of ratios of elements discussed above have a very important bearing upon some of the methods of control. For example, the removal of phosphates alone from the sewage will have an effect upon the processes of overenrichment only if phosphorus is indeed the element limiting production of organic matter. When nitrogen is limiting, as it is in New England coastal waters according to Ryther and Dunstan (1971),[423] the replacement of ṗ phorus by nitrogen compounds, such as nitrilotriacetate (NTA) could be more damaging to the ecosystem than continued use of phosphate-based detergents.

Pathogenic Microorganisms

The fecal coliform index is the most widely used microbiological index of sanitary quality of an estuary. Fecal coliform indices represent a compromise between the ideal of direct determination of bacterial and viral pathogens in time-consuming laboratory procedures, and the indirect, less indicative but practical exigencies. Laboratory methods for quantitative enumeration of virus currently are being developed and their present status is one of promise, but more time is needed for their evaluation. Bacterial pathogen detection frequently requires special laboratory attention.

Virus, in general, may exhibit considerably longer survival times in water and shellfish as compared to fecal coliform bacteria. Under these circumstances a negative *E. coli* test can give a false impression of the absence of viral pathogens (Slanetz et al. 1965,[424] Metcalf and Stiles 1968[415]). Fecal coliform multiplication may possibly occur in polluted waters leading to further difficulties in interpreting sanitary quality.

Disinfection of waste water by chlorine is effective in removing most pathogenic bacteria but unpredictable

TABLE IV-9—*Effects of Salinity and Temperature on the Oxygen Content of Water in Equilibrium with Air at Atmospheric Pressure*

Temperature C	Salinity o/oo	Oxygen mg/l	Salinity o/oo	Oxygen mg/l
25	30	6.8	0	8.1
20	30	7.4	0	8.9
10	30	9.1	0	10.9
0	30	11.65	0	14.15

Richards and Corwin 1956[421].

...ucing the number of viruses. Differences in resistance of bac... ...ia and virus to chlorination may result in the appear- ...n infectious virus in treated effluents devoid of bac- ...ria. Failure to demonstrate the presence of viruses would ...e the best way to insure their absence, but such capability ...its development of methods adequate for quantitative ...numeration of virus in water.

The pollution of estuaries with waste products has led to ...e contamination of shellfish with human pathogenic ...acteria and viruses. Outbreaks of infectious hepatitis and ...cute gastroenteritis derived from polluted shellfish have ...einforced concern over the dangers to public health associ- ...ted with the pollution of shellfish waters. The seriousness of ...iral hepatitis as a world problem has been documented by ...Mosley and Kendrick (1969).[416] Transmission of infectious ...epatitis as a consequence of sewage-polluted estuaries has ...ccurred through consumption of virus-containing shellfish, ...ither raw or improperly cooked. Nine outbreaks of infec- ...ious hepatitis have been attributed to shellfish (Liu 1970).[413] ...contamination of water by sewage leads to the closing of ...yster beds to commercial harvesting, denying public use ...f a natural resource and causing economic repercussions ...n the shellfish industry. (See the discussion of Shellfish in ...Section I on Recreation and Aesthetics.)

Sludge Disposal into Marine Waters

Dumping of sewage sludge in the ocean continues and this ...pr....e, although at present indispensable, constitutes a ...loss of one resource and potential danger for another. A study on the New York Bight sludge and spoil dumping area has shown that an accumulation of toxic metals and petroleum materials appear to have reduced the abundance of the benthic invertebrates that normally rework the sedi- ...ments in a healthy bottom community (Pearce 1969).[419]

Deep Sea Dumping

Biological degradation of organic waste materials is gen- erally affected by micro-biota and chemophysical environ- mental factors. The deep sea is increasingly considered for the disposal of organic waste materials. A recent study (Jannasch et al. 1971)[409] has shown that rates of bacterial activity in degrading organic materials was slowed by about two orders of magnitude at depths of 5,000 to 15,000 feet as compared to samples kept at equal temperatures (38°F) in the laboratory. Since (a) the disposal of organic wastes should be designed on the basis of rapid decomposi- tion and recycling, and (b) there is no control of the pro- cesses following deep-sea disposal, this environment cannot be considered a suitable or safe dumping site.

Potential Beneficial Uses of Sewage

Light loads of either organic-rich raw sewage or nutrient- ri... ...ological treatment (secondary) effluent increase bio- lo... ..., productivity. Except for short-term data on increased fish and shellfish production, beneficial effects have rarely

been sufficiently documented, but at the present time several active research programs are underway. Some degree of nutrient enrichment exists today in most estuaries close to centers of populations. These estuaries remain relatively productive and useful for fishing and recreation. Certain levels of ecosystem modification via organic and nutrient enrichment appear to be compatible with current water uses; however, subtle changes in ecosystems may be accom- panied by later, more extensive change.

The possibility of intensive use of essential plant nutrients in waste material to increase the harvestable productivity of estuarine coastal systems has been suggested as a logical way to treat sewage and simultaneously derive an economic benefit. Aquaculture systems would essentially be an ex- tension of the waste treatment process. Conceptually, aqua- culture is a form of advanced treatment. The limiting factor involves problems presented by toxic synthetic chemicals, petroleum, metals, and pathogenic microorganisms in effluents of conventional biological treatment plants.

Rationale for Establishing Recommendations

It is conceptually difficult to propose a level of nutrient enrichment that will not alter the natural flora because seasonal phytoplankton blooms with complex patterns of species succession are an integral part of the ecology of estuarine and coastal waters. The timing and intensity of blooms vary from year to year and patterns of species suc- cession are frequently different in successive years. The highly productive and variable ecology of estuaries makes it difficult to differentiate between the early symptoms of arti- ficial nutrient enrichment and natural cyclic phenomena. In addition, there have already been major quantitative and qualitative changes in the flora of marine waters close to centers of population. These changes are superimposed on the normal patterns of growth and may not in themselves impair the recreational and commercial use of waters.

Simulation modeling has been used to predict the total phytoplankton response to given nutrient inputs with success by O'Connor (1965)[418] and DiToro et al. (1971)[405] in the San Joaquin Estuary and by Dugdale and Whitledge (1970)[406] for an ocean outfall. Their models predict the phytoplankton response from the interaction of the kind and rate of nutrient loading and the hydrodynamic dis- persal rates. This technique, although not perfect, facilitates evaluation of the ecological impact of given nutrient loads, but does not help in deciding what degree of artificial en- richment is safe or acceptable.

Recommendations

• **Untreated or treated municipal sewage dis- charges should be recognized as a major source of toxic substances. Recommendations for these con- stituents will limit the amount of sewage effluent that can be dispersed into estuaries. Reduced degradation rates of highly dispersed materials**

should be considered if the effluent contains refractory organic material. Undegradable synthetic organic compounds do not cause oxygen depletion but can still adversely affect the ecosystem. Maintenance of dissolved oxygen standards will not prevent the potentially harmful buildup of these materials. Specific quantitative analyses should be done to identify and assess the abundance of these compounds.

• The addition of any organic waste to the marine environment should be carefully controlled to avoid decomposition which would reduce the oxygen content of the water below the levels specified in the recommendations for oxygen.

• Neither organic matter nor fertilizers should be added that will induce the production of organic matter by normal biota to an extent causing an increase in the size of any natural anoxic zone in the deeper waters of an estuary.

• The natural ratios of available nitrogen to total phosphorus should be evaluated under each condition, and the element actually limiting plant production should be determined. Control of the amount of the limiting element added to the water will generally control enrichment.

• If the maximum amounts of available nitrogen and phosphorus in domestic waste increase the concentration in receiving waters to levels of 50 micrograms per liter of phosphorus and 360 micrograms per liter of nitrogen, enough organic matter would be produced to exhaust the oxygen content of the water, at the warmest time of the year under conditions of poor circulation, to levels below those recommended (see p. 275). These concentrations of nutrients are clearly excessive.

• The potential presence of pathogenic bacteria and viruses must be considered in waters receiving untreated or treated municipal sewage effluents. The present quality standards for fecal coliform counts (see pp. 31-32) should be observed. The procedures for the examination of seawater and shellfish as recommended by Hosty et al. (1970)[408] should be used.

• Disposal of sludge into coastal waters may adversely affect aquatic organisms, especially the bottom fauna. Periodic examination samples should determine the spread of such an operation to aid in the control of local waste material loads. The probable transport by currents should be carefully considered. The dumping of· sludge into marine waters should be recognized as a temporary practice.

• Disposal of organic wastes into the deep-sea is not recommended until further studies on their fate, their effect on the deep-sea fauna, and the controllability of such a procedure have been completed.

SOLID WASTES, PARTICULATE MATTER, AND OCEAN DUMPING

Disposal of solid wastes has become one of the most urgent and difficult problems in crowded urban centers. Ocean disposal of these waste materials is receiving increased attention as land suitable for disposal becomes increasingly difficult to find.

Solid wastes are of many types and each may have a different impact on the marine environment. Household and commercial rubbish as well as automobiles and sewage sludge are disposed of at sea. Industrial wastes may be either solid or dissolved material, of varying toxicity. Harbor channels need continuous dredging, temporarily increasing the suspended sediment load, and the spoils often are dumped in coastal waters. Building rubble and stone also often are placed in the sea. The impact of disposal of these different materials into the ocean will range from innocuous to seriously damaging.

Particulate material is also discharged to the ocean by surface runoff, sewage outfalls, and storm sewers (Municipality of Metropolitan Seattle 1965).[464] Much of this material settles to the bottom at or near the discharge site (Gross 1970).[443] An increasingly important method of disposal is that of barging solids offshore to be dumped in coastal areas. Table IV-10 shows compilation of the amoun· of wastes barged to sea in 1968 on the Pacific, Atlantic and Gulf Coasts (Smith and Brown 1969).[476]

Dredge Spoils

Dredge spoils make up a major share of sea disposal operations. Their composition depends upon the source from which they were obtained. Saila et al. (1968)[472] were able to differentiate between dredged spoil from Providence Harbor dumped offshore and sediments of the natural bottom in the dumping area (Rhode Island Sound). Gross (1970)[443] suggests that dredge spoil generally consists of a mixture of sands, silts, and wastes which form the surface deposits in harbors. He compared minor element concen-

TABLE IV-10—Ocean Dumping: Types and Amounts, 1968

Waste type	(In tons) Atlantic	Gulf	Pacific	Total
Dredge spoils	15,808,000	15,300,000	7,320,000	38,428,000
Industrial wastes	3,013,200	696,000	981,300	4,690,500
Sewage sludge	4,477,000	0	0	4,477,000
Construction and demolition debris	574,000	0	0	574,000
Solid waste	0	0	26,000	26,000
Explosives	15,200	0	0	15,200
Total	23,887,400	15,966,000	8,327,300	48,210,700

Council on Environmental Quality 1970[444].

rations in harbor sediments, dredged wastes, and continental shelf sediments. The median values of observed con-
:e   ions were clearly different, although the ranges of
:o.. .trations overlapped.

The proportion of dredging spoils from polluted areas is llustrated in Table IV-11.

A variety of coastal engineering projects involve changes n suspended loads and sedimentation (Ippen 1966,[447] Nicker 1965[480]). Because important biotic communities nay inhabit the sites selected for these projects, conflicts arise concerning navigational, recreational, fisheries, conservation, and municipal uses of the areas (Cronin et al. 1969).[436] Although our knowledge about the effects is imited and the literature is widely scattered, Copeland and Dickens (1969)[433] have attempted to construct a picture of how dredging affects estuarine ecosystems from information gathered in the upper Chesapeake Bay, Maryland, Redfish Bay, Texas, and an intracoastal canal in South Carolina.

The biological effects of suspended loads, sedimentation, dredging methods and spoil disposal may range from gross damage, such as habitat destruction and smothering, to more subtle effects under low but chronic conditions of sedimentation over long periods of exposure. The channelization, dumping of spoils, dredging, and filling in the Gulf Coast estuaries had destroyed roughly 200,000 acres of swamp, marsh, and bay bottom areas by 1968 (Chapman 19^ '[32] Marshall 1968[459]).

    tures of clays, silts, fine sands, and organic matter, sometimes referred to as "faunally rich muddy sand," tend to support larger benthic populations than coarse clean unstable sands, gravels, or soft muds (Carriker 1967)[430] over or through which locomotion may be difficult (Yonge 1953).[482] Close relationships exist between the presence of organic matter, the mechanical nature of sediments, and infaunal feeding habits (Sanders 1956,[473] 1958,[474] McNulty et al. 1962,[461] Brett cited by Carriker 1967[430]).

Ten years after dredging Boca Ciega Bay invertebrate recolonization of canal sediments (92 per cent silt and clay; 3.4 per cent carbon) was negligible. None of 49 fish species caught in these canals (as compared to 80 species in undredged areas) was demersal, apparently because of the lack of benthic fish food organisms on or in the canal de-

posits (Taylor and Saloman 1968).[477] Breuer (1962)[429] noted that layers of dead oyster shell in South Bay corresponded to layers of deposited spoil from dredging and re-dredging of the Brownsville Ship Channel. He thought that this suggested destruction of South Bay oyster populations with each dredging operation.

Pfitzenmeyer (1970)[470] and Flemer et al. (1967)[441] noted a 71 per cent reduction in average number of individuals and a marked reduction in diversity and biomass in a spoil area in upper Chesapeake Bay after dredging ceased. One and one half years after dredging, the number of individuals and species diversity of the spoil disposal area, but not in the channel, were the same as those of the surrounding area.

In lower Chesapeake Bay, Harrison et al. (1964)[444] observed a transitory effect of a dredging and spoil disposal operation on infauna. Resettlement of the dredged and disposal areas was very rapid by active migration and hydrodynamic distribution of juveniles.

Mock (1967)[463] noted that an unaltered shore in Clear Lake, Texas, produced 2.5 times more post larval and juvenile brown shrimp (*Penaeus aztecus*) and 14 times more post larval and juvenile white shrimp (*Penaeus setiferus*) than a similar bulkheaded shore. In a laboratory study using similar substrates, Williams' (1958)[481] data suggested that the type of substrate may exert its influence through its effect on available cover, although a contributing factor may be the different food content of the substrate.

Bayless (1968)[427] observed higher average hatches of striped bass eggs (*Morone saxatilis*) on coarse sand (58.9 per cent) and a plain plastic pan (60.3 per cent) than on silt-sand (21 per cent), silt-clay-sand (4 per cent) or muck detritus (none). These results tend to support Mansueti's (1962)[458] and Huet's (1965)[446] contention that deposition of suspended matter may interfere with or prevent fish reproduction by destruction of demersal eggs in upper estuarine areas.

Sewage Sludges

Sewage sludges contain about 5 per cent solids which consist of about 55 per cent organic matter, 45 per cent aluminosilicates, and tend to contain concentrations of some heavy metals at least ten times those of natural sediments (Gross 1970).[443]

Sewage sludge has been dumped off New York Harbor since 1924 in the same area. Studies by Pearce (1970a,[465] b)[466] show that the normal bottom populations in an area of about 10 square miles have been eliminated and that the benthic community has been altered over an area of approximately 20 square miles. Even the nematodes, unusually tolerant to pollution, are relatively scarce in the smaller area. In areas adjacent to the sewage sludge disposal area the sea clams have been found to be contaminated by enteric bacteria and the harvest of these clams in this area has been prohibited. The oxygen content of the water near

TABLE IV-11—Estimated Polluted Dredge Spoils

	Total spoils (in tons)	Estimated percent of total polluted spoils⁰	Total polluted spoils (in tons)
Atlantic Coast	15,808,000	45	7,120,000
Gulf Coast	15,300,000	31	4,740,000
Pacific Coast	7,320,000	19	1,390,000
Total	38,428,000	34	13,250,000

s of polluted dredge spoils consider chlorine demand; BOD; COD; volatile solids; oil and grease; con.   .ns of phosphorous, nitrogen, and iron; silica content; and color and odor of the spoils.
Council on Environmental Quality 1970[454]

the bottom is very low, less than 10 per cent of saturation in August, the warmest time of year. Chemical analysis of the sludge deposits have shown not only high organic content but also high concentrations of heavy metals and petrochemicals. In this area of the New York Bight, fin-rot disease of fish has been observed and is being investigated (Pearce 1970b).[466] In laboratory tests it has been shown that sludge deposits can cause necrosis of lobster (*Homarus americanus*) and crab shells and tend to clog their gills so that survival of these species in contact with the sludge deposits is very brief. In other laboratory experiments, organisms given a choice of substrate tend to avoid the sludge material in favor of the walls of the container or other surfaces that were made available (Pearce 1970b).[466] These studies have indicated that the disposal of sewage sludge has had disastrous ecological effects on the populations living on or near the bottom.

Many aspects associated with sludge dumping in the New York Bight require further investigation. It is not known, for example, how much of the material being dumped there is accumulating and how much is being decomposed. The effects of heavy metals, of oxygen-demanding materials, and of other components are imperfectly understood. When the rate of delivery of organic waste materials to an aquatic environment exceeds its capacity to recover, the rate of deterioration can be rapid. If, or when, sewage sludge disposal in this particular area of the New York Bight is terminated studies could determine whether the bottom populations can repopulate the area.

Solid Wastes

The amount of household and commercial rubbish to be disposed of in the United States is about 5 lbs per capita per day and is expected to increase to 7-½ lbs per capita per day (for a larger population), by the end of the present decade. Proposals have been made to collect and bale waste for transportation to the sea where it would be dumped in waters 1000 meters deep or more. It would be necessary that the bales be compacted to a density greater than sea water so that they would sink, and that no loose floating objects would be released from the bale. Among the suggestions made is that the bales be wrapped in plastic to avoid any leaching from the contents.

Pearce (1971)[468] reports that bales of compacted garbage wrapped in plastic and reinforced paper disintegrated in a few weeks when placed in water 10 to 20 meters deep off the coast of New Jersey. Compacted bales of refuse were also anchored at a depth of 200 meters off the Virgin Islands Pearce (1970c).[467] These were retrieved and inspected after approximately three months of exposure. Little growth had occurred on the surface of the bales, but some polychaete worms had penetrated the bales to a depth of 2–3 cm., and the material within the bale had decomposed to a limited extent. Relatively high counts of total coliform bacteria (96,000 Most Probable Number, MPN) and of fecal coliforms (1,300 MPN) were found in materials retrieved from the interior of the bales, indicating prolonged survival or growth of these nonmarine forms and suggesting a possible hazard of introduction of pathogens to the sea. The ecological effects of disposing of these materials are inadequately known.

Disposal of solid wastes, including dredging spoils and sewage sludge into the deep waters off the edge of the Continental Shelf (more than 200 meters) has been frequently suggested as a way to protect the inshore biota. However, the rate of decomposition of organic material at the high pressure and low temperature of the deep sea is very much slower than it would be at the same low temperature at atmospheric pressure (Jannasch et al. 1971).[449] The organisms in the deep sea have evolved in an extremely constant environment. They are, therefore, unaccustomed to the unusual stresses which confront organisms in more variable situations typical of coastal waters. Biologists interested in studying the bottom populations of the deep sea are extremely concerned about altering these populations before there is an opportunity to study them thoroughly.

Industrial Wastes

A wide variety of industrial waste is being dumped at sea. If this is discharged as a solution or slurry from a moving ship or barge it will be diluted in the turbulent wake and by the normal turbulence of the sea (Ford and Ketchum 1952).[442] The recommendations for mixing zones (p. 231) and for the constituents of specific waste material included should be applied to each such operation.

One such operation which has been extensively studied is the disposal of acid-iron wastes in the New York Bight (Redfield and Walford 1951,[471] Ketchum et al. 1951,[451] Vacarro et al. 1972,[478] Wiebe et al. *in press* 1972[479]). Even though this disposal has proceeded for over twenty years, no adverse effects on the marine biota have been demonstrated. The acid is rapidly neutralized by sea water and the iron is precipitated as nontoxic ferric hydroxide. This is a flocculant precipitate and the only accumulation above normal background levels in the sediments appears to be in the upper end of the Hudson Canyon, close to the specified dumping area. The so-called "acid grounds" have become a favored area among local blue fishermen. More toxic materials would clearly present an entirely different set of problems. This illustrates the need for a rational approach to problems of ocean dumping.

Other Solid Wastes

Automobiles are sometimes dumped at sea, and some work has been done on an experimental basis in an effort to determine whether artificial reefs can be created from them to improve sport fishing. There is evidence that the number of fish caught over these artificial reefs is greater than over a flat level bottom, but it is not yet certain whe

this represents an aggregation of fishes already in the area or an actual increase in productivity.

Disposal of building rubble (brick, stone, and mortar) a is not widely practiced. Presumably, this material could form artificial reefs and attract populations of fish, both as a feeding ground and by providing some species with cover. Obviously, the bottom organisms present would be crushed or buried, but Pearce (1970a,[465] b)[466] found no permanent detrimental effects in the building rubble disposal site off New York City.

Suspended Particulate Materials

In addition to specific waste disposal operations, suspended particulate material, seston, may be derived from other sources, and have a variety of biological effects. Particulate material can originate from detritus carried by rivers, atmospheric fallout, biological activity, chemical reactions, and resuspension from the bottom as a result of currents, storms, or dredging operations. The particles introduced by rivers can be rock, mineral fragments, and clay serving as a substrate for microorganisms or affecting light transmission in the water column. In addition, organic matter fragments, which make up 20 to 40 per cent of particles in coastal waters (Biggs 1970,[428] Manheim et al. 1970[467]) may comprise 50 per cent to 80 per cent of suspended material further offshore. Particle concentrations generally range from 1 to 30 mg/l in coastal waters to about 0 1 mg/l at the surface in the open ocean. Higher concentrations occur near the bottom.

The estimated yearly sediment load from rivers to the world oceans is estimated at 20 to 36 $\times$ 10^8 tons with 80 per cent originating in Asia (Holeman 1968).[445] Much of this load is trapped in estuaries and held inshore by the general landward direction of subsurface coastal currents (Meade 1969).[462] Gross (1970)[443] suggests that 90 per cent or more of particles originating from rivers or discharged to the oceans settles out at the discharge site or never leaves the coastal zone.

Average seston values may more than double from natural causes during a tidal cycle. Biggs (1970)[428] observed concentrations in the upper Chesapeake Bay ranging from less than 20 mg/l to greater than 100 mg/l during a single day. Resuspension of bottom sediments by storm waves and currents induced by wind were responsible for this range of concentrations. Masch and Espey (1967)[460] found that the total suspended material concentrations in Galveston Bay, Texas, ranged from 72 mg/l in the surface water of the ship channel to over 150 g/l six inches above the bay bottom near dredging operations. Normal background concentrations in Galveston Bay during times of strong wind action were 200 to 400 mg/l. Background values observed by Mackin (1961)[456] in Louisiana marshes ranged from 20 to 2 g/l. Depending on the amount of overburden, operating times, and rate of discharges, Masch and Espey

(1967)[460] recorded suspended fixed solids concentrations in dredge discharges ranging from 3,000 to 29,100 mg/l.

The basic relationships between physical and chemical aspects of suspended and deposited sediments and the responses of estuarine and marine organisms are poorly understood (Sherk 1971).[475] However, there is general agreement that particulate material in suspension or settling on the bottom can affect aquatic organisms both directly and indirectly, by mortality or decreased yield.

Particles suspended in the water column can decrease light penetration by absorption and scattering and thus limit primary productivity. Resuspended sediments exert an oxygen demand on the order of eight times that of the same material in bottom deposits (Isaac 1965).[448] Jitts (1959)[450] found that 80 to 90 per cent of phosphate in solution was absorbed by silt suspensions which might also modify the rate of primary production. However, exchange rates and capacity of sediment can maintain a favorable level of phosphate (1 micromole/l) for plant production (Pomeroy et al. 1965).[469] Carritt and Goodgal (1954)[431] postulated a mechanism for phosphate removal, transport, and regeneration by the sediment-phosphate sorption complex at different temperatures, pH values, and salinities.

Evidence tends to support the contention that nutrient fertilization and possible release of toxic materials can occur with resuspension of bottom material in the water column (Gross 1970).[443] This may occur during dredging, disposal and dumping operations, reagitation during storms or floods and from beach erosion. In upper Chesapeake Bay total phosphate and nitrogen were observed to increase over ambient levels by factors of 50 to 1,000 near an overboard spoil disposal project, but no gross effects were observed in samples incubated with water from the spoil effluent (Flemer et al. 1967,[441] Flemer 1970[440]).

Oyster and clam eggs and larvae demonstrate a remarkable ability to tolerate the variable turbidities of the estuarine environment at concentrations up to 4.0 g/l (Carriker 1967,[430] Davis and Hidu 1969[438]). Survival and growth of these egg and larval stages reported by Davis (1960)[437] and Loosanoff (1962),[452] however, indicated a significant effect on survival at suspended particle concentrations of as little as 125 mg/l. Earlier life stages of the oyster tend to be more sensitive to lower concentrations of suspended material than adults. However, the effects on survival and growth cannot wholly be attributed to particle sizes and concentrations since different particle types may have markedly different effects at similar concentrations. The adult American oyster (*Crassostrea virginica*) appears to be a remarkably silt-tolerant organism when not directly smothered by deposited sediments (Lunz 1938,[454] 1942[455]). Significantly, mortality of adult oysters was not evident with suspended sediment concentrations as high as 700 mg/l (Mackin 1961),[456] but there was a drastic reduction in pumping rates (57 per cent at 100 mg/l of silt) observed by Loosanoff and Tommers (1948)[453] and Loosanoff

(1962[452]). Apparently adult oysters may pump at reduced rates throughout most of their lives when the background suspended particulate matter persists at values observed by Biggs (1970)[428] and Masch and Espey (1967[460]).

Organisms that colonize hard surfaces must contend with a sediment mat of varying thickness. While motile fauna may be able to adjust to short range vertical bottom alterations from scour or deposition, ".... the capacity and behavior of less motile estuarine benthos in adjustment to relatively rapid fluctuations in the bottom level are little known. Fixed epifauna, like oysters and barnacles, perish when covered by sediment, adjustment occurring only indirectly through later repopulation of the area from elsewhere" (Carriker 1967).[430]

The highly variable nature of suspended loads (Biggs 1970),[428] the resuspension of bottom accumulations by currents, tidal action and wind, and the feeding and filtering activities of benthic organisms complicate the determination of threshold values or limiting conditions for aquatic organisms. Data are difficult to compare because of differences in methods and approaches. This may indicate a lack of understanding of sedimentation and the difficulty in distinguishing between the effect of light attenuation by suspended particles and the effects of these particles on growth and physiology of estuarine and marine organisms (Municipality of Metropolitan Seattle 1965).[464] The observed responses of organisms may not be due to turbidity or total suspended sediment concentration, but to the number of particles, their densities, sizes, shapes, types, presence and types of organic matter and the sorptive properties of the particles.

Physical alterations in estuaries and offshore dumping have had obvious effects on estuarine and marine biological resources. These effects have been given little consideration in project planning, however, and little information exists concerning the magnitude of biological change because few adequate studies have been attempted (Sherk 1971).[475] Areas of high biological value, such as nursery grounds or habitats for commercially important species, must be protected from sediment damage (Municipality of Metropolitan Seattle 1965).[464] For example, the exceptionally high value of the Upper Chesapeake as a low salinity fish nursery area has been demonstrated (Dovel 1970).[439] Larvae and eggs are particularly sensitive to environmental conditions, and sediment-producing activities in this type of area should be restricted to seasons or periods of least probable effects.

Results reported from the study of this area, concerning seasonal patterns of biota, the nature of the sediments, and physical hydrography of the area, can be applied to the other areas being considered for dredging, disposal, and dumping. These data, in addition to careful pre-decision surveys or research conducted at the site under consideration should provide a guide to efforts to minimize damage and enhance desirable features of the system (Cronin 1970).[435]

Adequate knowledge of local conditions at sites selected for any sediment-producing activity is essential, however. This will generally require preproject surveys for each site selected because knowledge of ecological impacts of the activities is limited. Data should be obtained on the ".... biological values of the areas involved, seasonal patterns of the biota, the nature of the sediments, physical hydrography of the area, and the precise location of productive or potential shellfish beds, fish nursery areas and other areas of exceptional importance to human uses..." which are close to or in the site selected (Cronin 1970).[435]

Appropriate laboratory experiments are also required. These should have value in predicting effects of sedimentation in advance of dredging operations. Eventually, the results of these experiments and field observations should yield sets of environmental conditions and criteria, for adequate coastal zone management and competent guidance to preproject decision making (Sherk 1971).[475]

The presence of major benthic resources (e.g., oyster beds, clam beds) in or near the selected area should be cause for establishment of a safety zone or distance limit between them and the sediment-producing activity. This would control mortality caused by excessive deposition of suspended particulate material on the beds and prevent spread of spoil onto the beds from the disposal or dumping sites. Biggs (1970)[428] found that the maximum slope of deposited spoil was 1:100 and the average slope was 1:500 in the Upper Chesapeake. These slopes may prove useful in estimating safety zone limits on relatively flat bottoms. times, the safety zone would have to be quite large. For example, the areas in New York Bight which are devoid of naturally occurring benthos in the sewage sludge and dredging spoil disposal areas were attributed to toxins, low dissolved oxygen, and the spreading of the deposits (Pearce 1970a).[465] The presence or absence of bottom currents or density flows should be determined (Masch and Espey 1967).[460] If these are present, measures must be taken to prevent transport of deposits ashore or to areas of major benthic resources.

Tolerable suspended sediment levels or ranges should accommodate the most sensitive life stages of biologically important species. The present state of knowledge dictates that the critical organism must be selected for each site where environmental modification is proposed.

Recommendations

The disposal of waste materials at sea, or the transport of materials for the purpose of disposal at sea should be controlled. Such disposal should be permitted only when reasonable evidence is presented that the proposed disposal will not seriously damage the marine biota, interfere with fisheries operations or with other uses of the marine environment such as navigation and recreation,

cause hazards to human health and welfare. The following guidelines are suggested:

Disposal at sea of potentially hazardous materials such as highly radioactive material or agents of chemical or biological warfare should be avoided.

- Toxic wastes should not be discharged at sea in a way which would adversely affect the marine biota. The toxicity of such materials should be established by bioassay tests and the concentrations produced should conform to the conditions specified in the discussion of mixing zones (pp. 231–232).
- Disposal of materials containing settleable solids or substances that may precipitate out in quantities adversely affecting the biota should be avoided in estuarine or coastal waters.
- Solid waste disposal at sea should be avoided if floating material might accumulate in harbors or on the beaches or if such materials might accumulate on the bottom or in the water column in a manner that will deleteriously affect deep sea biota.

In connection with dredging operations or other physical modifications of harbors and estuaries which would increase the suspended sediment load, the following types of investigations should be undertaken:

- Evaluation of the range and types of particles to be resuspended and transported, where they will settle, and what substratum changes or modifications may be created by the proposed activities in both the dredged and the disposal areas.
- Determination of the biological activity of the water column, the sediment-water interface, and the substrate material to depths which contain burrowing organisms.
- Estimation of the potential release into the water column of sediments, those substances originally dissolved or complexed in the interstitial water of the sediments, and the beneficial or detrimental chemicals sorbed or otherwise associated with particles which may be released wholly or partially after resuspension.
- Establish the expected relationship between properties of the suspended load and the permanent resident species of the area and their ability to repopulate the area, and the transitory species which use the area only at certain seasons of the year.

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Section III—FRESHWATER AQUATIC LIFE AND WILDLIFE

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The biota of a natural aquatic ecosystem is the result of evolutionary processes in the course of which a delicate balance and complex interactions were established among various kinds of organisms and between those organisms and their environment. Some species can live in a wide range of environmental conditions and are found in many different systems throughout the world. Other species are restricted and their distribution is limited to certain habitats or in some cases to only one. Frequently, it is the latter group of species that have been most useful to man. Minor changes in their environments, especially if such changes are rapid, may upset the ecological balance and endanger the species.

Man has the ability to alter—to impair or improve—his env' nment and that of other organisms. His use of water to   se of wastes of a technological society and his other :.:erations of aquatic environments have degraded his water resources. Water pollutants may alter natural conditions by reducing the dissolved oxygen content, by changing the temperature, or by direct toxic action that can be lethal or, more subtly, can affect the behavior, reproduction, and physiology of the organisms. Although a substance may not directly affect a species, it may endanger its continued existence by eliminating essential sources of food and metabolites. Furthermore, conditions permitting the survival of a given organism at one stage of its life may be intolerable at another stage.

This Section evaluates criteria and proposes recommendations that reflect scientific understanding of the relationships between freshwater aquatic organisms and their environment. Anything added to or removed from natural waters will cause some change in the system. For each use f water there are certain water quality characteristics that should be met to ensure the suitability of the water for that use.

The following general recommendations apply to a wide variety of receiving systems and pollutants:

- More stringent methods of control or treatment, or both, of waste inputs and land drainage should be applied to improve water quality as the demand for use increases.

- In recognition of the limitations of water quality management programs, consideration should be given to providing reserve capacity of receiving waters for future use.
- Bioassays and other appropriate tests, including field studies, should be made to obtain scientific evidence on the effect of wastewater discharges on the environment. Test procedures are recommended in this report.
- A survey of the receiving system to assess the impact of waste discharges on the biological community should be made on a regular basis, particularly prior to new discharges. Such surveys especially should cover the seasons most critical to the biological community. Background laboratory data should include bioassays using important local aquatic organisms and associated receiving waters. In addition to the more comprehensive surveys, some form of biomonitoring in the receiving system should be carried out routinely. A suggested list of ecological considerations is included in the section on Biological Monitoring.
- One of the principal goals is to insure the maintenance of the biological community typical of that particular locale or, if a perturbed community exists, to upgrade the receiving system to a quality which will permit reestablishment of that community.

COMMUNITY STRUCTURE AND PROTECTION OF SIGNIFICANT SPECIES

The natural aquatic environment includes many kinds of plants and animals that vary in their life history and in their chemical and physical requirements. These organisms are interrelated in many ways to form communities. Aquatic environments are protected out of recreational and scientific interest, for aesthetic enjoyment, and to maintain certain organisms of special significance as a source of food. There are two schools of thought as to how this can be accomplished. One is to protect the significant species, the assumption being that by so doing, the entire system is protected. The other approach is to protect the aquatic com-

munity, the assumption being that the significant species are not protected unless the entire system is maintained.

Community Structure

Because chemical and physical environments are continually changing—sometimes gradually and sometimes catastrophically—many species are necessary to keep the aquatic ecosystems functioning by filling habitats vacated because of the disappearance of other species. Likewise, when one kind of organism becomes extremely abundant because of the disappearance of one or more species, predator species must be available to feed on the overabundant species and keep it from destroying the functioning of the community. In a balanced ecosystem, large populations of a single species rarely maintain themselves over a long time because predators quickly reduce their number.

Therefore, the diverse characteristics of a habitat are necessary to the maintenance of a functioning ecosystem in the process of evolution. In the fossil record are found many species that were more common at one time than they are today and others that have been replaced entirely. If it were not for diverse gene pools, such evolutionary replacement would not have been possible.

Some aquatic environments present unusual extremes in their chemical and physical characteristics. They support highly specialized species that function as ecosystems in which energy flows and materials cycle. If these species are not present and functioning in this manner, such areas may become aesthetically distasteful, as has occurred for example in the alkaline flats of the West and the acid bogs of the Northeast, Midwest, and East.

Rare habitats support rare organisms that become extinct or endangered species if their habitats are impaired or eliminated. In the aquatic world there are many species of algae, fish, and invertebrates that are maintained only in such rare, fragile habitats. Man must understand th- if he is to appreciate the process of evolution and ι. trend of ecological change that brings about drastic alterations to fauna and flora.

Protection of Significant Aquatic Species

An essential objective of freshwater quality recommendations is the protection of fish and other aquatic organisms for sport or commercial harvesting. This does not imply that all other aquatic species will be subject to potential extinction, or that an unaltered environment is the goal to be attained in all cases. The average person is usually interested in only a small number of aquatic species, principally fish; but it remains necessary to preserve, in certain unique or rare areas, a diversified environment both for scientific study and for maintaining species variety.

It is sometimes difficult to justify protection of isolated organisms not used by man unless it can be documented that they are ultimately essential to the production of desirable biota. In some instances it may be that a critical, sensitive species, irreplaceable in the food web of another more important species, is one known only to the biologist. In such instances, protection of the "less important" sensitive species could justifiably determine the water quality recommendation.

Because no single recommendation can protect all ꞌ portant sport and commercial species unless the ι. sensitive is protected, a number of species must be considered. The most sensitive species provide a good estimate of the range of sensitivity of all species.

ASSIMILATIVE CAPACITY OF FRESHWATER RECEIVING SYSTEMS

Waste discharges do not just go into water but rather into aquatic ecosystems. The capacity of such a system to receive and assimilate waste is determined by the physical, chemical, and biological interactions within the system. Thus the response is a function of the characteristics of both the ecosystem and the nature and quantity of the waste. Understanding the unique characteristics of each ecosystem will enable wise users to develop means to obtain maximum beneficial use with minimal damage to the system. Each aquatic ecosystem is sufficiently unique to require professional ecological advice to define the problems associated with waste discharge into a particular ecosystem. Such a procedure has not been customary in the past, and this has led to some unfortunate consequences, but the practice is becoming increasingly prevalent.

Aquatic systems receive from natural and man-made sources a variety of organic and inorganic materials. These materials through physical, chemical, and biological interaction are transported, rendered, converted, respired, incorporated, excreted, deposited and thus assimilated by the system. However, not all systems can receive and assimilate the same quantity or kinds of waste materials. The capacity of each system to transform waste without damage to the system is a function of the complexity of environmental factors.

Physical factors such as flow velocity, volume of water, bottom contour, rate of water exchange, currents, depth, light penetration, and temperature, govern in part the ability of a system to receive and assimilate waste materials.

This ability is a function of the reaeration capability of the system, the physical rendering of wastes, and other physical, chemical, and biological factors. Most flowing systems have a greater reaeration capacity than standing waters. Furthermore, flowing systems are open systems with continual renewal of water, whereas standing waters are closed systems and act as traps for pollutants.

Temperature plays a vital role in the rate of chemical reactions and the nature of biological activities in freshwater and in governing the receiving and assimilative capacity of a system. Most temperate lakes are thermally stratified part of the year, except when there are small differences between surface and bottom temperatures in the spring and fall. As a consequence little exchange occurs between layers during the period of stratification. In organically enriched lakes and reservoirs, depletion of soluble oxygen typically occurs in the bottom layer because there is little or no photosynthesis and little mixing with the oxygen-rich surface layer. As a result, substances are released from the sediments because certain compounds have a much greater solubility in a reduced state.

The unique chemical characteristics of water govern in part the kinds and quantities of waste a system may receive. Some of the important chemical characteristics are hardness, alkalinity, pH (associated with the buffering capacity), and nutrients such as carbon, nitrogen, and phosphorus. Because of synergistic or antagonistic interaction with receiving water, the effects of a waste on a wide variety of receiving systems are hard to predict.

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When a liquid discharge is made to a receiving system, a zone of mixing is created. Although recent public, administrative, and scientific emphasis has focused on mixing zones for the dispersion of heated discharges, liquid wastes of all types are included in the following considerations. (For a further discussion of Mixing Zones see Appendix II–A.)

DEFINITION OF A MIXING ZONE

A mixing zone is a region in which a discharge of quality characteristics different from those of the receiving water is in transit and progressively diluted from the source to the receiving system. In this region water quality characteristics necessary for the protection of aquatic life are based on time-exposure relationships of organisms. The boundary of a mixing zone is where the organism response is no longer time-dependent. At that boundary, receiving system water quality characteristics based on long-term exposure will protect aquatic life.

Recommendation

Although water quality characteristics in mixing zones may differ from those in receiving systems, to protect uses in both regions it is recommended that mixing zones be free of substances attributable to discharges or wastes as follows:

- materials which form objectionable deposits;
- scum, oil and floating debris;
- substances producing objectionable color, odor, taste, or turbidity;
- conditions which produce objectionable growth of nuisance plants and animals.

GENERAL PHYSICAL CONSIDERATIONS

The mass emission rates of the most critical constituents and their relationship to the recommended values of the material in the receiving water body are normally the primary factors determining the system-degradation potential of an effluent. Prior to establishment of a mixing zone the factors described in Waste Capacity of Receiving Waters (Section IV, pp. 228–232) and Assimilative Capacity (This Section, p. 111) should be considered and a decision made on whether the system can assimilate the discharge without damage to beneficial uses. Necessary data bases may include:

- Discharge considerations—flow regime, volume, design, location, rate of mixing and dilution, plume behavior and mass-emission rates of constituents including knowledge of their persistence, toxicity, and chemical or physical behavior with time.
- Receiving system considerations—water quality, local meteorology, flow regime (including low-fl' records), magnitude of water exchange at poin\ discharge, stratification phenomena, waste capacity of the receiving system including retention time, turbulence and speed of flow as factors affecting rate of mixing and passage of entrained or migrating organisms, and morphology of the receiving system as related to plume behavior, and biological phenomena.

Mathematical models based in part on the above considerations are available for a variety of ecosystems and discharges. (See Appendix II-A.) All such mathematical models must be applied with care to each particular discharge and the local situation.

Recommendation

To avoid potential biological damage or interference with other uses of the receiving system it is recommended that mixing zone characteristics be defined on a case-by-case basis after determination that the assimilative capacity of the receiving system can safely accommodate the discharge taking into consideration the physical, chemical, and biological characteristics of the discharge and the receiving system, the life history and behavior of organisms in the receiving syst and desired uses of the waters.

GENERAL BIOLOGICAL CONSIDERATIONS

Organisms in the water body may be divided into two g ⁓s from the standpoint of protection within mixing z   . (1) nonmobile benthic or sessile organisms; (2) weak and strong swimmers.

1. Nonmobile benthic or sessile organisms in mixing zones may experience long or intermittent exposures exceeding recommended values for receiving systems and therefore their populations may be damaged or eliminated in the local region. Minimum damage to these organisms is attained by minimizing exposure of the bottom area to concentrations exceeding levels resulting in harm to these organisms from long-term exposure. This may be accomplished by discharge location and design.

The mixing zone may represent a living space denied the subject organisms and this space may or may not be of significance to the biological community of the receiving system. When planning mixing zones, a decision should be made in each case whether the nonmobile benthic and sessile organisms are to be protected.

Recommendation

To protect populations of nonmobile benthic and sessile organisms in mixing zones it is recommended that the area of their habitat exposed to water quality poorer than recommended receiving system quality be minimized by discharge location an⁻ᵈ design or that intermittent time-exposure h   ⁚y relationships be defined for the organisms' we11-being.

2. Biological considerations to protect planktonic and swimming organisms are related to the time exposure history to which critical organisms are subjected as they are carried or move through a mixing zone. The integrated time exposure history must not cause deleterious effects, including post-exposure effects. In populations of important species, effects of total time exposure must not be deleterious either during or after exposure.

Weak swimmers and drifting organisms may be entrained into discharge plumes and carried through a mixing zone. In determining the time exposure history and responses of the organisms, the possibility of delayed effects, such as death, disease, and increased vulnerability to predation, should be investigated.

Strong swimmers are capable of moving out of, staying out of, or remaining in a mixing zone. Water quality characteristics which protect drifting organisms should also protect migrating fish moving through mixing zones. However, there are some discharges that attract animals into discharge channels and mixing zones where they are vulnerable to death or shock due to short-term changes in water quality, such as rapid temperature fluctuations. This vr ⁻ability should be recognized and occurrences that e.   ⸴ it should be guarded against (see Chlorine, page 189).

Some free-swimming species may avoid mixing zones and as a consequence the reduced living space may limit the population.

Free-swimming species may be attracted to a discharge. Chronic low-level exposure to toxicants may cause death or affect growth, reproduction or migratory instincts, or result in excessive body-burdens of toxicants hazardous for human consumption.

Recommendation

To protect drifting and both weak and strong swimming organisms in mixing zones it is recommended that scientifically valid data be developed to demonstrate that the organisms can survive without irreversible damage, the integrated time-exposure history to be based on maximum expected residence time so that deleterious effects on populations of important species do not occur.

MEETING THE RECOMMENDATIONS

In mixing zones the exposure of organisms to stress is of greater intensity but usually of shorter duration than in the receiving waters, assuming no attraction by the discharge. The objective of mixing zone water quality recommendations is to provide time exposure histories which produce negligible or no effects on populations of critical species in the receiving system. This objective can be met by: (a) determination of the pattern of exposure in terms of time and concentration in the mixing zone due either to activities of the organisms, discharge schedule, or currents affecting dispersion; and (b) determination that delayed effects do not occur.

Protection would be achieved if the time of exposure met the relationship $T/ET(x) \leq 1$ where T is the time of the organism's exposure in the mixing zone to a specified concentration, and $ET(x)$ is the effective time of exposure to the specified concentration, C, which produces (x) per cent response in a sample of the organisms, including delayed effects after extended observation. The per cent response, (x), is selected on the basis of what is considered negligible effects on the total population and is then symbolized $ET(25)$, $ET(5)$, $ET(0.1)$, etc.

Because concentrations vary within mixing zones, a more suitable quantitative statement than the simple relationship $T/ET(x) \leq 1$ is:

$$\frac{T_1}{ET(x) \text{ at } C_1} + \frac{T_2}{ET(x) \text{ at } C_2} + \frac{T_3}{ET(x) \text{ at } C_3} \cdots$$

$$+ \frac{\overline{T_n}}{ET(x) \text{ at } C_n} \leq 1$$

where the time of exposure of an organism passing through the mixing zone has been broken into increments, T_1, T_2, T_3, etc. The organism is considered to be exposed to concen-

tration C_1 during the time interval T_1, to concentration C_2 during the time interval T_2, etc. The sum of the individual ratios must then not exceed unity. (See caveat below, Short Time Exposure Safety Factors.)

Techniques for securing the above information, application to a hypothetical field situation, comments, caveats, and limitations are expressed in Appendix II–A, Mixing Zones, Development of Integrated Time Exposure Data, p. 403. Tabular data and formulae for summation of short-term effects of heated discharges on aquatic life are provided in the Heat and Temperature discussion, page 151.

SHORT TIME EXPOSURE SAFETY FACTORS

This concept of summation of short-term effects and extrapolation is an approach which tests the applicability of present bioassay methodology and precision and may not be universally applicable to all types of discharges. Conservatism in application should be practiced. When developing the summation of short-term thermal effects data, a safety factor of two degrees centigrade is incorporated. In development of summation of short-term toxicity effects data, a safety factor exists if a conservative physiological or behavioral response is used with effective time of exposure. However, when mortality is the response plotted, an application factor must be incorporated to provide an adequate margin of safety. This factor can most easily be applied by lowering the sum of the additive effects to some fraction of 1 so that the sum of $T_1/(ET(x)$ at $C_1) \cdots + T_n/(ET(x)$ at $C_n)$ then equals 0.9, or less. The value must be based on scientific knowledge of the organism's behavior and response to the contaminants involved.

Recommendation

When developing summation of short-term exposure effects it is recommended that safety factors, application factors, or conservative physiological or behavioral responses be incorporated into the bioassay or extrapolation procedures to provide an adequate margin of safety.

OVERLAPPING MIXING ZONES

If mixing zones are contiguous or overlap, the formula expressing the integrated time exposure history for single plumes should be adjusted. Synergistic effects should be investigated, and if not found, the assumption may be made that effects of multiple plumes are additive.

Recommendation

When two plumes are contiguous or overlap and synergistic effects do not occur, protection for aquatic life should be provided if the sum of the fractions of integrated time exposure effects for each plume total ≤0.5. Alternatively, protection should be provided if the sum of the fractions for

both plumes (or more than two contiguous or overlapping plumes) is ≤1. (See caveat above, Short Time Exposure Safety Factors.)

INTERIM GUIDELINE

In the event information on summation effects of the integrated time exposure history cannot be satisfactorily provided, a conservative single figure concentration can be used for all parts of the mixing zone until more detailed determinations of the time-exposure relationships are developed. This single, time-dependent median lethal concentration should be subject to the caveats found throughout this Section and Appendix II–A regarding delayed effects and behavioral modifications. Because of the variables involved, the single value must be applied in the light of local conditions. For one situation a 24-hour LC50 might be adequate to protect aquatic life. In another situation a 96-hour LC50 might provide inadequate protection.

CONFIGURATION AND LOCATION OF MIXING ZONES

The time-dependent three dimensional shape of a discharge plume varies with a multitude of receiving system physical factors and the discharge design. While time exposure water quality characteristics within mixing zones are designed to protect aquatic life, thoughtful placement of the discharge and planned control of plume behavior may increase the level of ecosystem protection, e.g., floating the plume on the surface to protect the deep water c channel; discharging in midstream or offshore to protect biologically-important littoral areas; piping the effluent across a river to discharge on the far side because fish historically migrate on the near side; or piping the discharge away from a stream mouth which is used by migrating species. Such engineering modifications can sometimes accomplish what is necessary to meet biological requirements.

Onshore discharges generally have more potential for interference with other uses than offshore discharges. For example the plume is more liable to impinge on the bottom in shallow areas of biological productivity and be closer to swimming and recreation areas.

PROPORTIONAL RELATIONSHIP OF MIXING ZONES TO RECEIVING SYSTEMS

Recommendations for mixing zones do not protect against the long-term biological effects of sublethal conditions. Thus water quality requirements necessary to protect all life stages and necessary functions of aquatic organisms such as spawning and larval development, are not provided in mixing zones, and it is essential to insure that adequate portions of every water body are free of mixing zones. The decision as to what portion and areas must be retained receiving water quality values is both a social and scien

decision. In reaching this decision, data input should include current and projected information on types and locations of intakes and discharges; percentage of shoreline n̶   ry to provide adequate spawning, nursery, and ̄eeuing areas; and other desired uses of the water.

Recommendation

It is recommended that the total area or volume of a receiving system assigned to mixing zones be limited to that which will: (1) not interfere with biological communities or populations of important species to a degree which is damaging to the ecosystem; (2) not diminish other beneficial uses disproportionately.

ZONES OF PASSAGE

In river systems, reservoirs, lakes, estuaries, and coastal waters, zones of passage are continuous water routes of such volume, area, and quality as to allow passage of free-swimming and drifting organisms so that no significant effects are produced on their populations.

Transport of a variety of organisms in river water and by tidal movements in estuaries is biologically important in a number of ways; e.g., food is carried to the sessile filter feeders and other nonmobile organisms; spatial distribution of organisms and reinforcement of depauperate populations is enhanced; embryos and larvae of some fish sp⸱ ⸱s develop while drifting. Anadromous and cata-d.   us species must be able to reach suitable spawning areas. Their young (and in some cases the adults) must be assured a return route to their growing and living areas. Many species make migrations for spawning and other purposes. Barriers or blocks which prevent or interfere with these types of essential transport and movement can be created by water of inadequate chemical or physical quality.

Water quality in the zone of passage should be such that biological responses to the water quality characteristics of the mixing zone are no longer time-dependent (see Definition of Mixing Zone on page 112). However, where a zone of passage is to be provided, bioassays determining time-exposure responses in the mixing zone should include additional requirements to assess organism behavior. In the mixing zone discussion above it is assumed that entrainment in the plume will be involuntary. However, if there is attraction due to plume composition, exposure in the plume could be very much longer than would be predicted by physical modeling. If avoidance reactions occur, migration may be thwarted. Thus, concentrations in both the mixing zone and the zone of passage should be reduced before discharge to levels below those at which such behavioral modifications affect the populations of the subject organisms.

Modern techniques of waste water injection such as diffusers and high velocity jets may form barriers to free passage due to responses of organisms to currents. Turbulence of flows opposing stream direction may create traps for those organisms which migrate upstream by orientation to opposing currents. These organisms may remain in the mixing zone in response to currents created by the discharge.

Recommendation

Because of varying local physical and chemical conditions and biological phenomena, no single-value recommendation can be made on the percentage of river width necessary to allow passage of critical free-swimming and drifting organisms so that negligible or no effects are produced on their populations. As a guideline no more than ⅔ the width of a water-body should be devoted to mixing zones thus leaving at least ⅓ free as a zone of passage.

Monitoring of aquatic environments has traditionally included obtaining physical and chemical data that are used to evaluate the effects of pollutants on living organisms. Biological monitoring has received less emphasis than chemical or physical monitoring, because biological assessments were once not as readily amenable to numerical expression and tended to be more time consuming and more expensive. This is no longer true. Aquatic organisms can serve as natural monitors of environmental quality and should be included in programs designed to provide continuous records of water quality, because they integrate all of the stresses placed on an aquatic system and reflect the combined effect. Chemical–physical assessments identify individual components, so the two types of assessments are mutually supporting rather than mutually exclusive.

A biological monitoring program is essential in determining the synergistic or antagonistic interactions of components of waste discharges and the resulting effects on living organisms. However, biological monitoring does not replace chemical and physical monitoring; each program provides information supplemental to the others.

PROGRAMS

An ideal biological monitoring program has four components: (1) field surveys, (2) in-plant biological monitoring, (3) bioassays, and (4) simulation techniques. Obviously no biological monitoring program is routine, nor does it necessarily have to include all of the above components. However, each of the components provides valuable and useful information.

FIELD SURVEYS

Field surveys are needed to obtain adequate data on biological, chemical, and physical water quality to determine the nature of the system and the possible adverse effects of waste discharges on beneficial uses of the system. Two methods for continuously monitoring the effects of pollution on a receiving water have been described. Patrick et al. (1954)[6]* described the use of diatoms as natural monitors of various types of pollution. Various species of shellfish,

especially oysters suspended in trays, have been described as an effective method of monitoring pollution (Galtsoff et al. 1947).[4] Field surveys should be carried out at suitable intervals depending on local conditions. For example, in determining the impact of a new or relocated municipal or industrial discharge, it is desirable to perform the following functions:

- survey the stream as a part of the site selection procedure;
- continue the field survey prior to construction to determine existing water quality: at this time it is also useful to make bioassays using simulated plant wastes and representative organisms from the receiving systems, and to establish biomonitoring stations;
- monitor the effects of construction;
- carry out bioassays using actual plant wastes and effluents after the plant is in operation, and make field surveys to determine any changes from pre-construction results.

BODY BURDENS OF TOXICANTS

Body burdens of toxicants that can be concentrated by biota should be measured regularly. These data can provide early warning before concentrations in water become readily available and can provide warnings of incipient effects in the biota being monitored.

IN-PLANT BIOLOGICAL MONITORING

Present information systems do not provide data rapidly enough to be of use in environmental management, because the constituents of a waste stream are likely to vary, from hour to hour and from day to day. Potentially harmful materials should be detected before they enter the receiving water and before substantial damage has been done to the ecosystem.

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* Citations are listed at the end of the Section. They can be located alphabetically within subtopics or by their superior numbers w! run consecutively across subtopics for the entire Section.

Several potentially useful methods for rapid in-plant monitoring are being explored (Sparks et al. 1969,[7] Waller and Cairns 1969[8]), and one rapid in-stream method is now c ional (Cairns et al. 1968,[2] Cairns and Dickson 1971[3]). These in-plant methods use changes in heart rate, respiration, and movements of fish within a container to detect sublethal concentrations of toxicants in a waste discharge. Continual information on toxicity of a waste should enable sanitary engineers to identify those periods likely to produce the most toxic wastes and to identify those components of the production process that contribute significantly to toxicity. This could be accomplished with bioassays as they are currently used, but rarely are enough samples taken over a period of time sufficient to give the range of information that would be available with continually operating bioassay techniques.

BIOASSAYS

Of equal importance to the river surveys and the in-plant and in-stream monitoring systems is the availability of toxicity information based on a predictive bioassay. The bioassay provides valuable information pertaining to the effects of potential or contemplated discharges on aquatic life. Acute bioassays are useful as a shortcut or predictive method of estimating safe concentrations by use of suitable application factors for many pollutants, as recommended throughout this Report.

However, determining only the acute lethal toxicity of wastes is no longer adequate. Good health and an ability to function vigorously are as important for aquatic ecosystems as they are for humans. The former end point of bioassays, viz., death, has been supplanted by more subtle end points such as the protection of respiration, growth, reproductive success, and a variety of other functional changes (Cairns 1967).[1] Acute toxicity determinations are being supplemented by long-term tests often involving an entire life cycle. The latter require more time and expense than short-term tests, but they provide better predictive information about biologically safe concentrations of various toxicants. Bioassays of organisms other than fish are becoming increasingly common because of the realization that elimination of the lower organisms can also have serious consequences.

SIMULATION TECHNIQUES

The fourth component now available to provide ecological information is the use of scale models. Models are used to study major ecological or environmental problems by simulating prospective new uses. Engineering scale models are common, but ecological scale models or environmental simulation systems are not yet as commonly used. Experimental streams and reservoirs have been constructed to predict toxicity of waste discharges, determine factors responsible for productivity of aquatic communities, and answer questions about plant site location (Haydu 1968,[5] Warren and Davis 1971[9]).

BIOASSAYS

Bioassays are used to evaluate a given pollutant in terms of existing water quality. Most pollution problems involve discharges of unknown and variable composition where more than one toxicant or stress is present. In evaluating criteria for specific toxicants, consideration must be given to other environmental influences such as dissolved oxygen, temperature, and pH.

Harmful effects of pollutants can be described by one or more of the following terms:

acute—involves a stimulus severe enough to bring about a response speedily, usually within four days for fish.

subacute—involves a stimulus less severe than an acute stimulus, producing a response in a longer time; may become chronic.

chronic—involves a lingering or continuous stimulus; often signifying periods of about one-tenth of the life span or more.

lethal—causes death by direct action.

sublethal—insufficient to cause death.

cumulative—brought about, or increased in strength, by successive additions.

Two broad categories of effect (Alderdice 1967)[10] may be distinguished: acute toxicity which is usually lethal, and chronic toxicity which may be lethal or sublethal.

MEASURES OF TOXICITY

Most of the available toxicity data are reported as the median tolerance limit (TLm or TL50) or median lethal concentration (LC50). Either symbol signifies the concentration that kills 50 per cent of the test organisms within a specified time span, usually in 96 hours. The customary 96-hour (four-day) time period is recommended as adequate for most routine tests of acute toxicity with fish. A threshold of acute toxicity will have been attained within this time in the majority of cases (Sprague 1969).[43] This *lethal threshold concentration* is usually noticeable in the data. Sometimes mortality continues, and tests of a week or longer would be necessary to determine the threshold. The lethal threshold

concentration should be reported if it is demonstrated, because it is better for comparative purposes than the arbitrary 96-hour LC50. Absence of any apparent threshold is equally noteworthy.

The median lethal concentration is a convenient reference point for expressing the acute lethal toxicity of a given toxicant to the average or typical test animal. Obviously it is in no way a safe concentration, although occasionally the two have been confused. Safe levels, which permit reproduction, growth, and all other normal life-processes in the fish's natural habitat, usually are much lower than the LC50. In this book, the recommended criteria are intended to be safe levels.

Substantial data on long-term effects and safe levels are available for only a few toxicants. Information is now accumulating on the effect of toxicants on reproduction, an important aspect of all long-term toxicity tests. Other information is being gathered on sublethal effects on growth, performance, avoidance reactions, and social behavior of fish. Also important is the sensitivity of organisms at various life stages. Many organisms are most sensitive in the larval, nymphal, molting, or fry stage; some are most sensitive in the egg and sperm stage.

It would be desirable if a single, universal, rapid, biological test could be used to measure directly sublethal effects of a pollutant. Data on sublethal responses of fish have been used, such as respiratory rates and "coughing," swimming speed, avoidance behavior, and specific physiological and biochemical changes in various organisms; and histological studies have been made. A review of these (Sprague 1971)[45] shows that no single test is meaningful for all kinds of pollutants. Therefore, it is recommended that routine assessment and prediction of safe levels be made by carrying out bioassays for acute lethal toxicity and multiplying the lethal concentration by a suitable application factor. The application factors used and recommended here have been derived principally from chronic or sublethal laboratory experiments or from well documented field studies of polluted situations.

Acceptable concentrations of toxicants to which organ are exposed continually must be lower than the hig...

concentrations that may be reached occasionally but briefly without causing damage. Both maximum short-time conce   tions and the more restrictive range of safe concentr.   .is for continuous exposure are useful. The recommendations in this Report are those considered safe for continuous exposure, although in some cases there has also been an indication of permissible higher levels for short periods.

In field situations and industrial operations, average 24-hour concentrations can be determined by obtaining composite or continuous samples. After 24 hours, the sample may be mixed and analyzed. The concentration found will represent the average concentration. Samples obtained this way are more reproducible and easier to secure than the instantaneous sample of maximum concentrations. However, average concentrations are of little significance if fish are killed by a sharp peak of concentration, and for that reason maximum concentrations must also be considered.

METHODS FOR BIOASSAYS

Although there are many types of assays, two are in general use:

1. the static bioassay in which the organisms are held in a tank containing the test solution, and
 .the continuous flow or flow-through bioassay in w......1 the test solution is renewed continually.

The difference between the two types is not always great, but one can have clear advantages over the other.

An outline of methods for routine bioassays has been given in "Standard Methods for the Examination of Water and Wastewater" (American Public Health Association, American Water Works Association, Water Pollution Control Federation, 1971,[11] hereafter referred to as Standard Methods 1971[48]). Cope (1961)[21] described bioassay reporting, and Cairns (1969)[20] presented a rating system for evaluating the quality of the tests. Sprague (1969,[43] 1970,[44] 1971[45]) reviewed research to develop more incisive testing methods. Their findings are utilized in this Report.

Procedure for acute bioassay with fish is now relatively standardized and usually incorporates:

● a series of replicate test containers, each with a different but constant concentration of the toxicant;
● a group of similar fish, usually 10, in each container;
● observations of fish mortality during exposures that last between one day and one week, usually four days; and
● final results expressed as LC50.

ier factors that are required for good bioassay practice arc priefly summarized in the references mentioned above.

CHECKLIST FOR PROCEDURES

Species

A selected strain of fish or other aquatic organisms of local importance should be used in bioassays conducted for the purpose of pollution monitoring. Preferably it should be a game or pan fish, which are usually among the more sensitive. Ability to duplicate experiments is enhanced by the use of a selected strain of test organisms (Lennon 1967).[31] A selected strain can also help to determine the difference between toxicants more reliably, and to detect discrepancies in results due to apparatus. A National Research Council subcommittee chaired by Dr. S. F. Snieszko is currently preparing a report, *Standards and guidelines for the breeding, care, and management of laboratory animals—Fish*, which will be useful in this area. Susceptibility to toxicants among different species of fish is generally less than might be expected—sometimes no greater than when a single species is tested in different types of water. For example, trout and certain coarse fishes were equally resistant to ammonia when tests continued for several days to give the less sensitive species time to react (Ball 1967a);[13] and even for zinc, the coarse fishes were no more than 3.8 times as resistant as trout (Ball 1967b).[14] Recommendations for the selected test fish will often provide protection to other aquatic animals and plants. There are exceptions to this generalization: for example, copper is quite damaging to algae and mollusks, and insecticides are especially dangerous to aquatic arthropods. Sufficient data exist to predict these situations. When they are expected, bioassays should be run with two kinds of invertebrates and two kinds of algae (Patrick et al. 1968).[41]

In the case of important bodies of water, there is good reason to test several kinds of aquatic organisms in addition to fish. Patrick et al. (1968)[41] made a comparative study of the effects of 20 pollutants on fish, snails, and diatoms and found that no single kind of organism was most sensitive in all situations. The short-term bioassay method for fish may also be used for many of the larger invertebrate animals. A greater volume of test·water and rate of flow, or both, may be required in relation to weight of the animals since their metabolic rate is higher on a weight basis.

Larvae of mollusks or crustaceans can be good test animals. The crustacean *Daphnia* is a good test animal and was widely used in comparative studies of toxicants by Anderson (1950).[12] Recently Biesinger and Christensen (*unpublished data*, 1971)[52] have carried out tests on the chronic effects of toxicants on growth, survival, and reproduction of *Daphnia magna*. Because of the rapid life cycle of *Daphnia*, experiments on chronic toxicity can be completed in about the same time as an acute toxicity test with fish.

Patrick et al. (1968)[41] have shown that diatoms, snails and fish exposed for roughly comparable periods of time and in similar environmental conditions very often have similar LC50's, but at other times these may differ greatly.

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However, for some toxicants diatoms were most sensitive; for others, fish; and for others, snails. When one is comparing data of this type, one questions whether a LC50 for a diatom population in which a number of divisions have occurred during the test period is comparable to that obtained for fish and snails in which no reproduction has occurred during the test period. In the sense that there are 50 per cent fewer cells in the LC50 concentration than there are in the diatom control culture, the test is somewhat equivalent to a test of acute toxicity that results in 50 per cent fewer surviving fish in the LC50 than in the control container. Also loss of ability to grow and divide might be just as fatal to a microbial population as death of a substantial number of its members would be to a fish population.

When the absolute time for the test is considered, there are also reasons for believing that exposure of diatoms to a toxicant through several generations might not constitute a chronic test, because it is quite possible that for toxicants to accumulate in a cell may require a period of exposure much more lengthy than that encompassed in the average test which only spans a few generations. This would be particularly true when the organisms were dividing rapidly and the additional protoplasm diluted the material being accumulated.

Dilution Water

Toxicants should be tested in the water that will receive the pollutant in question. In this way all modifying factors and combined toxicities will be present. It is not advisable to use tap water for dilution, because it may contain chlorine and other harmful materials such as copper, zinc, or lead from plumbing systems. Routine dechlorination does not insure complete removal of chlorine.

Variations in physical and chemical characteristics of water affect toxicity of pollutants. Effects of five environmental entities on the lethal threshold of ammonia were illustrated a decade ago (Lloyd 1961b).[34] Hardness of water is particularly important in toxicity of metals. Hydrogen ion concentration is an important modifying factor for ammonia and cyanide. Higher temperatures sometimes increase toxicity of a pollutant, but recent work shows that phenol, hydrogen cyanide, ammonia, and zinc may be more toxic at low temperatures (United Kingdom Ministry of Technology 1969).[50] Dissolved oxygen levels that are below saturation will increase toxicity, and this is predictable (Lloyd 1961a;[33] Brown 1968).[16]

The supply of dilution water must be adequate to maintain constant test conditions. In both static and continuous flow tests, a sufficiently large volume of test water must be used, and it must be replaced or replenished frequently. This is to provide oxygen for the organism and dilution of metabolic wastes, to limit changes in temperature and pH, and to compensate for degradation, volatilization, intake, and sorption of the toxicant. In static tests, there should be two or three liters of water per gram of fish, changed daily, or increased proportionally in volume for the number of days of the test. In continuous flow tests, the flow must provide at least two or three liters of water per gram of fish per day, and it must equal test-volume in five hours c less, giving 90 per cent replacement in half a day or less.

Acclimation

Acclimatizing the test organism to the specific water before the bioassay begins may have marked effect upon the outcome. Abrupt changes in quality of the water should be avoided. Time for acclimation of the organisms to the conditions of the diluent water should be as generous as possible, dependent on life span. At least two weeks is recommended for fish.

Test Methods

Test methods must be adequately described when the results are given. Several bioassay procedures are listed in Table III-1. Adequate and appropriate control tests must always be run (Sprague 1969).[43] Survival of the control organisms is a minimum indication of the quality of the test organisms. In addition, levels of survival and health in holding tanks should be indicated and the conclusions recorded.

TABLE III-1—*Recommended Literature Sources for Bioassa and Biomonitoring Procedures with Various Aquatic Organisms*

Kind of organism	Type of response	Appropriate situations for use	Reference
Fish and Macroinvertebrates	96-hour lethal concentration	To measure lethal toxicity of a waste of known or unknown composition. To serve as a foundation for extrapolating to presumably safe concentrations. To monitor industrial effluents.	Standard Methods 1971[48]
Fish and macroinvertebrates	Lethal threshold concentration	For research applications to document lethal thresholds.	Sprague 1969,[43] 1970[44]
Fish and invertebrates	Incipient lethal temperatures & ultimate incipient lethal temperatures	For research to determine lethal temperature ranges of a given species.	Fry 1947,[25] Brett 1952[15]
Fish	Respiratory movements as acute sublethal response	Quick (1-day) indication of possible sublethal effects. For research and monitoring.	Schaumburg et al. 1967[42]
Fish (i.e., fathead minnows, brook trout, bluegill)	Reproduction, growth, and survival	Chronic tests for research on safe concentrations.	Mount 1968,[37] Mount & Stephan 1967,[38] Brungs 1969,[18] McKim & Benoit 1971,[35] Eaton 1970[24]
Daphnia	Survival, growth, and reproduction	Rapid completion of chronic tests for testing special susceptibility of crustaceans	Anderson 1950,[13] Biesinger & Christensen (Unpublished data)[52]
Diatoms	Survival, growth, and reproduction	A sensitive, rapid, chronic test for research, prediction, or monitoring[a]	Patrick 1968[40]
Marine crustacean, larvae mollusks	Survival, growth, and development through immature stages	A sensitive, rapid, chronic test for research, prediction, or monitoring[a]	Woelke 1967[51]

[a] requires an operator with some specialized biological training.

Dissolved Oxygen

The problem of maintaining dissolved oxygen concen-
t   s suitable for aquatic life in the test water can be
d   it. The suggestions on test volume and replacement
times (see Dilution Water above) should provide for ade-
quate oxygen in most cases. However, with some pollutants,
insufficient oxygen may be present in the test water because
a biochemical and a chemical oxygen demand (BOD and
COD) may consume much of the available dissolved oxygen.
Aeration or oxygenation may degrade or remove the test
material. Devices for maintaining satisfactory dissolved
oxygen in static tests have been proposed and used with some
degree of effectiveness, and are described in Doudoroff
et al. (1951).[22]

Concentrations

Periodic measurements of concentration of the toxicant
should be made at least at the beginning and end of the
bioassay. If this is not possible, introduced concentrations
may be stated alone, but it should be realized that actual
concentrations in the water may become reduced.

In the flow-through type of bioassay, a large quantity of
test water can be made up and used gradually. More often
a device is used to add toxicant to a flow of water, and the
mixture is discharged into the test container, using apparatus
such as "dipping bird" dosers described by Brungs and
Mount (1967).[19] Other devices have been developed by
Stark (1967),[47] and Mount and Warner (1965),[39] using
tl   ser technique.

Evaluation of Results

Mortality rates at the longest exposure time should be
plotted on a vertical probit scale against concentrations of
toxicants on a horizontal logarithmic scale. The concen-
tration which causes 50 per cent mortality can be read and
used as LC50. Errors in LC50 can be estimated using the
simple nomograph procedures described by Litchfield and
Wilcoxon (1949).[32] A more refined estimate of error may
be made using the methods of Finney (1952),[25] which can
be programmed for a computer.

The value of the results would be improved if the LC50's
were estimated (by the above procedures) at frequent
exposure times such as 1, 2, 4, 8 ± 1, 14 ± 2, 24, 48, 72,
and 96 hours. A toxicity curve of time versus LC50 could
then be constructed on logarithmic axes. The lethal thresh-
old concentration could then be estimated in many cases
(Sprague 1969)[43] to provide a more valid single number
for description of acute toxicity than the arbitrary 96-hour
LC50.

For some purposes, such as basic research or situations
where short exposures are of particular concern, it would
be desirable to follow and plot separately the mortality of
the group of fish in each tank. In this way, the median
le   time can be estimated for a given concentration.
N.   ods for doing this are given in Appendix II-A.

APPLICATION FACTORS

Short-term or acute toxicity tests do not indicate concen-
trations of a potential toxicant that are harmless under
conditions of long-term exposure. Nevertheless, for each
toxicant there is obviously a numerical value for the ratio
of the safe concentration to the acutely lethal concentration.
Such values are called application factors. In some cases
this safe-to-lethal ratio is known with reasonable accuracy
from experimental work, as in the examples given in Table
III-2. However, for most toxicants, the safe level has not
been determined, and must be predicted by some approxi-
mate method. In these cases, the assumption has been
made in this Report, that the numerical value of the safe-
to-lethal ratio, the application factor, is constant for related
groups of chemicals. Values for the ratio will be recom-
mended. The safe level of a particular toxicant can then
be estimated approximately by carrying out an acute bio-
assay to determine the lethal concentration, then multi-
plying this by the suggested application factor. An appli-
cation factor does not make allowance for unknown factors.
It is merely a fractional or decimal factor applied to a
lethal concentration to estimate the safe concentration.

Ideally, an application factor should be determined for
each waste material in question. To do this, it is necessary
first to determine the lethal concentration of the waste
according to the bioassay procedures outlined above. To
obtain the application factor, the safe concentration of the
same waste must be determined for the same species by
thorough research on physiological, biochemical, and be-
havioral effects, and by studying growth, reproduction,
and production in the laboratory and field. The safe-to-
lethal ratio obtained could then be used as an application
factor in a given situation, by working from the measured
LC50 of a particular kind of waste to predict the safe
concentration.

TABLE III-2—*Ratios between the safe concentration and the*
lethal concentration which have been determined experi-
mentally for potential aquatic pollutants. Sources of data
are given in the sections on the individual pollutants.

Material	Species of animal	Safe-to-lethal ratio
LAS	Fathead minnow (Pimephales promelas)	Between 0.14 and 0.28 (=about 0.21)
Chlorine	Fathead minnow	0.16
	Gammarus	0.16
Sulfides	Fathead minnow and white sucker (Catostomus commersoni)	0.1±
	Walleye pike (Stizostedion vitreum v.)	0.22±
Copper	Several species of fish	close to 0.1
Trivalent chromium	Fathead minnow	0.037
Hexavalent chromium	Fathead minnow	0.03
	Brook trout (Salvelinus fontinalis)	0.012
	Rainbow trout (Salmo gairdneri)	0.04
Malathion	Fathead minnow and bluegill (Lepomis machrochirus)	0.03
Carbaryl	Fish species	0.02
Nickel	Fathead minnow	0.02
Lead	Rainbow and Brook trout	<0.02
Zinc	Fathead minnow	0.005

In this approach, a 96-hour LC50 is determined for the pollutant using water from the receiving stream for dilution. The test organisms selected should be among the most sensitive species, or an important local species at a sensitive life stage, or a species whose relative sensitivity is known. This procedure takes into consideration the effects of local water quality and the stress or adverse effects of wastes already present in the stream. The LC50 thus found is then multiplied by the application factor for that waste to determine its safe concentration in the specific stream or section of stream. Such bioassays should be repeated at least monthly or when changes in process or rate of waste discharge are observed.

For example, if the 96-hour LC50 is 0.5 milligrams per liter (mg/l) and the concentration of the waste found to be safe is 0.01 mg/l, the ratio would be:

$$\frac{\text{Safe Concentration}}{\text{96-hour } LC50} = \frac{0.01}{0.50} = \frac{1}{50}$$

In this instance, the safe-to-lethal ratio is 0.02. It can be used as an application factor in other situations. Then, in a given situation involving this waste, the safe concentration in the receiving stream would be found by multiplying the four-day LC50 by 0.02.

This predictive procedure based on lethal concentrations is useful, because the precise safe level of many pollutants is not known because of the uncertainty about toxicity of mixed effluents and the difference in sensitivity among fish and fish food organisms. Henderson (1957)[27] and Tarzwell (1962)[40] have discussed various factors involved in developing application factors. Studies by Mount and Stephan (1967),[38] Brungs (1969),[18] Mount (1968),[37] McKim and Benoit (1971),[36] and Eaton (1970)[24] in which continuous exposure was used, reveal that the safe-to-lethal ratio that permits spawning ranges over nearly two orders of magnitude. Exposure will not be constant in most cases, and higher concentrations usually can be tolerated for short periods.

Lethal threshold concentrations, which may require more than 96-hour exposures, may be beneficially used (Sprague 1969)[43] to replace 96-hour LC50 in the above procedures, and there is a trend today to use such threshold concentrations (Eaton 1970).[24]

At present, safe levels have been determined for only a few wastes, and as a result only a few application factors are known. Because the determination of safe levels of pollutants is an involved process, interim procedures for estimating tolerable concentrations of various wastes in receiving waters must be used. To meet this situation, three universal application factors selected on the basis of present knowledge, experience, and judgment are recommended at the end of this section. Where toxicants have a nonpersistent nature (a half life of less than 4 days) or noncumulative effects, an application factor of 0.1 of the 96-hour LC50 should not be exceeded at any time or place after mixing with the receiving waters. The 24-hour average of the concentration of these toxicants should not exceed 0.05 of the LC50 if aquatic life is to be protected. For toxic materials which are persistent or cumulative the concentrations should not exceed 0.05 of the 96-hour LC50 at any time or place, and the 24-hour average concentration should not exceed 0.01 of the 96-hour LC50 in order to protect aquatic life. It is proposed that these general application factors be applied to LC50 values determined in the manner described above to set tolerable concentrations of wastes in the receiving stream.

MIXTURES OF TWO OR MORE TOXICANTS

The toxicity of a mixture of pollutants may be estimated by expressing the actual concentration of each toxicant as a proportion of its lethal threshold concentration (usually equal to the 96-hour LC50) and adding the resulting numbers for all the toxicants. If the total is 1.0 or greater, the mixture will be lethal.

The system of adding different toxicants in this way is based on the premise that their lethal actions are additive. Unlikely as it seems, this simple rule has been found to govern the combined lethal action of many pairs and mixtures of quite dissimilar toxicants, such as copper and ammonia, and zinc and phenol in the laboratory (Herbert and Vandyke 1964,[29] Jordan and Lloyd 1964,[30] Brown et al. 1969).[17] The rule holds true in field studies (Herbert 1965,[28] Sprague et al. 1965).[46] The method of addition is useful and reasonably accurate for predicting thresholds lethal effects in mixtures.

There is also evidence of a lower limit for additive lethal effects. For ammonia and certain other pollutants, levels below 0.1 of the lethal concentration do not seem to contribute to the lethal action of a mixture (Brown et al. 1969,[17] Lloyd and Orr 1969).[35] This lower cutoff point of 0.1 of the LC50 should be used when it is necessary to assess the lethal effects of a mixture of toxicants.

SUBLETHAL EFFECTS

Sublethal or chronic effects of mixtures are of great importance. Sublethal concentrations of different toxicants should be additive in effect. Here again, it would be expected that for any given toxicant there would be some low concentration that would have no deleterious effect on an organism and would not contribute any sublethal toxicity to a mixture, but there is little research on this subject. Biesinger and Christensen (*unpublished data* 1971),[52] concluded that subchronic concentrations of 21 toxicants were close to being additive in causing chronic effects on reproduction in *Daphnia*. Copper and zinc concentrations of about 0.01 of the LC50 are additive in causing avoidance reactions (Sprague et al. 1965).[46] On the other hand, somewhat lower metal concentrations of about 0.003 of the LC50 do not seem to be additive in affecting reproduction of

(Eaton *unpublished data* 1971).[63] Perhaps there is a lower cutoff point than 0.01 of the LC50 for single pollutants co- -ibuting to sublethal toxicity of a mixture.

ın interim solution, it is recommended that the contribution of a single pollutant to the sublethal toxicity of a mixture should not be counted if it is less than 0.2 of the recommended level for that pollutant. Applying this to a basic recommended level of 0.05 (see the Recommendation that follows) of the LC50 would yield a value of 0.01 of the LC50, corresponding to the possible cutoff point suggested above.

It is expected that certain cases of joint toxicity will not be covered by simple addition. The most obvious exception would be when two toxicants combine chemically. For example, mixed solutions of cyanides and metals could cause addition of toxicity or very different effects if the metal and cyanide combined (Doudoroff et al. 1966).[23] A thorough understanding of chemical reactions is necessary in these cases.

For further discussions of bioassays and the difficulties posed in assessing sublethal effects of toxicants on organisms, see Section IV, pp. 233–237.

Recommendations for the Use of Application Factors to Estimate Safe Concentrations of Toxic Wastes in Receiving Streams

Where specific application factors have been determined fo given material, they should be used instead of the safe co ntration levels of wastes given below:

(a) Concentration of materials that are nonpersistent or have noncumulative effects should not exceed 0.1 of the 96-hour LC50 at any time or place after mixing with the receiving waters. The 24-hour average of the concentration of these materials should not exceed 0.05 of the LC50 after mixing.

(b) For toxicants which are persistent or cumulative, the concentrations should not exceed 0.05 of the 96-hour LC50 at any time or place, nor should the 24-hour average concentration exceed 0.01 of the 96-hour LC50.

(c) When two or more toxic materials are present at the same time in the receiving water, it should be assumed unless proven otherwise that their individual toxicities are additive and that some reduction in the permissible concentrations is necessary. The amount of reduction required is a function of both the number of toxic materials present and their concentrations in respect to the permissible concentrations. The following relationship will assure that the

combined amounts of the several substances do not exceed a permissible concentration:

$$\frac{C_a}{L_a}+\frac{C_b}{L_b}+\cdots+\frac{C_n}{L_n}\leq1.0$$

This formula may be applied where C_a, C_b, ... C_n are the measured or expected concentrations of the several toxic materials in the water, and L_a, L_b, ... L_n are the respective concentrations recommended or those derived by using recommended application factors on bioassays done under local conditions. Should the sum of the several fractions exceed 1.0, a local restriction on the concentration of one or more of the substances is necessary.

C and L can be measured in any convenient chemical unit as proportions of the LC50 or in any other desired way, as long as the numerator and denominator of any single fraction are in the same units. To remove natural trace concentrations and low nonadditive concentrations from the above formula, any single fraction which has a value less than 0.2 should be removed from the calculation.

Example:

Small quantities of five toxicants are measured in a stream as follows:

3 micrograms/liter (μg/l) of zinc; 3 μg/l of phenol; 3 μg/l of un-ionized ammonia as calculated from Figure III-10 (see Ammonia, p. 186); 1 μg/l of cyanide; and 1 μg/l of chlorine.

A bioassay with zinc sulphate indicates that the 96-hour LC50 is 1.2 mg/l. The application factor for zinc is 0.005; therefore, the allowable limit is 0.005 × 1.2=0.006 mg/l. Initial bioassays with phenol, ammonia, and cyanide indicate that the recommended values are the safe concentrations stated in other sections of the Report, not the fractions of LC50; so the limits are 0.1 mg/l, 0.02 mg/l, and 0.005 mg/l. The permissible limit for chlorine (page 189) is 0.003 mg/l. Therefore, the total toxicity is estimated as follows for zinc, phenol, ammonia, cyanide, and chlorine, respectively:

$$\frac{0.003}{0.006}+\frac{0.003}{0.1}+\frac{0.003}{0.02}+\frac{0.001}{0.005}+\frac{0.001}{0.003}$$
$$=0.5+0.03+0.15+0.2+0.33$$

The second and third terms, i.e., phenol and ammonia, should be deleted since they are below the minimum of 0.2 for additive effects. This leaves 0.5+0.2+0.33 = 1.03, indicating that the total sublethal effect of these three toxicants is slightly above the permissible level and that no higher concentration of any of the three is safe. Thus none can be added as a pollutant.

PHYSICAL MANIPULATION OF THE ENVIRONMENT

Numerous activities initiated to maximize certain uses of water resources often adversely affect water quality and minimize other uses. These activities have caused both benefit and harm in terms of environmental quality. The common forms of physical alteration of watersheds are channelization, dredging, filling, shoreline modifications (of lakes and streams), clearing of vegetation, rip-rapping, diking, leveling, sand and gravel removal, and impounding of streams.

Channelization is widespread throughout the United States, and many studies have been conducted documenting its effects. Channelization usually increases stream gradient and flow rates. The quiet areas or backwaters are either eliminated or cut off from the main flow of the stream, the stream bed is made smooth, thus reducing the habitats available to benthic organisms, and surrounding marshes and swamps are more rapidly drained. The steeper gradient increases velocity allowing the stream to carry a greater suspended load and causing increased turbidity. The rate of organic waste transformation per mile is usually reduced, and destruction of spawning and nursery areas often occurs. Trautman (1939),[67] Smith and Larimore (1963),[65] Peters and Alvord (1964),[64] Welker (1967),[69] Martin (1969),[63] and Gebhards (1970)[58] have discussed the harmful effects of channelization on some fish populations and the effect on stimulation of less desirable species.

Dredging undertaken to increase water depth often destroys highly productive habitats such as marshes (Marshall 1968,[62] Copeland and Dickens 1969).[56] The spoils from dredging activities are frequently disposed of in other shallow sites causing further loss of productive areas. For example, Taylor and Saloman (1968)[66] reported that since 1950 there has been a 20 per cent decrease in surface area of productive Boca Ciega Bay, Florida, due to fill areas. It has become common practice to fill in marshy sites near large metropolitan areas (e.g., San Francisco Bay, Jamaica Bay) to provide for airport construction and industrial development.

In addition to the material that is actually removed by the dredging process, a considerable amount of waste is suspended in the water resulting in high turbidities (Mackin 1961).[61] If the dredged sediments are relatively nontoxic, gross effects on motile aquatic life may not be noticeable, but benthic communities may be drastically affected by the increased redeposition of silt (Ingle 1952).[59]

In many instances either high nutrient or toxic sediments are suspended or deposited during the dredging process. This action may kill aquatic organisms by exposure to the toxicants present or by the depletion of dissolved oxygen concentrations, or both. Brown and Clark (1968)[54] noted a dissolved oxygen reduction of 16 to 83 per cent when oxidizable sediments were resuspended. In many cases disturbed sediments containing high nutrient concentrations may stimulate undesirable forms of phytoplankton or *Cladophora*. Gannon and Beeton (1969)[57] categorized harbor sediments in five groups. Those most severely polluted were toxic to various animals and did not stimulate growth of phytoplankton. Other sediments were toxic but stimulated plant growth. The least polluted sediments were not toxic and stimulated growth of phytoplankton but not *Cladophora*.

Three basic aspects must be considered in evaluating the impact of dredging and disposal on the aquatic environment: (1) the amount and nature of the dredgings, (2) the nature and quality of the environments of removal and disposal, and (3) the ecological responses. All vary widely in different environments, and it is not possible to identify an optimal dredging and disposal system. Consequently, the most suitable program must be developed for each situation. Even in situations where soil is deposited in diked enclosures or used for fill, care must be taken to monitor overflow, seepage, and runoff waters for toxic and stimulatory materials.

Artificial impoundments may have serious environmental impact on natural aquatic ecosystems. Dams and other artificial barriers frequently block migration and may destroy large areas of specialized habitat. Aquatic organisms are frequently subjected to physical damage if they are allowed to pass through or over hydroelectric power units and other man-made objects when properly designed barriers are not provided. At large dams, especially t designed for hydroelectric power, water drawn from

pool behind the dam is frequently taken from great depths, resulting in the release to the receiving stream of waters low ˙˙ dissolved oxygen and excessively cold. This can be a pr   a, particularly in areas where nonnative fish are tocked.

Cutting down forests, planting the land in crops, and partially covering the surface of a watershed by building roads, houses, and industries can have detrimental effects on water ways. Wark and Keller (1963)[68] showed that in the Potomac River Basin (Washington, D.C.) reducing the rest cover from 80 per cent to 20 per cent increased the annual sediment yield from 50 to 400 tons per square mile per year. The planting of land in crops increased the sediment yield from 70 to 300 tons per square mile per year, or a fourfold increase as the land crops increased from 10 per cent to 50 per cent. Likens et al. (1970)[60] showed that cutting down the forest in the Hubbard Brook area (Ver-

mont) caused substantial changes in the streams. The sediment load increased fourfold over a period from May 1966 to May 1968. Furthermore, the particulate matter drained from the deforested watershed became increasingly inorganic in content, thus reducing the value of the sediment as a food source. The nutrient content of the water was also affected by cutting down the forests. The nitrate concentration increased from 0.9 mg/l prior to the cutting of vegetation to 53 mg/l two years later. Temperatures of streams in deforested areas were higher, particularly during the summer months, than those of streams bordered by forests (Brown and Krygier 1970).[55]

Prior to any physical alterations of a watershed, a thorough investigation should be conducted to determine the expected balance between benefits and adverse environmental effects.

SUSPENDED AND SETTLEABLE SOLIDS

Suspended and settleable solids include both inorganic and organic materials. Inorganic components include sand, silt, and clay originating from erosion, mining, agriculture, and areas of construction. Organic matter may be composed of a variety of materials added to the ecosystem from natural and man-made sources. These inorganic and organic sources are discussed in the Panel Report on Marine Aquatic Life and Wildlife (Section IV), and the effects of land–water relationships are described in the report on Recreation and Aesthetics (Section I).

SOIL AS A SOURCE OF MINERAL PARTICLES

Soil structure and drainage patterns, together with the intensity and temporal distribution of rainfall that directly affect the kind and amount of protective vegetative cover, determine the susceptibility of a soil to erosion. Where rain occurs more or less uniformly throughout the year, protective grasses, shrubs, or trees develop (Leopold, et al. 1964).[78] Where rainfall occurs intermittently, as in arid areas, growth of protective plants is limited thus allowing unchecked erosion of soils.

Wetting and drying cause swelling and shrinking of clay soils and leave the surface susceptible to entrainment in surface water flows. Suspended soil particle concentrations in rivers, therefore, are at their peak at the beginning of flood flows. Data on the concentration of suspended matter in most of the significant streams of the United States are presented in the U.S. Geological Survey Water Supply Papers.

Streams transport boulders, rocks, pebbles, and sand by intermittent rolling motions, or by intermittent suspension and deposition as particles are entrained and later settled on the bed. Fine particles are held in suspension for long periods, depending on the intensity of the turbulence. Fine silt particles, when dispersed in fresh waters, remain almost continuously suspended, and suspension of dispersed clay mineral particles may be maintained even by the thermally induced motions in water. These fine mineral particles are the soil materials of greatest significance to the turbidity values of a particular water.

The suspended and settleable solids and the bed of a water body must be considered as interrelated, interacting parts. For example, Langlois (1941)[77] reported that in Lake Erie the average of 40 parts per million (ppm) of suspended matter in the water was found to change quickly to more than 200 ppm with a strong wind. He further explained that this increase is attributed to sediments resuspended by wave action. These sediments enter from streams or from shoreline erosion.

Suspended clay mineral particles are weakly cohesive in fresh river waters having either unusually low dissolved salt concentrations or high concentrations of multivalent cations. Aggregations of fine particles form and settle on the bed to form soft fluffy deposits when such waters enter a lake or impoundment. However, clay mineral particles are ʳ persed or only weakly cohesive in most rivers.

EFFECTS OF SUSPENDED PARTICLES IN WATER

The composition and concentrations of suspended particles in surface waters are important because of their effects on light penetration, temperature, solubility products, and aquatic life (Cairns 1968).[72] The mechanical or abrasive action of particulate material is of importance to the higher aquatic organisms, such as mussels and fish. Gills may be clogged and their proper functions of respiration and excretion impaired. Blanketing of plants and sessile animals with sediment as well as the blanketing of important habitats, such as spawning sites, can cause drastic changes in aquatic ecosystems. If sedimentation, even of inert particles, covers substantial amounts of organic material, anaerobic conditions can occur and produce noxious gases and other objectionable characteristics, such as low dissolved oxygen and decreases in pH.

Absorption of sunlight by natural waters is strongly affected by the presence of suspended solids. The intensity of light (I) at any distance along a light ray (L) is, for a uniform suspension, expressed by the formula:

$$I = I_0{}^{-kcL},$$

where I_0 is the intensity just below the water surface (L =

: is the extinction coefficient for the suspended solids, and is the concentration of suspended solids. L can be related c water depth by the zenith angle, i, the angle of el. on, r, and the index of refraction of water, 1.33, by nell's rule:

$$\sin r = \frac{\sin i}{1.33}$$

The depth, D, is $L \cos r$. Refraction makes the light path more nearly vertical under water than the sun's rays, except when the sun's rays are themselves normal to the water surface.

The growth of fixed and suspended aquatic plants can be limited by the intensity of sunlight. An example of the decrease in the photic zone was calculated for San Francisco Bay (Krone 1963),[76] where k was 1.18×10^3 square centimeters per gram. For a typical suspended solids concentration of 50×10^{-6} grams per cubic centimeter, for an algae requiring 20 foot candles or more for its multiplication, and under incident sunlight of 13,000 foot candles the photic zone did not exceed 1.1 meters. A reduction in suspended solids concentration to 20×10^{-6} g/cm^3 increased the maximum depth of the photic zone to 2.8 meters.

Because suspended particles inhibit the penetration of sunlight, water temperatures are affected, and increasing turbidity results in increasing absorption near the water surface so that turbid waters warm more rapidly at the ur than do clearer waters. Warming and the accompa. g decrease in density stabilize water and may inhibit vertical mixing. Lower oxygen transfer value from air to water results when surface waters are heated. This action combined with inhibited vertical mixing reduces the rate of oxygen transfer downward. Still or slowly moving water is most affected.

The rate of warming, dT/dt, at any distance from the surface along a light path, L, in water having uniform suspended material is

$$\frac{dT}{dt} = -\left[\frac{Ikc}{\rho C}\right]^{-kcL}$$

where ρ is the water density and C is the specific heat of the water. This equation shows that an increase in suspended sediment concentration increases the rate of warming near the surface and decreases exponentially with depth. The biological significance of this relationship is in the effect on time of formation, vertical distribution of thermal stratification, and stability of the upper strata. Increasing turbidity could change the stratification patterns of a lake and thus change the temperature distribution, oxygen regime, and composition of the biological communities.

ADSORPTION OF TOXIC MATERIALS

ended mineral particles have irregular, large surface areas, with electrostatic charges. As a consequence, clay minerals may sorb cations, anions, and organic compounds. Pesticides and heavy metals may be absorbed on suspended clay particles and strongly held with them. The sorption of chemicals by suspended matter is particularly important if it leads to a buildup of toxic and radioactive materials in a limited area with the possibility of sudden release of these toxicants. One such example has been reported by Benoit et al. (1967).[70] Gannon and Beeton (1969)[75] reported that sediments with the following characteristics dredged from various harbors on the Great Lakes were usually toxic to various organisms: COD 42,000 mg/l, volatile solids 4,000 mg/l, ammonia 0.075 mg/g, phosphate-P 0.65 mg/g.

The capacity of minerals to hold dissolved toxic materials is different for each material and type of clay mineral. An example illustrates the magnitudes of sorptive capacities: the cation exchange capacity (determined by the number of negatively charged sites on clay mineral surfaces) ranges from a few milliequivalents per hundred grams (me/100 g) of mineral for kaolinite clay to more than 100 me/100 g for montmorillonite clay. Typical estuarial sediments, which are mixtures of clay, silt, and sand minerals, have exchange capacities ranging from 15 to 60 me/100 g (Krone 1963).[76] The large amounts of such material that enter many estuaries and lakes from tributary streams provide continually renewed sorptive capacity that removes materials such as heavy metals, phosphorus, and radioactive ions. The average new sediment load flowing through the San Francisco Bay-Delta system, for example, has a total cation exchange capacity of a billion equivalents per year.

The sorptive capacity effectively creates the large assimilative capacity of muddy waters. A reduction in suspended mineral solids in surface waters can cause an increase in the concentrations of dissolved toxic materials contributed by existing waste discharges.

EFFECTS ON FISH AND INVERTEBRATES

The surface of particulate matter may act as a substratum for microbial species, although the particle itself may or may not contribute to their nutrition. When the presence of particulate matter enables the environment to support substantial increased populations of aquatic microorganisms, the dissolved oxygen concentration, pH, and other characteristics of the water are frequently altered.

There are several ways in which an excessive concentration of finely divided solid matter might be harmful to a fishery in a river or a lake (European Inland Fisheries Advisory Commission, EIFAC 1965).[73] These include:

- acting directly on fish swimming in water in which solids are suspended, either killing them or reducing their growth rate and resistance to disease;
- preventing the successful development of fish eggs and larvae;

- modifying natural movements and migrations of fish;
- reducing the food available to fish;
- affecting efficiency in catching the fish.

With respect to chemically inert suspended solids and to waters that are otherwise satisfactory for the maintenance of freshwater fisheries, EIFAC (1965)[73] reported:

- there is no evidence that concentrations of suspended solids less than 25 mg/l have any harmful effects on fisheries;
- it should usually be possible to maintain good or moderate fisheries in waters that normally contain 25 to 80 mg/l suspended solids; other factors being equal, however, the yield of fish from such waters might be somewhat lower than from those in the preceding category;
- waters normally containing from 80 to 400 mg/l suspended solids are unlikely to support good freshwater fisheries, although fisheries may sometimes be found at the lower concentrations within this range;
- only poor fisheries are likely to be found in waters that normally contain more than 400 mg/l suspended solids.

In addition, although several thousand parts per million suspended solids may not kill fish during several hours or days exposure, temporary high concentrations should be prevented in rivers where good fisheries are to be maintained. The spawning grounds of most fish should be kept as free as possible from finely divided solids.

While the low turbidities reported above reflected values that should protect the ecosystem, Wallen (1951)[80] reported that fish can tolerate higher concentrations. Behavioral reactions were not observed until concentrations of turbidity neared 20,000 mg/l, and in one species reactions did not appear until turbidities reached 100,000 mg/l. Most species tested endured exposures of more than 100,000 mg/l turbidity for a week or longer, but these same fishes finally died at turbidities of 175,000 to 225,000 mg/l. Lethal turbidities caused the death of fishes within 15 minutes to two hours exposure. Fishes that succumbed had opercular cavities and gill filaments clogged with silty clay particles from the water.

In a study of fish and macroinvertebrate populations over a four-year period in a stream receiving sediment from a crushed limestone quarry, Gammon (1970)[74] found that inputs that increased the suspended solids load less than 40 mg/l (normal suspended solids was 38 to 41 mg/l and volatile suspended solids 16 to 30 mg/l) resulted in a 25 per cent reduction in macroinvertebrate density in the stream below the quarry. A heavy silt input caused increases of more than 120 mg/l including some decomposition of sediment, and resulted in a 60 per cent reduction in density

of macroinvertebrates. Population diversity indices were unaffected because most species responded to the same degree. The standing crop of fish decreased dramatica¹¹ when heavy sediment occurred in the spring; but fish mained in pools during the summer when the input was heavy and vacated the pools only after deposits of sediment accumulated. After winter floods removed sediment deposits, fish returned to the pools and achieved levels of 50 per cent of the normal standing crop by early June.

Not all particulate matter affects organisms in the same way. For example, Smith, et al. (1965)[79] found that the lethal action of pulp-mill fiber on walleye fingerlings (*Stizostedion vitreum vitreum*) and fathead minnows (*Pimephales promelas*) was influenced by the type of fiber. In 96-hour bioassays, mortality of the minnows in 2,000 ppm suspensions was 78 per cent in conifer groundwood, 34 per cent in conifer kraft, and 4 per cent in aspen groundwood. High temperatures and reduced dissolved oxygen concentrations increased the lethal action of fiber.

Buck (1956)[71] studied the growth of fish in 39 farm ponds having a wide range of turbidities. The ponds were cleared of fish and then restocked with largemouth black bass (*Micropterus salmoides*), bluegill (*Lepomis macrochirus*), and redear sunfish (*Lepomis microlophus*). After two growing seasons the yields of fish were:

- clear ponds (less than 25 mg/l suspended solids)   161.5 lb/acre
- intermediate (25–100 mg/l suspended solids)   94.0 lb/acre
- muddy (more than 100 mg/l suspended solids)   29.3 lb/acre

The rate of reproduction was also reduced by turbidity, and the critical concentration for all three species appeared to be about 75–100 mg/l. In the same paper, Buck reported that largemouth black bass (*Micropterus salmoides*), crappies (*Pomoxis*), and channel catfish (*Ictalurus punctatus*) grew more slowly in a reservoir where the water had an average turbidity of 130 mg/l than in another reservoir where the water was always clear.

Floating materials, including large objects as well as very fine substances, can adversely affect the activities of aquatic life. Floating logs shut out sunlight and interfere particularly with surface feeding fish. Logs may also leach various types of organic acids due to the action of water. If they have been sprayed with pesticides or treated chemically, these substances may also leach into the water. As the logs float downstream their bark often disengages and falls to the bed of the stream, disturbing benthic habitats. Aquatic life is also affected by fine substances, such as sawdust, peelings, hair from tanneries, wood fibers, containers, scum, oil, garbage, and materials from untreated municipal an·dustrial wastes, tars and greases, and precipitated chemic....

ecommendations

T' combined effect of color and turbidity should
1. change the compensation point more than
10 per cent from its seasonally established norm,
nor should such a change place more than 10
per cent of the biomass of photosynthetic orga-
nisms below the compensation point.

• Aquatic communities should be protected if the
following maximum concentrations of suspended
solids exist:

High level of protection	25 mg/l
Moderate protection	80 mg/l
Low level of protection	400 mg/l
Very low level of protection	over 400 mg/l

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The true color of a specific water sample is the result of substances in solution; thus it can be measured only after suspended material has been removed. Color may be of organic or mineral origin and may be the result of natural processes as well as manufacturing operations. Organic sources include humic materials, peat, plankton, aquatic plants, and tannins. Inorganic substances are largely metallic, although iron and manganese, the most important substances, are usually not in solution. They affect color as particles. Heavy-metal complexes are frequent contributors to the color problem.

Many industries (such as pulp and paper, textile, refining, chemicals, dyes and explosives, and tanning) discharge materials that contribute to the color of water. Conventional biological waste treatment procedures are frequently ineffective in removing color. On the other hand, such treatment processes have caused an accentuation of the level of color during passage through the treatment plant. Physicochemical treatment processes are frequently preferable to biological treatment if color removal is critical (Eye and Aldous 1968,[81] King and Randall 1970[83]).

The tendency for an accentuation of color to occur as a result of complexing of a heavy metal with an organic substance may also lead to problems in surface waters. A relatively color-free discharge from a manufacturing operation, may, upon contact with iron in a stream, produce a highly colored water that would significantly affect aquatic life (Hem 1960,[82] Stumm and Morgan 1962[86]).

The standard platinum-cobalt method of measuring color is applicable to a wide variety of water samples (Standard Methods 1971).[85] However, industrial wastes frequently produce colors dissimilar to the standard platinum-cobalt color, making the comparison technique of limited value. The standard unit of color in water is that level produced by 1 mg/l of platinum as chloroplatinate ion (Standard Methods 1971).[85] Natural color in surface waters ranges from less than one color unit to more than 200 in highly colored bodies of water (Nordell 1961).[84]

That light intensity at which oxygen production in photosynthesis and oxygen consumption by respiration of the plants concerned are equal is known as the compensation point, and the depth at which the compensation point occurs is called the compensation depth. For a given body of water this depth varies with several conditions, including season, time of day, the extent of cloud cover, conditio᠎ the water, and the taxonomic composition of the flor᠎ volved. As commonly used, the compensation point refers to that intensity of light which is such that the plant's oxygen production during the day will be sufficient to balance the oxygen consumption during the whole 24-hour period (Welch 1952).[87]

Recommendation

The combined effect of color and turbidity should not change the compensation point more than 10 per cent from its seasonally established norm, nor should such a change place more than 10 per cent of the biomass of photosynthetic organisms below the compensation point.

DISSOLVED OXYGEN

Oxygen requirements of aquatic life have been extensively studied. Comprehensive papers have been presented by Doudoroff and Shumway (1967),[89] Doudoroff and Warren 1965),[91] Ellis (1937),[93] and Fry (1960).[94] (Much of the research on temperature requirements also considers oxygen, and references cited in the discussion of Heat and Temperature, p. 151, are relevant here.) The most comprehensive review yet to appear has been written by Doudoroff and Shumway for the Food and Agriculture Organization FAO) of the United Nations (1970).[90] This FAO report provides the most advanced summary of scientific research on oxygen needs of fish, and it has served as a basis for most of the recommendations presented in this discussion. In particular, it provided the criteria for citing different levels of protection for fish, for change from natural levels of oxygen concentration, and for the actual numerical values recommended. Much of the text below has been quoted verbatim or condensed from the FAO report. Its recommendations have been modified in only two ways: the insertion of a floor of 4 mg/l as a minimum, and the suggestion that natural minima be assumed to be equal to saturation levels if the occurrence of lower minima cannot be definitely established. Doudoroff and Shumway covered oxygen concentrations below the floor of 4 mg/l; however, the 4 mg/l floor has been adopted in this report for reasons explained below.

Levels of Protection

Most species of adult fish can survive at very low concentrations of dissolved oxygen. Even brook trout (*Salvelinus fontinalis*) have been acclimated in the laboratory to less than 2 mg/l of O_2. In natural waters, the minimum concentration that allows continued existence of a varied fish fauna, including valuable food and game species, is not high. This minimum is not above 4 mg/l and may be much lower.

However, in evaluating criteria, it is not important to know how long an animal can resist death by asphyxiation at low dissolved oxygen concentrations. Instead, data on the oxygen requirements for egg development, for newly hatched larvae, for normal growth and activity, and for completing all stages of the reproductive cycle are pertinent. Upon review of the available research, one fact becomes clear: *any* reduction of dissolved oxygen can reduce the efficiency of oxygen uptake by aquatic animals and hence reduce their ability to meet demands of their environment. There is evidently no concentration level or percentage of saturation to which the O_2 content of natural waters can be reduced without causing or risking some adverse effects on the reproduction, growth, and consequently, the production of fishes inhabiting those waters.

Accordingly, no single, arbitrary recommendation can be set for dissolved oxygen concentrations that will be favorable for all kinds of fish in all kinds of waters, or even one kind of fish in a single kind of water. Any reduction in oxygen may be harmful by affecting fish production and the potential yield of a fishery.

The selection of a level of protection (Table III-3) is a socioeconomic decision, not a biological one. Once the level of protection is selected, appropriate scientific recommendations may be derived from the criteria presented in this discussion.

Basis for Recommendations

The decision to base the recommendations on O_2 concentration minima, and not on average concentrations, arises from various considerations. Deleterious effects on fish seem to depend more on extremes than on averages. For example, the growth of young fish is slowed markedly if the oxygen concentration falls to 3 mg/l for part of the day, even if it rises as high as 18 mg/l at other times. It could be an inaccurate and possibly controversial task to carry out the sets of measurements required to decide whether a criterion based on averages was being met.

A daily fluctuation of O_2 is to be expected where there is appreciable photosynthetic activity of aquatic plants. In such cases, the minimum O_2 concentration will usually be found just before daybreak, and sampling should be done at that time. Sampling should also take into account the possible differences in depth or width of the water body. The guiding principle should be to sample the places where

aquatic organisms actually live or the parts of the habitat where they should be able to live.

Before recommendations are proposed, it is necessary to evaluate criteria for the natural, seasonal O_2 minimum from which the recommendations can be derived. Natural levels are assumed to be the saturation levels, unless scientific data show that the natural levels were already low in the absence of man-made effects.

Certain waters in regions of low human populations can still be adequately studied in their natural or pristine condition. In these cases the minimum O_2 concentration at different seasons, temperatures, and stream discharge volumes can be determined by direct observation. Such observed conditions can also be useful in estimating seasonal minima in similar waters in similar geographical regions where natural levels can no longer be observed because of waste discharges or other man-made changes.

In many populated regions, some or all of the streams and lakes have been altered. Direct determination of natural minima may no longer be possible. In these cases the assumption of year-round saturation with O_2 is made in the absence of other evidence.

Supersaturation of water with dissolved oxygen may occur as the result of photosynthesis by aquatic vegetation. There is some evidence that this may be deleterious to aquatic animals because of gas bubble disease (see Total Dissolved Gases, p. 135).

Despite the statements in previous paragraphs that there is no single O_2 concentration which is *favorable* to all species and ecosystems, it is obvious that there are, nevertheless, very low O_2 concentrations that are *unfavorable* to almost all aquatic organisms. Therefore, a floor of 4 mg/l is recommended except in situations where the natural level of dissolved oxygen is less than 4 mg/l in which case no further depression is desirable. The value of 4 mg/l has been selected because there is evidence of subacute or chronic damage to several fish below this concentration. Doudoroff and Shumway (1970)[90] review the work of several authors as given below, illustrating such damage. Fathead minnows (*Pimephales promelas*) held at 4 mg/l spawned satisfactorily; only 25 per cent of the resultant fry survived for 30 days, compared to 66 per cent survival at 5 mg/l. At an oxygen level of 3 mg/l, survival of fry was even further reduced to 5 per cent (Brungs 1972[101] *personal communication*). Shumway et al. (1964)[98] found that the dry weight of coho salmon (*Oncorhynchus kisutch*) alevins (with yolk sac removed) was reduced by 59 per cent when they had been held at 3.8 mg/l of oxygen, compared to weights of the controls. The embryos of sturgeon (*Acipenser*) suffered complete mortality at oxygen concentrations of 3.0 to 3.5 mg/l, compared to only 18 per cent mortality at 5.0 to 5.5 mg/l (Yurovitskii 1964).[100] Largemouth bass (*Micropterus salmoides*) embryos reared at 25 C showed survival equal to controls only at oxygen levels above 3.5 mg/l (Dudley 1969).[92] Efficiency of food conversion by juvenile bass was nearly independent of O_2 at 5 mg/l and higher, but growth rate was reduced by 16.5 per cent at 4 mg/l, and 30 per cent at 3 mg/l (Stewart et al. 1967).[99] Similar reductions in growth of underyearling coho salmon occurred at the same O_2 concentrations (Herrmann et al. 1962).[95] Although many other experiments have shown little or no damage to performance of fish at 4 mg/l, or lower, the evidence given above shows appreciable effects on embryonic and juvenile survival and growth for several species of fish sufficient to justify this value.

Warm- and Coldwater Fishes

There are many associations and types of fish fauna throughout the country. Dissolved oxygen criteria for coldwater fishes and warmwater game fishes are considered together in this report. There is no evidence to suggest that the more sensitive warmwater species have lower O_2 requirements than the more sensitive coldwater fishes. The difference in O_2 requirements is probably not greater than the difference of the solubility of O_2 in water at the maximum temperatures to which these two kinds of fish are normally exposed in summer (Doudoroff and Shumway 1970).[90] In warmwater regions, however, the variety of fishes and fish habitats is relatively great, and there are many warmwater species that are exceedingly tolerant of O_2 deficiency.

Unusual Waters

There are certain types of waters that naturally hav oxygen content, such as the "black waters" draining swamps of the Southeastern United States. (Other examples include certain deep ocean waters and eutrophic waters that support heavy biomass, the respiration of which reduces O_2 content much of the time.) A special situation prevails in the deep layers (hypolimnion) of some lakes. Such layers do not mix with the surface layers for extended periods and may have reduced O_2, or almost none. Fish cannot live in the deep layers of many such lakes during a large part of the year, although each lake of this kind must be considered as a special case. However, the recommendation that *no* oxygen-consuming wastes should be released into the deep layers still applies, since there may be no opportunity for reaeration for an entire season.

Organisms Other Than Fish

Most research concerning oxygen requirements for freshwater organisms deals with fish; but since fish depend upon other aquatic species for food, it is necessary to consider the O_2 requirements of these organisms. This Section makes the assumption that the O_2 requirements of other components of the aquatic community are compatible with fish (Doudoroff and Shumway 1970).[90] There are certain exceptions where exceedingly important invertebrate organisms may be very sensitive to low O_2, more sensitive than t species in that habitat (Doudoroff and Shumway 1...

he situation is somewhat more complicated for inverte-
·ates and aquatic plants, inasmuch as organic pollution that
.uF ·eduction of O_2 also directly increases food material.
o\ ·., it appears equally true for sensitive invertebrates
for fish that *any* reduction of dissolved O_2 may have de-
terious effects on their production. For example, Nebeker
972)[97] has found that although a certain mayfly (*Ephemera
nulans*) can survive at 4.0 mg/l of oxygen for four days,
ıy reduction of oxygen below saturation causes a decrease
successful transformation of the immature to the adult
age.

ılmonid Spawning

For spawning of salmonid fishes during the season when
ɪgs are in the gravel, there are even greater requirements
r O_2 than those given by the high level of protection.
iee Table III–3 for description of levels.) This is because
ıe water associated with the gravel may contain less oxygen
ıan the water in the stream above the gravel. There is
ɔundant evidence that salmonid eggs are adversely affected
. direct proportion to reduction in O_2. The oxygen criteria
r eggs should be about half way between the nearly
.aximum and high levels of protection.

ΓΑΡΙΕ III–3—*Guidelines for Selecting Desired Type and
L   ɪf Protection of Fish Against Deleterious Effects of
Reduced Oxygen Concentrations*

evel of protection	Intended type of protection	Possible application
˙rly Maximumᵃ	For virtually unimpaired productivity and unchanged quality of a fishery.	Appropriate for conservation areas, parks, and water bodies of high or unique value. Requires, practically speaking, that little or no deoxygenating wastes be added to natural waters. Nor must there be any activities such as unfavorable land use which would reduce O₂ levels.
ɡh...............	Not likely to cause appreciable change in the ecosystem, nor material reduction of fish production. Some impairment is risked, but appreciable damage is not to be expected at these levels of oxygen.	Could be appropriate for fisheries or aquatic ecosystems of some importance, which should not be impaired by other uses of water.
ıderate..........	Fisheries should persist, usually with no serious impairment, but with some decrease in production.	Could be used for fisheries which are valued, but must co-exist with major industries or dense human population.
˙...............	Should permit the persistence of sizeable populations of tolerant species and successful passage of most migrantsᵇ. Much reduced production or elimination of sensitive fish is likely.	Appropriate for fisheries that have some commercial or recreational value, but are so unimportant compared with other water uses, that their maintenance cannot be a major objective of pollution control. This type of protection should however, provide for survival of sensitive species in adult or subadult life stages for short periods during the year, if oxygen levels at other times are satisfactory for growth, reproduction, etc.

Note that there could be a higher level of protection that would require oxygen to be near natural level at all times,
ıerea˙ ˙˙ maximum requires only that oxygen should not fall below the lowest level characteristic of the season.
ᵇ Bı   protect migrating salmonids, which would require at least a Moderate level of protection, for zones of
ɪtaɡ.

Interaction with Toxic Pollutants or Other Environmental Factors

It is known that reduced oxygen levels increase the
toxicity of pollutants. A method for predicting this inter-
action has been given by Brown (1968),[98] and a theoretical
background by Lloyd (1961).[76] The disposal of toxic pol-
lutants must be controlled so that their concentrations will
not be unduly harmful at prescribed acceptable levels of
O_2, temperature, and pH. The levels of oxygen recom-
mended in this Section are independent of the presence of
toxic wastes, no matter what the nature of the interaction
between these toxicants and O_2 deficiencies. Carbon dioxide
is an exception, because its concentration influences the
safe level of oxygen. The recommendations for O_2 are
valid when the CO_2 concentration is within the limits
recommended in the section on CO_2.

Application of Recommendations

As previously stated, the recommendations herein differ
in two important respects from those widely used. First,
they are not fixed values independent of natural conditions.
Second, they offer a choice of different levels of protection
of fishes, the selection of any one of which is primarily a
socioeconomic decision, not a biological one.

Table III–4 presents guidelines for the protection of
fishes at each of four levels. Each column shows the level
to which the dissolved O_2 can be reduced and still provide
the stated level of protection for local fisheries. The values
can be derived from the equations given in the recommen-
dations. These equations have been calculated to fit the
curves shown in the figure on page 264 of Doudoroff and
Shumway (1970),[90] which serve as the basis of the recom-
mendations. To use Table III–4, the estimated natural
seasonal minimum should first be determined on the basis
of available data or from expert judgment. This may be
taken to be the minimum saturation value for the season,
unless there is scientific evidence that losses of O_2 levels
prevailed naturally. The word "season" here means a
period based on local climatic and hydrologic conditions,
during which the natural thermal and dissolved O_2 regime
of a stream or lake can be expected to be fairly uniform.
Division of the year into equal three-month periods, such
as December–February, March–May, is satisfactory. How-
ever, under special conditions, the designated seasons could
be periods longer or shorter than three months, and could
in fact be taken as individual months. The selected periods
need not be equal in length.

When the lowest natural value for the season has been
estimated, the desired kind and level of protection should
then be selected according to the guidelines in Table III–3.
The recommended minimum level of dissolved oxygen may
then be found in the selected column of Table III–4, or as
given by the formula in the recommendation.

TABLE III-4—Example of Recommended Minimum Concentrations of Dissolved Oxygen

Estimated natural seasonal minimum concentration of oxygen in water	Corresponding temperature of oxygen-saturated fresh water	Recommended minimum concentrations of O₂ for selected levels of protection			
		Nearly maximal	High	Moderate	Low
5	(a) (a)	5	4.7	4.2	4.0
6	46C(a) (115F)(a)	6	5.6	4.8	4.0
7	36C (96.8F)	7	6.4	5.3	4.0
8	27.5C (81.5F)	8	7.1	5.8	4.3
9	21C (69.8F)	9	7.7	6.2	4.5
10	16C (60.8F)	10	8.2	6.5	4.6
12	7.7C (45.9F)	12	8.9	6.8	4.8
14	1.5C (34.7F)	14	9.3	8.8	4.9

* Included to cover waters that are naturally somewhat deficient in O₂. A saturation value of 5 mg/l might be found in warm springs or very saline waters. A saturation value of 6 mg/l would apply to warm sea water (32 C = 90 F).

Note: The desired kind and level of protection of a given body of water should first be selected (across head of table). The estimated seasonal minimum concentration of dissolved oxygen under natural conditions should then be determined on the basis of available data, and located in the left hand column of the table. The recommended minimum concentration of oxygen for the season is then taken from the table. All values are in milligrams of O₂ per liter. Values for natural seasonal minima other than those listed are given by the formula and qualifications in the section on recommendations.

Examples

• It is desired to give moderate protection to trout (Salvelinus fontinalis) in a small stream during the summer. The maximum summer temperature is 20 C (68 F); the salt content of the water is low and has negligible effect on the oxygen saturation value. The atmospheric pressure is 760 millimeters (mm) Hg. Oxygen saturation is therefore 9.2 mg/l. This is assumed to be the natural seasonal minimum in the absence of evidence of lower natural concentrations. Interpolating from Table III-4 or using the recommended formula, reveals a minimum permissible concentration of oxygen during the summer of 6.2 mg/l. If a high level of protection had been selected, the recommendation would have been 7.8 mg/l. A low level of protection, providing little or no protection for trout but some for more tolerant fish, would require a recommendation of 4.5 mg/l. Other recommendations would be calculated in a similar way for other seasons.

• It is decided to give moderate protection to largemouth bass (Micropterus salmoides) during the summer. Stream temperature reaches a maximum of 35 C (95 F) during summer, and lowest seasonal saturation value is accordingly 7.1 mg/l. The recommendation for minimum oxygen concentration is 5.4 mg/l.

• For low protection of fish in summer in the same stream described above (for largemouth bass), the recommendation would be 4.0 mg/l, which is also the floor value recommended.

• It is desired to protect marine fish in full-strength sea water (35 parts per thousand salinity) with a maximum seasonal temperature of 16 C (61 F). The saturation value of 8 mg/l is assumed to be the natural dissolved oxygen minimum for the season. For a high level of protection, the recommendation is 7.1 mg/l, for a moderate level of protection it is 5.8 mg/l, and for a low level of protection it is 4.3 mg/l.

It should be stressed that the recommendations are the minimum values for any time during the same season.

Recommendations

(a) For nearly maximal protection of fish a... other aquatic life, the minimum dissolved oxygen in any season (defined previously) should not be less than the estimated natural seasonal minimum concentration (defined previously) characteristic of that body of water for the same season. In estimating natural minima, it is assumed that waters are saturated, unless there is evidence that they were lower in the absence of man-made influences.

(b) For a high level of protection of fish, the minimum dissolved oxygen concentration in any season should not be less than that given by the following formula in which M = the estimated natural seasonal minimum concentration characteristic of that body of water for the same season, as qualified in (a):

$$\text{Criterion}^* = 1.41M - 0.0476M^2 - 1.11$$

(c) For a moderate level of protection of fish, the minimum dissolved oxygen concentration in any season should not be less than is given by the following formula with qualifications as in (b):

$$\text{Criterion}^* = 1.08M - 0.0415M^2 - 0.202$$

(d) For a low level of protection of fish, minimum O₂ in any season should not be less t. given by the following formula with qualifications as in (b):

$$\text{Criterion}^* = 0.674M - 0.0264M^2 + 0.577$$

(e) A floor value of 4 mg/l is recommended except in those situations where the natural level of dissolved oxygen is less than 4 mg/l, in which case no further depression is desirable.

(f) For spawning grounds of salmonid fishes, higher O₂ levels are required as given in the following formula with qualifications as in (b):

$$\text{Criterion}^* = 1.19M - 0.0242M^2 - 0.418$$

(g) In stratified eutrophic and dystrophic lakes, the dissolved oxygen requirements may not apply to the hypolimnion and such lakes should be considered on a case by case basis. In other stratified lakes, recommendations (a), (b), (c), and (d) apply; and if the oxygen is below 4 mg/l, recommendation (e) applies. In unstratified lakes recommendations apply to the entire circulating water mass.

(i) All the foregoing recommendations apply to all waters except waters designated as mixing zones

* All values are instantaneous, and final value should be expr----d to two significant figures.

ee section on Mixing Zones p. 112). In locations
here supersaturation occurs, the increased levels
o' 'en should conform to the recommendations
1 . liscussion of Total Dissolved Gases, p. 139.

TAL DISSOLVED GASES (SUPERSATURATION)

Excessive total dissolved gas pressure (supersaturation) is
relatively new aspect of water quality. Previously, super-
turation was believed to be a problem that was limited to
e water supplies of fish culture facilities (Shelford and
lee 1913).[135] Lindroth (1957)[126] reported that spillways
hydroelectric dams in Sweden caused supersaturation,
id recently Ebel (1969)[112] and Beiningen and Ebel (1968)[103]
tablished that spillways at dams caused gas bubble disease
be a limiting factor for aquatic life in the Columbia and
iake Rivers. Renfro (1963)[133] and others reported that
.cessive algal blooms have caused gas bubble disease in
ntic water. DeMont and Miller (*in press*)[110] and Maious
al. (1972)[127] reported gas bubble disease among fish and
ollusks living in the heated effluents of steam generating
ations. Therefore, modified dissolved gas pressures as a
sult of dams, eutrophication, and thermal discharges
esent a widespread potential for adversely affecting fish
id aquatic invertebrates. Gas bubble disease has been
udied frequently since Gorham (1898,[119] 1899[120]) pub-
ihed his initial papers, with the result that general knowl-
lge of the causes, consequences, and adverse levels are
lea···te to evaluate criteria for this water quality char-
:t(..

Gas bubble disease is caused by excessive total dissolved
is pressure *but it is not caused by the dissolved nitrogen gas
one* (Marsh and Gorham 1904,[128] Shelford and Allee
)13,[135] Englehorn 1943,[115] Harvey et al. 1944a,[121] Doudoroff
)57,[111] Harvey and Cooper 1962).[123] Englehorn (1943)[115]
nalyzed the gases contained in the bubbles that were
rmed in fish suffering from gas bubble disease and found
iat their gas composition was essentially identical to air.
his was confirmed by Shirahata (1966).[136]

liologic Factors

Gas bubble disease (GBD) results when the uncompen-
ited total gas pressure is greater in the water than in the
.r, but several important factors influence the etiology of
BD. These factors include: exposure time and physical
:ctors such as hydrostatic pressure; other compensating
irces and biological factors such as species or life stage
ilerance or levels of activity; and any other factors that
ifluence gas solubility. Of these factors perhaps none are
lore commonly misunderstood than the physical roles of
)tal dissolved gas pressure* and hydrostatic pressure. The
illowing discussion is intended to clarify these roles.

---

* In this Section gas tension will be called gas pressure and total
as t~ ~ion will be called total dissolved gas pressure (TDGP). This
b   one as a descriptive aid to readers who are not familiar with
ie t~...inology and yet need to convey these principles to laymen.

Each component gas in air exerts a measurable pressure,
and the sum of these pressures constitutes atmospheric or
barometric pressure, which is equivalent per unit of surface
area at standard conditions to a pressure exerted by a
column of mercury 760mm high or a column of water
about 10 meters high (at sea level, excluding water vapor
pressure). The pressure of an individual gas in air is called
a *partial pressure*, and in water it is called a *tension*; both
terms are an acknowledgement that the pressure of an indi-
vidual gas is only part of the total atmospheric pressure.
Likewise, each component gas will dissolve in water inde-
pendently of all other gases, and when at equilibrium with
the air, the pressure (tension) of a specific dissolved gas is
equivalent to its partial pressure in the air. This relationship
is evident in Table III-5 which lists the main constituents
of dry air and their approximate partial pressures at sea
level.

When supersaturation occurs, the diffusion pressure im-
balance between the dissolved gas phase and the atmos-
pheric phase favors a net transfer of gases from the water to
the air. Generally this transfer cannot be accomplished fast
enough by diffusion alone to prevent the formation of gas
bubbles. However, a gas bubble cannot form in the water
unless gas nuclei are present (Evans and Walder 1969,[116]
Harvey et al. 1944b[122]) and unless the total dissolved gas
pressure exceeds the sum of the compensating pressures such
as hydrostatic pressure. Additional compensating pressures
include blood pressure and viscosity, and their benefits
may be significant.

Gas nuclei are probably unavoidable in surface water
or in animals, because such nuclei are generated by any
factor which decreases gas solubility, and because extreme
measures are required to dissolve gas nuclei (Evans and
Walder 1969;[116] Harvey et al. 1944b).[122] Therefore, hydro-
static pressure is a major preventive factor in gas bubble
disease.

The effect of hydrostatic pressure is to oppose gas bubble
formation. For example, one cannot blow a bubble out of
a tube immersed in water until the gas pressure in the tube
slightly exceeds the hydrostatic pressure at the end of the
tube. Likewise a bubble cannot form in water, blood, or

TABLE III-5—*Composition of Dry Air and Partial Pressures
of Selected Gases at Sea Level*

Gas	Molecular[a] percentage in dry air	Times atmospheric pressure	Individual gas[b] pressure in air or water at sea level
N₂..........	78.084	×760 mm Hg	=593.438 mm Hg
O₂..........	20.946	"	159.189 "
Ar..........	0.934	"	7.098 "
CO₂..........	0.033	"	0.250 "
Ne..........	0.00181	"	0.0138 "
He..........	0.00052	"	0.0039 "
			759.9927 mm Hg

a Glueckauf (1951[118]).
b At standard conditions excluding corrections for water vapor pressure.

tissue until the total gas pressure therein exceeds the sum of atmospheric pressure (760mm Hg) plus hydrostatic pressure plus any other restraining forces. This relationship is illustrated in Figure III-1 which shows, for example, that gas bubbles could form in fresh water to a depth of about one meter when the total dissolved gas pressure is equal to 1.10 atmospheres; but they could not form below that point.

Excessive total dissolved gas pressure relative to ambient atmospheric pressure, therefore, represents a greater threat to aquatic organisms in the shallow but importantly productive littoral zone than in the deeper sublittoral zone. For example, if fish or their food organisms remain within a meter of the surface in water having a total dissolved gas pressure of 1.10 atmospheres, they are theoretically capable of developing gas bubble disease, especially if their body processes further decrease gas solubility by such means as physical activity, metabolic heat, increased osmolarity, or decreased blood pressure.

Hydrostatic pressure only opposes bubble formation; it does not decrease the kinetic energy of dissolved gas molecules except at extreme pressures. If this were not the case, aerobic animal life would be eliminated at or below a water depth equivalent to the pressure of oxygen, because there would be no oxygen pressure to drive O_2 across the gill membrane and thence into the blood. For a more detailed discussion of this subject, the reader is referred to Van Liere and Stickney's (1963)[138] and Randall's (1970a)[131] excellent reviews.
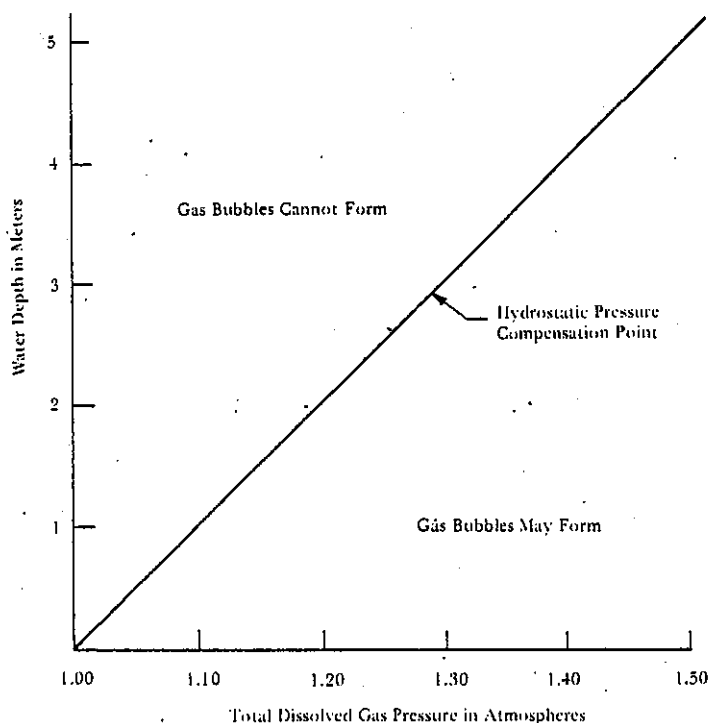

FIGURE III-1—Relationship of Total Dissolved Gas Pressure to Hydrostatic Pressure in Preventing Gas Bubble Formation

A final example will clarify the importance of total dissolved gas pressure. Eutrophic lakes often become supersaturated with photosynthetic dissolved oxygen, and such lakes commonly approach (or exceed) 120 per cent saturation values for oxygen. But this only represents additional dissolved gas pressure of about 32mm Hg ($O_2 = 159.19$ mm Hg$\times 0.2 = 31.83$ mm Hg) which equals:

$$\frac{760 \text{ mm Hg} + 31.83 \text{ mm Hg}}{760 \text{ mm Hg}} = 1.041 \text{ atmospheres of total dissolved gas pressure}$$

This imbalance apparently can be compensated in part by metabolic oxygen consumption, blood pressure, or both. On the other hand, a 1,000-fold increase in the neon saturation level would only increase the total dissolved gas pressure by about 1.8 mm Hg or:

$$\frac{1.8 \text{ mm Hg} + 760 \text{ mm Hg}}{760 \text{ mm Hg}} = 1.002 \text{ atmospheres}$$

This would not cause gas bubble disease.

The opposite situation can occur in spring water, where dissolved oxygen pressure is low and dissolved nitrogen and other gas pressures are high. In an actual case (Schneider *personal communication*),[144] dissolved nitrogen was reported to be 124 per cent of its air saturation value, whereas oxygen was 46 per cent of its air saturation value; total gas pressure was 1.046 of dry atmospheric pressure. Fish were living in this water, and although they probably suffered from hypoxia, they showed no symptoms of gas bubble dise?

How dissolved gases come out of solution and bubbles (cavitate) is a basic physical and physiological topic which is only summarized here. Harvey et al. (1944b)[122] determined that bubble formation is promoted by boundary zone or surface interfaces which reduce surface tension and thereby decrease the dissolved gas pressure required for cavitation. For this reason, one usually sees gas bubbles forming first and growing fastest on submersed interfaces, such as tank walls, sticks, or the external surfaces of aquatic life.

Gas nuclei are apparently required for bubble formation, and these are considered to be ultra micro bubbles (Evans and Walder 1969).[116] These nuclei apparently represent an equilibrium between the extremely high compressive energy of surface tension and the pressure of contained gases. Lack of gas nuclei probably accounts for instances when extremely high but uncompensated dissolved gas pressures failed to cause bubble formation (Pease and Blinks 1947,[130] Hemmingsen 1970).[124] Gas nuclei are produced by anything that decreases gas solubility or surface tension (Harvey et al. 1944b,[122] Hills 1967,[125] Evans and Walder 1969)[116] and they can be eliminated at least temporarily by extremely high pressure which drives them back into solution (Evans and Walder 1969).[116]

Possible causes of gas nuclei formation in organisms include negative pressures in skeletal or cardiac muscle d

ronounced activity (Whitaker et al. 1945),[141] eddy currents
in the blood vascular system, synthetic or biologically pro-
duc... surface-active compounds, and possible salting-out
effe... during hemoconcentration (as in saltwater adap-
...tion). Once a bubble has formed, it grows via the diffusion
f all gases into it.

Many factors influence the incidence and severity of gas
ubble disease. For example, the fat content of an animal
may influence its susceptibility. This has not been studied
in fish, but Boycott and Damant (1908),[106] Behnke (1942),[102]
and Gersh et al. (1944)[117] report that fat mammals are
more susceptible than lean mammals to the "bends" in
high-altitude decompression. This may be particularly sig-
ificant to non-feeding adult Pacific salmon which begin
their spawning run with considerable stored fat. This may
also account in part for differences in the tolerances of
different age groups or fish species. Susceptibility to gas
ubble disease is unpredictable among wild fish, particularly
when they are free to change their water depth and level of
ctivity.

as Bubble Disease Syndrome and Effects

Although the literature documents many occurrences of
as bubble disease, data are usually missing for several
nportant physical factors, such as hydrostatic pressure,
arometric pressure, relative humidity, salinity, temper-
ture or other factors leading to calculation of total dis-
ol... as pressure. The most frequently reported parameter
...s been the calculated dissolved nitrogen (N_2) concen-
ation or its percentage saturation from which one can
stimate the pressure of inert gases. Thus the reported N_2
alues provide only a general indication of the total dis-
olved gas pressure, which unfortunately tends to convey
he erroneous concept that N_2 is the instigative or only sig-
ificant factor in gas bubble disease.

Gas bubbles probably form first on the external surfaces
f aquatic life, where total hydrostatic pressure is least and
where an interface exists. Bubbles within the body of ani-
als probably form later at low dissolved gas pressures,
ecause blood pressure and other factors may provide ad-
itional resistance to bubble formation. However, at high
issolved gas pressure (>1.25 atm) bubbles in the blood
ay be the first recognizable symptom (Schneider *personal
ommunication*).[144] In the case of larval fishes, zooplankton,
r other small forms of aquatic life, the effect of external
ubbles may be a blockage of the flow of water across the
ills and asphyxiation or a change in buoyancy (Shirahata
966).[136] The latter probably causes additional energy
xpenditure or floatation, causing potentially lethal exposure
o ultraviolet radiation or potential predation.

The direct internal effects of gas bubble disease include a
ariety of symptoms that appear to be related primarily to
he l of total dissolved gas pressure, the exposure time,
nd ... *in vivo* location of lowest compensatory pressure.

The following is a résumé of Shirahata's (1966)[136] results.
As the uncompensated total dissolved gas pressure increases,
bubbles begin to appear on the fish, then within the skin,
the roof of the mouth, within the fins, or within the ab-
dominal cavity. Gas pockets may also form behind the eye-
ball and cause an exophthalmic "pop-eyed" condition.
Probably gas emboli in the blood are the last primary
symptoms to develop, because blood pressure and plasma
viscosity oppose bubble formation. At some as yet undefined
point, gas emboli become sufficiently large and frequent
to cause hemostasis in blood vessels, which in turn may
cause extensive tissue damage or complete hemostasis by
filling the heart chamber with gas. The latter is the usual
direct cause of death.

Exophthalmus or "pop-eye" and eye damage can be
caused by several factors other than gas bubble disease
and one should be duly cautious when tempted to diagnose
gas bubble disease based solely on these criteria. While the
above symptoms can be caused by excessive dissolved gas
pressure (Westgard 1964),[140] they can also be caused by
malnutrition, abrasion, and possibly by infection. Unfortu-
nately there is no known definitive way to distinguish be-
tween latent eye damage caused by previous exposure to
excessive dissolved gas pressure and other causes.

Secondary, latent, or sublethal effects of gas bubble
disease in fish include promoting other diseases, necrosis, or
other tissue changes, hemorrhages, blindness, and repro-
ductive failure (Harvey and Cooper 1962,[123] Westgard
1964,[140] Pauley and Nakatani 1967,[129] and Bouck et al.
1971).[105] There is no known evidence that supersaturation
causes a nitrogen narcosis in fish (such as can be experienced
by scuba divers), as this requires high dissolved gas pressures
probably above 10 atm. However, one can expect that fish
afflicted with gas bubble disease or the above secondary
effects might have their normal behavior altered.

There is no definitive evidence that fishes can detect
supersaturation (Shelford and Allee 1913),[135] or that they
actively avoid it by seeking hydrostatic pressure compen-
sation (Ebel 1969).[112] However, the potential capacity to
avoid supersaturation or to compensate by sounding is
limited among anadromous species by the necessity of
ascending their home river and by dams with relatively
shallow fish ladders. This may also apply to other species
that reproduce in or otherwise live in shallow-water niches.
Physiological adaptation to supersaturation seems unlikely,
and this contention is supported by the preliminary studies
of Coutant and Genoway (1968).[109]

Interaction between gas bubble disease and other stresses
is highly likely but not clearly established. Fish were more
susceptible to a given level of total dissolved gas pressure
when wounded (Egusa 1955).[114] The thermal tolerance of
Pacific salmon was reduced when N_2 levels were 125 to
180 per cent in the case of juveniles (Ebel et al. 1971),[113]
and when N_2 levels were >118 per cent in the case of adults
(Coutant and Genoway 1968).[109] Chemicals or other factors

that influence body activity or cardiovascular activity may also influence blood pressure (Randall 1970b),[132] and this would be expected to influence the degree to which the dissolved gas pressure is in excess, and hence the tolerance to gas bubble disease.

Variation in biological response is a prominent aspect of gas bubble disease, which should not be surprising in view of the numerous influential factors. Some of this variation might be explained by physiological differences between life stages or species, degree of fatness, blood pressure, blood viscosity, metabolic heat, body size, muscular activity, and blood osmolarity. For example, susceptibility to gas bubble disease may be inversely related to blood (or hemolymph) pressure. There is wide variation in blood pressure between life stages, between fish species, and between invertebrate species. Based on aortic blood pressures alone, one can hypothesize that largemouth bass (*Micropterus salmoides*) might be more susceptible to gas bubble disease than chinook salmon (*Oncorhynchus tshawytscha*) if other factors are equal. This contention is also supported by the observations that gas bubbles form in the blood of bullfrogs more easily than in rats (Berg et al. 1945),[104] possibly because of differences in blood pressure (Brand et al. 1951).[107]

Tolerance to supersaturation also varies between body sizes or life stages; Shirahata (1966)[136] relates this, in part, to an increase in cardiac and skeletal muscle activity. Larger fish were generally more sensitive to supersaturation than were smaller fish in most studies (Wiebe and McGavock 1932,[142] Egusa 1955,[114] Shirahata 1966,[136] Harvey and Cooper 1962).[123] Wood (1968)[143] has the opposite view, but he provides no supporting evidence. Possibly larger fish are more susceptible to gas bubble disease in part because they can develop greater metabolic heat than smaller fish. In this regard, Carey and Teal (1969)[108] reported that large tuna may have a muscle temperature as much as 10 C above the water temperature.

Data are quite limited on the tolerance of zooplankters and other aquatic invertebrates to excessive dissolved gas pressure. Evans and Walder (1969)[116] demonstrated that invertebrates can develop gas bubble disease. Unpublished observations by Nebeker* demonstrate that *Daphnia* sp. and *Gammarus* sp. are susceptible to gas bubble disease. On the other hand, it is widely known that some aquatic invertebrates are capable of diel migrations that may expose them to a considerable change in dissolved gas pressure; but apparently these organisms can tolerate or otherwise handle such changes. In view of the paucity of data, nothing firm can be said regarding the general tolerance of invertebrates to supersaturation.

Analytical Considerations

The apparatus and method of Van Slyke et al. (1934)[139] are still the standard analytical tools for most gas analyses. Scholander et al. (1955)[134] and others have developed simil: methods with modifications to accomodate their special needs. More recently, Swinnerton et al. (1962)[137] published a gas analysis method that utilizes gas-liquid chromatography. However, both of these basic methods have drawbacks, because they either require special expertise or do not otherwise meet the field needs of limnologists and fisheries or pollution biologists.

A new device by Weiss* measures the differential gas pressure between the air and the water within fifteen minutes. This portable device is simple to operate, easy and inexpensive to build, and gives direct readings in mm Hg. Unpublished data by Weiss show that this instrument has an accuracy comparable to the Van Slyke and the chromatographic procedures. The instrument consists of a gas sensor (150 ft. coil of small diameter, thin-walled, silicone rubber tube) connected to a mercury manometer. The sensor is placed underwater where the air in the tubing equilibrates with the dissolved gases in the water. The resulting gas pressure is read directly via the mercury manometer which gives a positive value for supersaturated water and a negative value for water that is not fully saturated.

Total Dissolved Gas Pressure Criteria

Safe upper limits for dissolved gases must be based on total dissolved gas pressures (sum of all gas tensions) and not solely on the saturation value of dissolved nitrogen gas alone. Furthermore, such limits must provide for the safety of aquatic organisms that inhabit or frequent the shallow littoral zone, where an existing supersaturation could be worsened by heating, photosynthetic oxygen production, or other factors. There is little information on the chronic sublethal effects of gas bubble disease and almost all the research has been limited to species of the family Salmonidae. Likewise, gas tolerance data are unavailable for zooplankters and most other aquatic invertebrates. Therefore, it is necessary to judge safe limits from data on mortality of selected salmonid fishes that were held under conditions approximating the shallow water of a hypothetical littoral zone. These data are:

1. Shirahata (1966)[136] reported that advanced fry of rainbow trout (*Salmo gairdneri*) experienced 10 per cent mortality when N_2 was about 111 per cent of its saturation value. He concludes that, ". . . the nitrogen contents which did not cause any gas disease were . . . less than 110 per cent to the more advanced fry."

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2. Harvey and Cooper (1962)[123] reported that fry of ockeye salmon (*Oncorhynchus nerka*) suffered latent effects necrosis and hemorrhages) for some time after normal gas [illegible]ere said to have been restored.

3. Coutant and Genoway (1968)[109] reported that sexully precocious spring chinook salmon (*Oncorhynchus tshawytcha*) weighing 2 to 4 kg, experienced extensive mortality n six days when exposed at or above 118 per cent of N_2 aturation; these salmon experienced no mortality when N_2 was below 110 per cent of saturation.

Whether or not other species or life stages of aquatic life may be more or less sensitive than the above salmonids remains to be proven. In the meantime, the above refernces provide the main basis for establishing the following otal dissolved gas recommendations.

ecommendations

Available data for salmonid fish suggest that quatic life will be protected only when *total* disolved gas pressure in water is no greater than 110 per cent of the existing atmospheric pressure. Any prolonged artificial increase in total dissolved gas pressure should be avoided in view of the incomplete body of information.

CARBON DIOXIDE

[illegible]on dioxide exists in two major forms in water. It may [illegible]ter into the bicarbonate buffering system at various oncentrations depending on the pH of the water. In addition, "free" carbon dioxide may also exist, and this component affects the respiration of fish (Fry 1957).[151] Because of respiratory effects, free carbon dioxide is the form conidered most significant to aquatic life.

The concentration of free carbon dioxide, where oxygen-demanding wastes are not excessive, is a function of pH, emperature, alkalinity, and the atmospheric pressure of carbon dioxide. Doudoroff (1957)[147] reported that concenrations of free carbon dioxide above 20 mg/l occur rarely, even in polluted waters; and Ellis (1937)[150] found that the free carbon dioxide content of Atlantic Coast streams ranged between zero and 12 mg/l. Ellis (1937)[150] and Hart (1944)[152] both reported that in 90 to 95 per cent of the fresh waters n the United States that support a good and diverse fish population the free carbon dioxide concentrations fall below [illegible] mg/l.

An excess of free carbon dioxide may have adverse effects on aquatic life. Powers and Clark (1943)[156] and Warren (1971)[157] reported that fish are able to detect and to respond to slight gradients in carbon dioxide tension. Brinley (1943)[146] and Höglund (1961)[154] observed that fish may avoid free carbon dioxide levels as low as 1.0 to 6.0 mg/l.

Elevated carbon dioxide concentrations may interfere with the ability of fish to respire properly and may thus affect dissolved oxygen uptake. Doudoroff and Katz (1950)[148] and Doudoroff and Shumway (1970)[149] reported that where dissolved oxygen uptake interference does occur, the free carbon dioxide concentrations which appreciably affect this are higher than those found in polluted waters. In bioassay tests using ten species of warmwater fish, Hart (1944)[152] found that the gizzard shad (*Dorosoma cepedianum*) was the most sensitive and was unable to remove oxygen from water 50 per cent saturated with dissolved oxygen in the presence of 88 mg/l of free carbon dioxide. The less sensitive, largemouth bass (*Micropterus salmoides*) was unable to extract oxygen when the carbon dioxide level reached 175 mg/l. Below 60 mg/l of free carbon dioxide, most species of fish had little trouble in extracting dissolved oxygen from the water.

High concentrations of free carbon dioxide cause pronounced increases in the minimum dissolved oxygen requirement of coho salmon (*Oncorhynchus kisutch*), but these fish acclimatized rapidly to carbon dioxide concentrations as high as 175 mg/l at 20 C when the dissolved oxygen level was near saturation (McNeil 1956).[155]

Basu (1959)[145] found that for most fish species, carbon dioxide affected the fishes' ability to consume oxygen in a predictable manner. He further indicated that temperature affected carbon dioxide sensitivity, being less at higher water temperatures.

The ability of fish to acclimatize to increases in carbon dioxide concentrations as high as 60 mg/l with little effect has been indicated by Haskell and Davies (1958).[153] Doudoroff and Shumway (1970)[149] indicate that the ability of fish to detect low free carbon dioxide concentrations, the presence of low carbon dioxide levels in most waters, and the ability of fish to acclimatize to carbon dioxide in the water probably prevent this constituent from becoming a major hazard.

Recommendation

Concentrations of free carbon dioxide above 20 mg/l occur rarely. Fish acclimatize to increases in carbon dioxide levels as high as 60 mg/l with little effect. However, fish are able to detect and respond to slight gradients and many avoid free carbon dioxide levels as low as 1.0 to 6.0 mg/l.

ACIDITY, ALKALINITY, AND pH

NATURAL CONDITIONS AND SIGNIFICANCE

Acidity in natural waters is caused by carbon dioxide, mineral acids, weakly dissociated acids, and the salts of strong acids and weak bases. The alkalinity of a water is actually a measure of the capacity of the carbonate-bicarbonate system to buffer the water against change in pH. Technical information on alkalinity has recently been reviewed by Kemp (1971).[162]

An index of the hydrogen ion activity is pH. Even though pH determinations are used as an indication of acidity or alkalinity or both, pH is not a measure of either. There is a relationship between pH, acidity, and alkalinity (Standard Methods 1971):[164] water with a pH of 4.5 or lower has no measurable alkalinity, and water with a pH of 8.3 or higher has no measurable acidity. In natural water, where the pH may often be in the vicinity of 8.3, acidity is not a factor of concern. In most productive fresh waters, the pH falls in a range between 6.5 and 8.5 (except when increased by photosynthetic activity). Some regions have soft waters with poor buffering capacity and naturally low pH. They tend to be less productive. Such conditions are found especially in dark colored waters draining from coniferous forests or muskegs, and in swampy sections of the Southeast. For a variety of reasons, some waters may exhibit quite extreme pH values. Before these are considered natural conditions, it should be ascertained that they have not actually resulted from man-made changes, such as stripping of ground cover or old mining activities. This is important because the recommendations refer to estimated natural levels.

TOXICITY TO AQUATIC LIFE

Some aquatic organisms, especially algae, have been found to live at pH 2 and lower, and others at pH 10 and higher; however, such organisms are relatively few. Some natural waters with a pH of 4 support healthy populations of fish and other organisms. In these cases the acidity is due primarily to carbon dioxide and natural organic acids, and the water has little buffering capacity. Other natural waters with a pH of 9.5 also support fish but are not usually highly productive.

The effects of pH on aquatic life have been reviewed in detail in excellent reports by the European Inland Fisheries Advisory Commission (1969)[160] and Katz (1969).[161] Interpretations and summaries of these reviews are given in Table III-6.

ADVERSE INDIRECT EFFECTS OR SIDE EFFECTS

Addition of either acids or alkalies to water may be harmful not only by producing acid or alkaline conditions, but also by increasing the toxicity of various components in the waters. For example, acidification of water may release free carbon dioxide. This exerts a toxic action additional to that of the lower pH. Recommendations for pH are valid if carbon dioxide is less than 25 mg/l (see the discussion of Carbon Dioxide, p. 139).

A reduction of about 1.5 pH units can cause a thousa fold increase in the acute toxicity of a metallocyaniae complex (Doudoroff et al. 1966).[159] The addition of strong alkalies may cause the formation of undissociated NH_4OH or un-ionized NH_3 in quantities that may be toxic (Lloyd 1961,[163] Burrows 1964).[158] Many other pollutants may change their toxicity to a lesser extent. It is difficult to predict whether toxicity will increase or decrease for a given direction of change in pH.

Weakly dissociated acids and bases must be considered in terms of their toxicities, as well as their effects on pH and alkalinity.

The availability of many nutrient substances varies with the hydrogen ion concentration. Some trace metals become more soluble at low pH. At higher pH values, iron tends to become unavailable to some plants, and hence the production of the whole aquatic community may be affected.

The major buffering system in natural waters is the carbonate system that not only neutralizes acids and bases to reduce the fluctuations in pH, but also forms a reservoir of carbon for photosynthesis. This process is indispensable, because there is a limit on the rate at which carbon dioxide can be obtained from the atmosphere to replace that in the water. Thus the productivity of waters is closely correlated to the carbonate buffering system. The addition of mineral acids preempts the carbonate buffering capacity, and

TABLE III-6—A Summary of Some Effects of pH on Freshwater Fish and Other Aquatic Organisms

	Known effects
.5–12.0....	Some caddis flies (Trichoptera) survive but emergence reduced.
.0–11.5....	Rapidly lethal to all species of fish.
1.5–11.0....	Rapidly lethal to salmonids. The upper limit is lethal to carp (Cyprinus carpio), goldfish (Carassius auratus), and pike. Lethal to some stoneflies (Plecoptera) and dragonflies (Odonata). Caddis fly emergence reduced.
1.0–10.5....	Withstood by salmonids for short periods but eventually lethal. Exceeds tolerance of bluegills (Lepomis macrochirus) and probably goldfish. Some typical stoneflies and mayflies (Ephemera) survive with reduced emergence.
.5–10.0....	Lethal to salmonids over a prolonged period of time and no viable fishery for coldwater species. Reduces populations of warmwater fish and may be harmful to development stages. Causes reduced emergence of some stoneflies.
1.0–9.5....	Likely to be harmful to salmonids and perch (Perca) if present for a considerable length of time and no viable fishery for coldwater species. Reduced populations of warmwater fish. Carp avoid these levels.
1.5–9.0.....	Approaches tolerance limit of some salmonids, whitefish (Coregonus), catfish (Ictaluridae), and perch. Avoided by goldfish. No apparent effects on invertebrates.
.0–8.5....	Motility of carp sperm reduced. Partial mortality of burbot (Lota lota) eggs.
0–8.0....	Full fish production. No known harmful effects on adult or immature fish; but 7.0 is near low limit for Gammarus reproduction and perhaps for some other crustaceans.
.5–7.0.....	Not lethal to fish unless heavy metals or cyanides that are more toxic at low pH are present. Generally full fish production, but for fathead minnow (Pimephales promelas), frequency of spawning and number of eggs are somewhat reduced. Invertebrates except crustaceans relatively normal, including common occurrence of mollusks. Microorganisms, algae, and higher plants essentially normal.
.0–6.5.....	Unlikely to be toxic to fish unless free carbon dioxide is present in excess of 100 ppm. Good aquatic populations with varied species can exist with some exceptions. Reproduction of Gammarus and Daphnia prevented, perhaps other crustaceans. Aquatic plants and microorganisms relatively normal except fungi frequent.
.5–6.0.....	Eastern brook trout (Salvelinus fontinalis) survive at over pH 5.5. Rainbow trout (Salmo gairdneri) do not occur. In natural situations, small populations of relatively few species of fish can be found. Growth rate of carp reduced. Spawning of fathead minnow significantly reduced. Mollusks rare.
.0–5.5.....	Very restricted fish populations but not lethal to any fish species unless CO₂ is high (over 25 ppm), or water contains iron salts. May be lethal to eggs and larvae of sensitive fish species. Prevents spawning of fathead minnow. Benthic invertebrates moderately diverse, with certain black flies (Simuliidae), mayflies (Ephemerella), stoneflies, and midges (Chironomidae) present in numbers. Lethal to other invertebrates such as the mayfly. Bacterial species diversity decreased; yeasts and sulfur and iron bacteria (Thiobacillus-Ferrobacillus) common. Algae reasonably diverse and higher plants will grow.
.5–5.0.....	No viable fishery can be maintained. Likely to be lethal to eggs and fry of salmonids. A salmonid population could not reproduce. Harmful, but not necessarily lethal to carp. Adult brown trout (Salmo trutta) can survive in peat waters. Benthic fauna restricted, mayflies reduced. Lethal to several typical stoneflies. Inhibits emergence of certain caddis fly, stonefly, and midge larvae. Diatoms are dominant algae.
.0–4.5.....	Fish populations limited; only a few species survive. Perch, some coarse fish, and pike can acclimate to this pH, but only pike reproduce. Lethal to fathead minnow. Some caddis flies and dragonflies found in such habitats; certain midges dominant. Flora restricted.
.5–4.0.....	Lethal to salmonids and bluegills. Limit of tolerance of pumpkinseed (Lepomis gibbosus), perch, pike, and some coarse fish. All flora and fauna severely restricted in number of species. Cattail (Typha) is only common higher plant.
.0–3.5.....	Unlikely that any fish can survive for more than a few hours. A few kinds of invertebrates such as certain midges and alderflies, and a few species of algae may be found at this pH range and lower

original biological productivity is reduced in proportion to the degree that such capacity is exhausted. Therefore, the minimum essential buffering capacity and tolerable pH limits are important water quality considerations.

Because of this importance, there should be no serious depletion of the carbonate buffering capacity, and it is recommended that reduction of alkalinity of natural waters should not exceed 25 per cent.

Recommendations

Suggested maximum and minimum levels of protection for aquatic life are given in the following recommendations. A single range of values could not apply to all kinds of fish, nor could it cover the different degrees of graded effects. The selection of the level of protection is a socioeconomic decision, not a biological one. The levels are defined in Table III–3 (see the discussion of Dissolved Oxygen).

Nearly Maximum Level of Protection

- pH not less than 6.5 nor more than 8.5. No change greater than 0.5 units above the estimated natural seasonal maximum, nor below the estimated natural seasonal minimum.

High Level of Protection

- pH not less than 6.0 nor more than 9.0. No change greater than 0.5 units outside the estimated natural seasonal maximum and minimum.

Moderate Level of Protection

- pH not less than 6.0 nor more than 9.0. No change greater than 1.0 units outside the estimated natural seasonal maximum and minimum.

Low Level of Protection

- pH not less than 5.5 nor more than 9.5. No change greater than 1.5 units outside the estimated natural seasonal maximum and minimum.

Additional Requirements for All Levels of Protection

- If a natural pH is outside the stated range of pH for a given level of protection, no further change is desirable.
- The extreme range of pH fluctuation in any location should not be greater than 2.0 units. If natural fluctuation exceeds this, pH should not be altered.
- The natural daily and seasonal patterns of pH variation should be maintained, although the absolute values may be altered within the limits specified.
- The total alkalinity of water is not to be decreased more than 25 per cent below the natural level.

Surface water at some time and place may contain a trace or more of any water-soluble substance. The significance and the effects of small concentrations of these substances are discussed separately throughout this Report. The presence and relative abundance of these constituents in water is influenced by several factors, including surface runoff, geochemistry of the watershed, atmospheric fallout including snow and rainfall, man-created effluents, and biological and chemical processes in the water itself. Many of these dissolved materials are essential to the life processes of aquatic organisms. For a general discussion of the chemistry of fresh water the reader is referred to Hutchinson (1957)[167] and Ruttner (1963).[172]

A general term describing the concentration of dissolved materials in water is *total dissolved solids*. The more conspicuous constituents of total dissolved solids in natural surface waters include carbonates, sulfates, chlorides, phosphates, and nitrates. These anions occur in combination with such metallic cations as calcium, sodium, potassium, magnesium, and iron to form ionizable salts (Reid 1961).[170]

Concentrations and relative proportions of dissolved materials vary widely with locality and time. Hart et al. (1945)[166] reported that in the inland waters of the United States which support a mixed biota, 5 per cent have a dissolved solids concentration under 72 mg/l; about 50 per cent under 169 mg/l; and 95 per cent under 400 mg/l. Table III-7 provides information on ranges and median concentrations of the major ions in United States streams.

The quantity and quality of dissolved solids are major factors in determining the variety and abundance of plants and animals in an aquatic system. They serve as nutrients in productivity, osmotic stress, and direct toxicity. A major change in quantity or composition of total dissolved solids changes the structure and function of aquatic ecosystems. Such changes are difficult to predict.

Concentrations of dissolved solids affecting freshwater fish by osmotic stress are not well known. Mace (1953)[169] and Rounsefell and Everhart (1953)[171] reported that the upper limit may range between 5,000 and 10,000 mg/l total dissolved solids, depending on species and prior acclimatization. The literature indicates that concentrations of total dissolved solids that cause osmotic stress in adult fish are higher than the concentrations existing in most fresh waters of the United States. Many dissolved materials are toxic at concentrations lower than those where osmotic effect can be expected. (See Toxic Substances, p. 172, and Acidity, Alkalinity, and pH, p. 140.)

Hardness of surface waters is a component of total dissolved solids and is chiefly attributable to calcium and magnesium ions. Other ions such as strontium, barium, manganese, iron, copper, zinc, and lead add to hardness, but since they are normally present in minor concentrations their effect is usually minimal. Generally, the biological productivity of a water is directly correlated with its hardness. However, while calcium and magnesium contribute to hardness and productivity, many other elements (w' present in concentrations which contribute a substa. measure of hardness) reduce biological productivity and are toxic. Hardness per se has no biological significance because biological effects are a function of the specific concentrations and combinations of the elements present.

The term "hardness" serves a useful purpose as a general index of water type, buffering capacity, and productivity. Waters high in calcium and magnesium ions (hard water) lower the toxicity of many metals to aquatic life (Brown 1968;[165] Lloyd and Herbert 1962).[168] (See Figure III-9 in the discussion of Metals, p. 178.) However, the term "hardness" should be avoided in delineating water quality

TABLE III-7—*Major Dissolved Constituents of River Waters Representing About 90 Percent of Total Stream Flow in the United States*

Constituent	Median mg/l	Range mg/l
Total dissolved solids	169	72–400
Bicarbonate (HCO₃)	90	40–180
Sulfate (SO₄)	32	11–90
Chloride (Cl)	9	3–170
Calcium (Ca)	28	15–52
Magnesium (Mg)	7	3.5–14
Sodium and potassium (Na and K)	10	6–85

Source: After Hart et al. (1945)[166]

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:quirements for aquatic life. More emphasis should be laced on specific ions.

.e   iendation

Total dissolved materials should not be changed o the extent that the biological communities characteristic of particular habitats are significantly changed. When dissolved materials are altered, bioassays and field studies can determine the limits that may be tolerated without endangering the structure and function of the aquatic ecosystem.

Losses of oil that can have an adverse effect on water quality and aquatic life can occur in many of the phases of oil production, refining, transportation, and use. Pollution may be in the form of floating oils, emulsified oils, or solution of the water soluble fraction of these oils.

The toxicity of crude oil has been difficult to interpret since crude oil may contain many different organic compounds and inorganic elements. The composition of such oils may vary from region to region, and petroleum products produced can be drastically different in character in line with their different intended uses (Purdy 1958).[198] The major components of crude oil can be categorized as aliphatic normal hydrocarbons, cyclic paraffin hydrocarbons, aromatic hydrocarbons, naphtheno-aromatic hydrocarbons, resins, asphaltenes, heteroatomic compounds, and metallic compounds (Bestougeff 1967).[175] The aromatic hydrocarbons in crude oil appear to be the major group of acutely toxic compounds (Blumer 1971,[176] Shelton 1971).[199]

Because the biological effects of oils and the relative merits of control measures are discussed in detail in Section IV (p. 257) of this Report, only effects of special interest or pertinence to fresh water are discussed here. The effects of floating oil on wildlife are discussed on p. 196.

OIL REFINERY EFFLUENTS

Copeland and Dorris (1964)[180] studied primary productivity and community respiration in a series of oil refinery effluent oxidation ponds. These ponds received waste waters which had been in contact with the crude oil and various products produced within the refinery. Surface oils were skimmed. In the series of oxidation ponds, primary productivity and community respiration measurements clearly indicated that primary producers were limited in the first ponds, probably by toxins in the water. Oxidation ponds further along in the series typically supported algal blooms. Apparently degradation of the toxic organic compounds reduced their concentration below the threshold lethal to the algae. Primary productivity was not greater than community respiration in the first ponds in the series. Minter (1964)[195] found that species diversity of phytoplankton was lowest in the first four ponds of the series of ten. A "slug" of unknown toxic substance drastically reduced the species diversity in all ponds. Zooplankton volumes increased in the latter half of the pond series, presumably as a result of decreasing toxicity. Benthic fauna species diversity in streams receiving oil refinery effluents was low near the outfall and progressively increased downstream as biological assimilation reduced the concentration of toxins (Wilhm and Dorris 1966,[206] Harrel et al. 1967,[184] Mathis and Dorris 1968[191]).

Long-term, continuous-flow bioassays of biologically treated oil refinery effluents indicated that complex refineries produce effluents which contain cumulative toxins of substances that cause accumulative deleterious effects (Graham and Dorris 1968).[182] Subsequent long-term tinuous-flow bioassays of biologically treated oil refi. effluents indicated that passage of the effluent through activated carbon columns does not remove the fish toxicants. Of the fathead minnows (*Pimphales promelas*) tested, half were killed in 14 days, and only 10 per cent survived 30 days (Burks 1972[207] *personal communication*). Trace organic compounds identified in extracts from the effluent were a homologous series of aliphatic hydrocarbons ($C_{11}H_{22}$ through $C_{18}H_{38}$) and isomers of cresol and xylenol. Since the soluble fractions derived from oil refineries are quantitatively, and to some extent qualitatively, different from those derived from oil spills, care must be taken to differentiate between these two sources.

FREE AND FLOATING OIL

Free oil or emulsions may adhere to the gills of fish, interfering with respiration and causing asphyxia. Within limits, fish are able to combat this by defensive mucous secretions (Cole 1941).[179] Free oil and emulsions may likewise coat aquatic plants and destroy them (McKee and Wolf 1963).[193]

Fish and benthic organisms may be affected by soluble substances extracted from the oils or by coating 'n emulsified oils. Water soluble compounds from cru   r

manufactured oils may also contain tainting substances which affect the taste of fish and waterfowl (Krishnawami and Kupchanko 1969).[189]

icity tests for oily substances provide a broad range of results which do not permit rigorous safety evaluations. The variabilities are due to differences in petroleum products tested, non-uniform testing procedures, and species differences. Most of the research on the effects of oils on aquatic life has used pure compounds which exist only in low percentages in many petroleum products or crude oils.

Table III–8 illustrates the range of reported toxicities. For halo-, nitro-, or thio-derivatives, the expected toxicity would be greater.

Because of the basic difficulties in evaluating the toxicity, especially of the emulsified oils, and because there is some evidence that oils may persist and have subtle chronic effects (Blumer 1971),[176] the maximum allowable concentration of emulsified oils should be determined on an individual basis and kept below 0.05 of the 96-hour LC50 for sensitive species.

TABLE III–8—Toxicity Ranges

Chemical	ppm. conc.	Effect	Species	Investigator
Aniline	379	none	Daphnia magna	Anderson 1944[17]
Benzene	31	96 hr LC50	Pimephales promelas	Pickering & Henderson 1966[197]
	22	96 hr LC50	Lepomis macrochirus	..."......."...
	32	96 hr LC50	Carassius auratus	..."......."...
Cresol	10	96 hr LC50	Lepomis macrochirus	Cairns & Scheier 1959[178]
Cyclohexane	30	96 hr LC50	Pimephales promelas	Pickering & Henderson 1966[197]
	31	96 hr LC50	Lepomis macrochirus	..."......."...
	33	..."...	Carassius auratus	"......."...
	48	..."...	Lebistes reticulatus	..."......."...
Ethylbenzene	40	..."...	Pimephales promelas	..."......."...
	29	..."...	Lepomis macrochirus	..."......."...
	73	..."...	Carassius auratus	..."......."...
	78	..."...	Lebistes reticulatus	..."......."...
Heptane	4924	48 hr LC50	Gambusia affinis	Wallen et al. 1957[205]
Isoprene	75	96 hr LC50	Pimephales promelas	Pickering & Henderson 1966[197]
	39	..."...	Lepomis macrochirus	..."......."...
	180	..."...	Carassius auratus	..."......."...
	140	..."...	Lebistes reticulatus	..."......."...
Nep...ad	5.6	..."...	Lepomis macrochirus	Cairns & Scheier 1958[177]
	6.6–7.5	..."...	Physa heterostropha	..."......."...
Naphthalene	165	48 hr LC50	Gambusia affinis	Wallen et al. 1957[205]
Toluene	1260	..."...		..."...
	44	96 hr LC50	Pimephales promelas	Pickering & Henderson 1966[197]
	24	..."...	Lepomis macrochirus	..."......."...
	62	..."...	Carassius auratus	..."......."...
	66	..."...	Lebistes reticulatus	..."......."...
Gasoline	91	48 hr LC50	Alosa sapidissima	Tagatz 1961[233]
	40	96 hr LC50	Salmo gairdneri	Mernck et al. 1956[194]
Cutting oil #2	14,500	96 hr LC50	Salmo gairdneri	Turnbull et al. 1954[204]
Diesel fuel	167	48 hr LC50	Alosa sapidissima	Tagatz 1961[203]
Bunker oil	2417	..."...	Alosa sapidissima	..."......."...
Bunker C oil	1700	168 hr LC50	Salmo salar	Sprague and Carson manuscript 1970[200]

SEDIMENTED OIL

Ludzack et al. (1957)[190] found that the sediment in the Ottawa River in Ohio downstream from a refinery consisted of up to 17.8 per cent oil. Hunt (1957)[187] and Hartung and Klingler (1968)[185] reported on the occurrence of sedimented oil in the Detroit River. North et al. (1965)[196] found sedimented oils after an oil pollution incident in marine coves in Baja California. Forbes and Richardson (1913)[181] reported 2.5 per cent oils in the bottom deposits of the Illinois River. McCauley (1964)[192] reported finding oily bottom de **·**ts after oil pollution near Boston. Thus, while the re   s may be scattered, the evidence is clear that the

existence of sedimented oils in association with oil pollution is widespread.

There is an increasing body of evidence indicating that aliphatic hydrocarbons are synthesized by aquatic organisms and find their way into sediments in areas which have little or no history of oil pollution (Han et al. 1968,[183] Avigan and Blumer 1968[174]). Hydrocarbons have been reported in the recent sediments of lakes in Minnesota (Swain 1956)[202] and the Gulf of Mexico (Stevens et al. 1956).[201]

Areas which contain oily sediments usually have an impoverished benthic fauna; it is not clear to what extent oil contributes to this, because of the presence of other pollutants (Hunt 1962).[188] However, there are recurring reports

of a probable relationship between sedimented oils and altered benthic communities. Sedimented oils may act as concentrators for chlorinated hydrocarbon pesticides (Hartung and Klingler 1970),[186] but the biological implications indicate that additional study is required.

Because of the differences in toxicities of sedimented oils and because of limited knowledge on quantities which are harmful to aquatic life, it is suggested that the concentration of hexane extractable substances (exclusive of elemental sulfur) in air-dried sediments not be permitted to increase above 1,000 mg/kg on a dry weight basis.

Recommendations

Aquatic life and wildlife should be protected where:
- there is no visible oil on the surface;
- emulsified oils do not exceed 0.05 of the 96-hour LC50;
- concentration of hexane extractable substances (exclusive of elemental sulfur) in air–dried sediments does not increase above 1,000 mg/kg on a dry weight basis.

Discharges from municipal wastewater treatment plants, a variety of industrial wastes and organic compounds, as well as biological organisms, can impart objectionable taste, odor, or color to the flesh of fish and other edible aquatic organisms. Such tainting can occur in waters with concentrations of the offending material lower than those recognized as being harmful to an animal (Tables III–9 and III–10).

BIOLOGICAL CAUSES OF TAINTING

Thaysen (1935)[231] and Thaysen and Pentelow (1936)[232] demonstrated that a muddy or earthy taste can be imparted to the flesh of trout by material produced by an odiferous s es of *Actinomyces*. Lopinot (1962)[224] reported a serious 1 nd municipal water supply tainting problem on the Mississippi River in Illinois during a period when actinomycetes, *Oscillatoria*, *Scenedesmus*, and *Actinastrum* were abundant. *Oscillatoria princeps* and *O. agardhi* in plankton of a German lake were reported by Cornelius and Bandt (1933)[213] as causing off-flavor in lake fish. Aschner et al. (1967)[210] concluded that the benthic alga, *O. tenuis*, in rearing ponds in Israel was responsible for imparting such a bad flavor to carp (*Cyprinus carpio*) that the fish were unacceptable on the market. Henley's (1970)[221] investigation of odorous metabolites of Cyanophyta showed that *Anabaena circinalis* releases geosmin and indicated that this material was responsible for the musty or earthy odor often characteristic of water from reservoirs with heavy algal growths in summer and fall.

Oysters occasionally exhibit green coloration of the gills due to absorption of the blue-green pigment of the diatom, *Navicula*, (Ranson 1927).[225]

TAINTING CAUSED BY CHEMICALS

Phenolic compounds are often associated with both water and fish tainting problems (Table III–9). However, Albersmeyer (1957)[208] and Albersmeyer and Erichsen (1959)[209] found that, after being dephenolated, both a carbolated oil light oil still imparted a taste to fish more pronounced t.   . that produced by similar exposures to naphthalene

and methylnaphthalene (phenolated compounds). They concluded that other hydrocarbons in the oils were more responsible for imparting off-flavor than the phenolic materials in the two naphthalenes tested.

Refineries (Fetterolf 1962),[215] oily wastes (Zillich 1969),[236] and crude oil (Galtsoff et al. 1935)[219] have been associated with off-flavor problems of fish and shellfish in both freshwater and marine situations (Westman and Hoff 1963).[234] Krishnawami and Kupchanko (1969)[223] demonstrated that rainbow trout (*Salmo gairdneri*) adsorbed enough compounds from a stream polluted with oil slicks and oil refinery effluents to exhibit a definite oily taste and flavor. In waters receiving black liquor from kraft pulp mills, the gills and mantles of oysters developed a gray color (Galtsoff et al. 1947).[218] The authors also found this condition in oysters grown in waters receiving domestic sewage. Newton (1967)[237] confined trout in live-cages and correlated inten-

TABLE III–9—Wastewaters Found to have Lowered the Palatability of Fish Flesh

Wastewater source	Concentration in water affecting palatability of fish	Species	Reference
2,4-D mfg. plant	50–100 mg/l	Trout	Shumway 1966[223]
Coal—coking	0.02–0.1 mg/l	Freshwater fish	Bandt 1955[211]
Coal—tar	0.1 mg/l	Freshwater fish	Bandt 1955[211]
Kraft process (untreated)	1–2% by vol.	Salmon	Shumway and Chadwick 1971[229]
Kraft process (treated)	9–12% by vol.	Salmon	Shumway and Palensky, unpublished data[239]
Kraft and neutral sulfite process		Trout	Newton 1967[237]
Municipal dump runoff		Channel catfish (Ictalurus punctatus)	Thomas and Hicks 1971[233]
Municipal untreated sewage (2 locations)		Channel catfish	Thomas and Hicks 1971[233]
Municipal wastewater treatment plants (4 locations)		Channel catfish	Thomas and Hicks 1971[233]
Municipal wastewater treatment plant (Primary)	11–13% by vol.	Freshwater fish	Shumway and Palensky, unpublished data[239]
Municipal wastewater treatment plant (Secondary)	20–26% by vol.	Freshwater fish	Shumway and Palensky, unpublished data[239]
Oily wastes		Trout	Zillich 1969[236]
Refinery		Trout	Fetterolf 1962[215]
Sewage containing phenols	0.1 mg/l	Freshwater fish	Bandt 1955[211]
Slaughterhouses (2 locations)		Channel catfish	Thomas and Hicks 1971[233]

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TABLE III-10—*Concentrations of Chemical Compounds in Water That Can Cause Tainting of the Flesh of Fish and Other Aquatic Organisms*

Chemical	Estimated threshold level in water (mg/l)	Reference*
acetophenone	0.5	d
acrylonitrile	18	g
cresol	0.07	g
m-cresol	0.2	g
o-cresol	0.4	g
p-cresol	0.12	g
cresylic acid (meta para)	0.2	d
N-butylmercaptan	0.06	g
o-sec. butylphenol	0.3	d
p-tert. butylphenol	0.03	d
o-chlorophenol	0.0001 to 0.015	b, d, e
p-chlorophenol	0.01 to 0.05	d, g, e
2,3-dichlorophenol	0.084	g
2,4-dichlorophenol	0.001 to 0.014	d, f, g
2,5-dichlorophenol	0.023	g
2,6-dichlorophenol	0.035	g
2-methyl, 4-chlorophenol	0.075	g
2-methyl, 6-chlorophenol	0.003	g
o-phenylphenol	1	d
2,4,6-trichlorophenol	0.003 to 0.05	g
phenol	1 to 10	d, e
phenols in polluted river	0.02 to 0.15	a
diphenyl oxide	0.05	d
β,β-dichlorodiethyl ether	0.09 to 1.0	d, g
o-dichlorobenzene	0.25	d
ethylbenzene	<0.25	d
ethanethiol	0.24	g
ethylacrylate	0.6	g
formaldehyde	95	g
kerosene	0.1	d
kerosene plus kaolin	1	i
isopropylbenzene	<0.25	d
naphtha	0.1	d
naphthalene	1	a
naphthol	0.5	a
2-naphthol	0.3	g
dimethylamine	7	g
α-methylstyrene	0.25	d
oil, emulsifiable	>15	d
pyridine	5 to 28	a, g
pyrocatechol	0.8 to 5	a, g
pyrogallol	20 to 30	a
quinoline	0.5 to 1	a
p-quinone	0.5	a
styrene	0.25	d
toluene	0.25	d
outboard motor fuel, as exhaust	2.6 gal/acre-foot	c, h
guaiacol	0.082	g

* Reference key:
  a Bandt 1955[211]
  b Boetius 1954[212]
  c English et al. 1963[214]
  d Fetterolf 1964[215] published the results of A. W. Winston, Jr. of the Dow Chemical Company. The data are also available in an undated mimeographed release of the company
  e Schulze 1961[227]
  f Shumway 1966[228]
  g Shumway, D. L. and J. R. Palensky,[239] unpublished data (1971).
  h Surber, et al. 1965[230]
  i Westman and Hoff 1963[234]

sity of off-flavor with proximity to the discharge of a paper mill using both the neutral sulfite and kraft processes.

Shellfish have the ability to concentrate and store metals at levels greater than the concentrations in the water (see Section I, pp. 36–37, and Section IV, p. 240). Oyster flesh can become green-colored from copper accumulation. The

copper content of normal-colored oyster flesh from uncontaminated areas varied from 0.170 to 0.214 mg copper per oyster, or from 8.21 to 13.77 mg per 100 grams dry weight (Galtsoff and Whipple 1931;[220] Galtsoff 1964[217]). Oyster growing in adjacent areas slightly contaminated with copper salts had green-colored flesh and contained from 1.27 to 2.46 mg copper per oyster, or from 121 to 271 mg per 100 grams dry weight.

If an effluent containing a variety of components is associated with a tainting problem, identification of the taint-producing component or components is necessary for efficient isolation and removal in waste treatment. For example, Shumway (1966)[228] exposed salmon to various concentrations of wastes and waste components discharged from a plant producing pesticides. Although concentrations of the combined wastes at about 50 to 100 mg/l were found to impart objectionable flavor to test fish, one of the major components of the plant waste, 2,4-dichlorophenol, was found capable of impairing flavor at exposure levels of about 1 to 3 μg/l.

A preliminary laboratory study (English et al. 1963)[214] showed that outboard motor exhaust damages the quality of water in several ways, the most noticeable of which are unpleasant taste and odor in the water and off-flavoring of fish flesh. A later field study (Surber et al. 1965)[230] determined the threshold level of tainting of fish in pond and lake waters to be about 2.6 gal/acre-foot of fuel as exhaust, accumulating over a 2-month period. The gasoline used was regular grade, and the lubricating oil (½ pint/g: was a popular brand of packaged outboard motor oil.

UPTAKE AND LOSS OF FLAVOR-IMPAIRING MATERIALS

Experiments involving method and rates of uptake and loss of flavor-impairing materials by aquatic organisms have been reported by few investigators. From data available it is obvious that rates are highly variable. Thaysen and Pentelow (1936)[232] exposed trout to extract from odoriferous *Actinomyces*. They showed that fish exposed to 10 ppm of extract acquired an off-flavor in one hour. The exposed fish were also removed and held in uncontaminated water for periods up to five days. The level of tainting, which showed no diminution after 27 hours, became less marked after 2 to 3 days, and no tainting could be detected after 5 days in fresh water.

Shumway and Palensky (*unpublished data*)[239] exposed trout to three separate concentrations of each of the following chemicals, o-cresol, 2,4-dichlorophenol, pyridine, and n-butylmercaptan, for periods up to 168 hours. With all four chemicals, maximum off-flavor generally occurred in 33.5 hours or less. In a few exceptions, a gradual increase in off-flavor appeared to occur with increasing time up to 168 hours, although the magnitude of increase in off-fla~ with time was minor in nature. In tests with o-chlorophe:

Boetius (1954)[212] reported that eels required up to 11 days exposure before flavor impairment was detected. The time re   ·ed to impair flavor was found to be related to the e.   ·re concentration, with low concentrations requiring longer exposure periods.

Shumway (1966)[228] found that the flesh of salmon exposed experimentally to industrial wastes containing mainly phenols acquired maximum off-flavor in 35 hours or less, with much of the tainting occurring within the first 6 hours. After the salmon were transferred to uncontaminated water, most of the acquired off-flavor was lost within 20 hours, although some off-flavor remained up to 72 hours.

In other tests, Shumway and Palensky (*unpublished data*)[239] observed flavor impairment in trout after 24-hour exposure to 2,4-dichlorophenol. After only 33.5 hours in uncontaminated water, the flavor of the trout had returned to the preexposure level, with most of the reduction in off-flavor occurring within 6.5 hours.

Korschgen et al. (1970)[222] transferred carp (*Cyprinus carpio*) to uncontaminated ponds from two sites, one of which received effluents from a major municipality and one of which received little or no effluent. Retention up to 18 days in the holding ponds failed to improve the flavor of the carp from the contaminated site. These authors also reported that channel catfish (*Ictalurus punctatus*) transferred from the Ohio River to control water lost about half of their off-flavor in 7 days and nearly all of it in 21 days.

I IFICATION OF CAUSES OF OFF-FLAVORED ORGANISMS

Determination that a tainting problem exists, or identification of a taint-causing material, involves field or laboratory exposure periods and organoleptic tests. When properly conducted, these tests are reliable but time-consuming. Wright (1966)[235] reported on the use of gas chromatography in conjunction with organoleptic tests. The chromatographic scans were compared with scans of industrial process waste streams to identify the taint-producing wastes. Gas chromatographic techniques are employed routinely in food technology laboratories investigating flavor and odor properties (Rhoades and Millar 1965).[226]

EXPOSURE AND ORGANOLEPTIC TESTS

Field exposure tests (bioassays) are used to determine the existence or the magnitude of a tainting problem in a water body. Fish or other edible aquatic life are held for a period of time in cages at selected locations in and around a suspected problem area or waste discharge and eventually evaluated for flavor. Laboratory bioassays are normally utilized to determine the tainting potential of wastes, waste components, or specific chemicals. Although either static c   tinuous-flow bioassays can be used in laboratory tests, co.....nuous-flow systems are considered far superior to static

tests. Exposure bioassays are followed by the organoleptic evaluation of the flesh of the test organisms.

In their studies of tainted organisms, investigators have used a number of different bioassay and flavor-evaluation procedures, some of which have produced poorly defined results. The following guidelines are based primarily on the successful procedures of Shumway and Newton (*personal communications*).[238]

Test Fish

The flesh of the fish to be exposed should be mild and consistent in flavor. For convenience in holding and taste testing, fish weighing between 200 and 400 grams are desirable, although smaller or larger fish are acceptable. Largemouth bass (*Micropterus salmoides*), yellow perch (*Perca flavescens*), channel catfish, bluegill (*Lepomis macrochirus*), trout, salmon flatfishes (Pleuronectiformes), and others have proven to be acceptable test fish.

Exposure Period

In general, test fish should be exposed for a period not less than 48 hours. Shorter or longer exposures will be advisable in some situations, although possible stress, disease, and mortality resulting from longer retention of test fish and maintenance of holding facilities may negate advantages of long exposure.

Exposure Conditions

The following conditions are desirable in laboratory bioassays:

Dissolved oxygen........near saturation
Temperature...........10–15 C for salmonids, and 20–25 C for warmwater fish
pH....................6.0–8.0, or pH of receiving water
Light..................intensity held at a low level
Water................uncontaminated, or quality of the receiving water; never distilled water

Preparation of Test Fish and Evaluation

Exposed fish and control fish, either fresh or fresh-frozen and subsequently thawed, are individually double-wrapped in aluminum foil, placed in an oven and cooked at about 375 F for 15 to 30 minutes, as size requires. Large fish may be portioned for cooking. No seasoning of any kind is added. Portions of the cooked fish may be placed in small coded cups and served warm to the judges for flavor evaluation. A known "reference" may be provided to aid judges in making comparisons. A minimum of ten experienced judges, each seated in an isolation booth or similar area, smell, taste, and score each sample. This method offers tighter control of variables and conforms more to off-flavor evaluations conducted in food laboratories than the more informal procedure below.

An alternative method is to place the cooked fish, still partially wrapped in foil to preserve the heat and flavor, on a large table. The judges start concurrently and work their way around the table, recording aroma and flavor. If a judge tastes more than six samples during a test, a lessening of organoleptic acuity may occur.

When investigating the potential of a substance to produce taint, a word-evaluation scale for intensity of off-flavor ranging from no off-flavor to extreme off-flavor, has proven successful with trained, experienced judges. Numerical values from 0 to 6 are applied to the word scale for derivation of off-flavor indices and statistical evaluation.

When using the above method, less experienced judges tend to over-react to slight off-flavor. For this reason, in less formal tests evaluating the effect of a substance on the palatability of the organism, an hedonic scale accompanied by word-judgments describing palatability is appropriate, i.e., 0—excellent, 1—very good, 2—good, 3—fair, 4—just acceptable, 5—not quite acceptable, 6—very poor, inedible, and 7—extremely poor, repulsive. Scores of the judges on each sample are averaged to determine final numerical or word-judgment values.

To determine whether there are acceptability differences between controls and test organisms, a triangle test may be used in which two samples are alike and one is different. Judges are asked to select the like samples, to indicate the degree of difference, and to rate both the like and the odd samples on a preference scale.

STATISTICAL EVALUATION

The triangle test is particularly well adapted to statistical analysis, but the organoleptic testing necessary is more extensive than when hedonic scales are used.

Application of the two-way analyses of variance to hedonic-scale data is an acceptable test, but professional assistance with statistical procedures is desirable. Reliance on the word-judgment system is sufficient for general information purposes.

Recommendations

- To prevent tainting of fish and other edible aquatic organisms, it is recommended that substances which cause tainting should not be present in water in concentrations that lower the acceptability of such organisms as determined by exposure bioassay and organoleptic tests.
- Values in Tables III–9 and III–10 are recommended as guidelines in determining what concentrations of wastes and substances in water may cause tainting of the flesh of fish or other aquatic organisms.

Living organisms do not respond to the quantity of heat but to degrees of temperature or to temperature changes caused by transfer of heat. The importance of temperature to acquatic organisms is well known, and the composition of aquatic communities depends largely on the temperature characteristics of their environment. Organisms have upper and lower thermal tolerance limits, optimum temperatures for growth, preferred temperatures in thermal gradients, and temperature limitations for migration, spawning, and egg incubation. Temperature also affects the physical environment of the aquatic medium, (e.g., viscosity, degree of ice cover, and oxygen capacity. Therefore, the composition of aquatic communities depends largely on temperature characteristics of the environment. In recent there has been an accelerated demand for cooling w...ers for power stations that release large quantities of heat, causing, or threatening to cause, either a warming of rivers, lakes, and coastal waters, or a rapid cooling when the artificial sources of heat are abruptly terminated. For these reasons, the environmental consequences of temperature changes must be considered in assessments of water quality requirements of aquatic organisms.

The "natural" temperatures of surface waters of the United States vary from 0 C to over 40 C as a function of latitude, altitude, season, time of day, duration of flow, depth, and many other variables. The agents that affect the natural temperature are so numerous that it is unlikely that two bodies of water, even in the same latitude, would have exactly the same thermal characteristics. Moreover, a single aquatic habitat typically does not have uniform or consistent thermal characteristics. Since all aquatic organisms (with the exception of aquatic mammals and a few large, fast-swimming fish) have body temperatures that conform to the water temperature, these natural variations create conditions that are optimum at times, but are generally above or below optima for particular physiological, behavioral, and competitive functions of the species present.

Because significant temperature changes may affect the position of an aquatic or wildlife community, an ..ced change in the thermal characteristics of an eco-

system may be detrimental. On the other hand, altered thermal characteristics may be beneficial, as evidenced in most fish hatchery practices and at other aquacultural facilities. (See the discussion of Aquaculture in Section IV.)

The general difficulty in developing suitable criteria for temperature (which would limit the addition of heat) lies in determining the deviation from "natural" temperature a particular body of water can experience without suffering adverse effects on its biota. Whatever requirements are suggested, a "natural" seasonal cycle must be retained, annual spring and fall changes in temperature must be gradual, and large unnatural day-to-day fluctuations should be avoided. In view of the many variables, it seems obvious that no single temperature requirement can be applied uniformly to continental or large regional areas; the requirements must be closely related to each body of water and to its particular community of organisms, especially the important species found in it. These should include invertebrates, plankton, or other plant and animal life that may be of importance to food chains or otherwise interact with species of direct interest to man. Since thermal requirements of various species differ, the social choice of the species to be protected allows for different "levels of protection" among water bodies as suggested by Doudoroff and Shumway (1970)[272] for dissolved oxygen criteria. (See Dissolved Oxygen, p. 131.) Although such decisions clearly transcend the scientific judgments needed in establishing thermal criteria for protecting selected species, biologists can aid in making them. Some measures useful in assigning levels of importance to species are: (1) high yield to commercial or sport fisheries, (2) large biomass in the existing ecosystem (if desirable), (3) important links in food chains of other species judged important for other reasons, and (4) "endangered" or unique status. If it is desirable to attempt strict preservation of an existing ecosystem, the most sensitive species or life stage may dictate the criteria selected.

Criteria for making recommendations for water temperature to protect desirable aquatic life cannot be simply a maximum allowed change from "natural temperatures." This is principally because a change of even one degree from

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an ambient temperature has varying significance for an organism, depending upon where the ambient level lies within the tolerance range. In addition, historic temperature records or, alternatively, the existing ambient temperature prior to any thermal alterations by man are not always reliable indicators of desirable conditions for aquatic populations. Multiple developments of water resources also change water temperatures both upward (e.g., upstream power plants or shallow reservoirs) and downward (e.g., deepwater releases from large reservoirs), so that "ambient" and "natural" are exceedingly difficult to define at a given point over periods of several years.

Criteria for temperature should consider both the multiple thermal requirements of aquatic species and requirements for balanced communities. The number of distance requirements and the necessary values for each require periodic reexamination as knowledge of thermal effects on aquatic species and communities increases. Currently definable requirements include:

- maximum sustained temperatures that are consistent with maintaining desirable levels of productivity;
- maximum levels of metabolic acclimation to warm temperatures that will permit return to ambient winter temperatures should artificial sources of heat cease;
- temperature limitations for survival of brief exposures to temperature extremes, both upper and lower;
- restricted temperature ranges for various stages of reproduction, including (for fish) gonad growth and gamete maturation, spawning migration, release of gametes, development of the embryo, commencement of independent feeding (and other activities) by juveniles; and temperatures required for metamorphosis, emergence, and other activities of lower forms;
- thermal limits for diverse compositions of species of aquatic communities, particularly where reduction in diversity creates nuisance growths of certain organisms, or where important food sources or chains are altered;
- thermal requirements of downstream aquatic life where upstream warming of a cold-water source will adversely affect downstream temperature requirements.

Thermal criteria must also be formulated with knowledge of how man alters temperatures, the hydrodynamics of the changes, and how the biota can reasonably be expected to interact with the thermal regimes produced. It is not sufficient, for example, to define only the thermal criteria for sustained production of a species in open waters, because large numbers of organisms may also be exposed to thermal changes by being pumped through the condensers and mixing zone of a power plant. Design engineers need

particularly to know the biological limitations to their design options in such instances. Such considerations may reveal nonthermal impacts of cooling processes that may outweigh temperature effects, such as impingement of fish upon intake screens, mechanical or chemical damage to zooplankton in condensers, or effects of altered current patterns on bottom fauna in a discharge area. The environmental situations of aquatic organisms (e.g., where they are, when they are there, in what numbers) must also be understood. Thermal criteria for migratory species should be applied to a certain area only when the species is actually there. Although thermal effects of power stations are currently of great interest, other less dramatic causes of temperature change including deforestation, stream channelization, and impoundment of flowing water must be recognized.
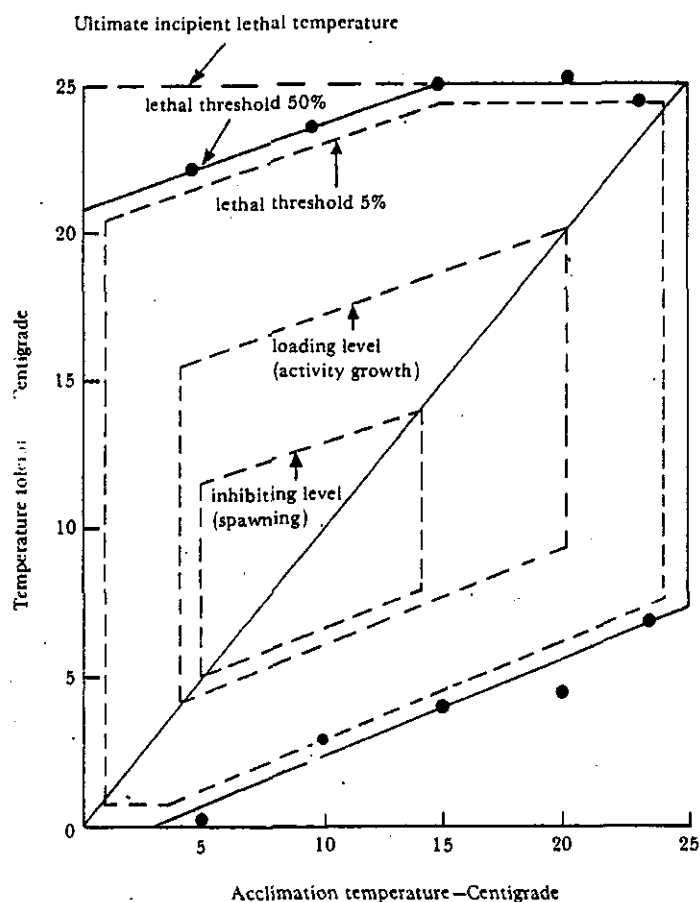
DEVELOPMENT OF CRITERIA

Thermal criteria necessary for the protection of species or communities are discussed separately below. The order of presentation of the different criteria does not imply priority for any one body of water. The descriptions define preferred methods and procedures for judging thermal requirements, and generally do not give numerical values (except in Appendix II–C). Specific values for all limitations would require a biological handbook that is far beyond the scope of this Section. The criteria may seem complex, but they represent an extensively developed framework of knowledge about biological responses. (A sample application of the criteria begins on page 166, Use of Temperature Criteria.)

TERMINOLOGY DEFINED

Some basic thermal responses of aquatic organisms will be referred to repeatedly and are defined and reviewed briefly here. Effects of heat on organisms and aquatic communities have been reviewed periodically (e.g., Bullock 1955,[259] Brett 1956;[253] Fry 1947,[276] 1964,[278] 1967;[279] Kinne 1970[296]). Some effects have been analyzed in the context of thermal modification by power plants (Parker and Krenkel 1969;[308] Krenkel and Parker 1969;[298] Cairns 1968;[261] Clark 1969;[263] and Coutant 1970c[269]). Bibliographic information is available from Kennedy and Mihursky (1967),[294] Raney and Menzel (1969),[313] and from annual reviews published by the Water Pollution Control Federation (Coutant 1968,[265] 1969,[266] 1970a,[267] 1971[270]).
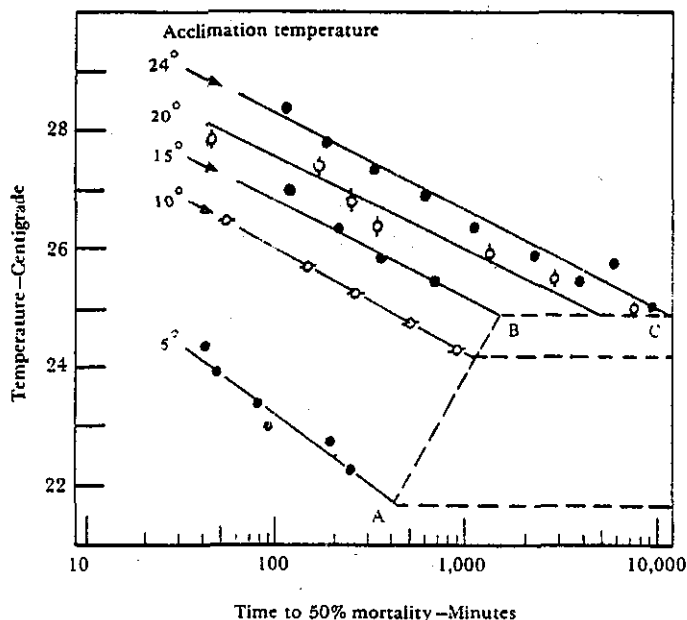
Each species (and often each distinct life-stage of a species) has a characteristic tolerance range of temperature as a consequence of acclimations (internal biochemical adjustments) made while at previous holding temperature (Figure III–2; Brett 1956[253]). Ordinarily, the ends of this range, or the lethal thresholds, are defined by survival of 50 per cent of a sample of individuals. Lethal thresholds typically are referred to as "incipient lethal temperatures," and temperature beyond these ranges would be considered "t

treme." The tolerance range is adjusted upward by acclimation to warmer water and downward to cooler water, al··· ·gh there is a limit to such accommodation. The lo ·nd of the range usually is at zero degrees centigrade 32 F) for species in temperate latitudes (somewhat less for saline waters), while the upper end terminates in an "ultimate incipient lethal temperature" (Fry et al. 1946[231]). This ultimate threshold temperature represents the "breaking point" between the highest temperatures to which an animal can be acclimated and the lowest of the extreme temperatures that will kill the warm-acclimated organism. Any rate of temperature change over a period of minutes

After Brett 1952 [252]

FIGURE III–3—*Median resistance times to high temperatures among young chinook (Oncorhynchus tshawytscha) acclimated to temperatures indicated. Line A-B denotes rising lethal threshold (incipient lethal temperatures) with increasing acclimation temperature. This rise eventually ceases at the ultimate lethal threshold (ultimate upper incipient lethal temperature), line B-C.*

to a few hours will not greatly affect the thermal tolerance limits, since acclimation to changing temperatures requires several days (Brett 1941).[251]

At the temperatures above and below the incipient lethal temperatures, survival depends not only on the temperature but also on the duration of exposure, with mortality occurring more rapidly the farther the temperature is from the threshold (Figure III–3). (See Coutant 1970a[267] and 1970b[268] for further discussion based on both field and laboratory studies.) Thus, organisms respond to extreme high and low temperatures in a manner similar to the dosage-response pattern which is common to toxicants, pharmaceuticals, and radiation (Bliss 1937).[249] Such tests seldom extend beyond one week in duration.

MAXIMUM ACCEPTABLE TEMPERATURES FOR PROLONGED EXPOSURES

Specific criteria for prolonged exposure (1 week or longer) must be defined for warm and for cold seasons. Additional criteria for gradual temperature (and life cycle) changes during reproduction and development periods are discussed on pp. 162–165.

After Brett 1960 [254]

FIGURE III–2—*Upper and lower lethal temperatures for young sockeye salmon (Oncorhynchus nerka) plotted to show the zone of tolerance. Within this zone two other zones are represented to illustrate (1) an area beyond which growth wo··'·* be poor to none-at-all under the influence of the loading e·· ·)f metabolic demand, and (2) an area beyond which te·...·erature is likely to inhibit normal reproduction.*

SPRING, SUMMER, AND FALL MAXIMA FOR PROLONGED EXPOSURE

Occupancy of habitats by most aquatic organisms is often limited within the thermal tolerance range to temperatures somewhat below the ultimate upper incipient lethal temperature. This is the result of poor physiological performance at near lethal levels (e.g., growth, metabolic scope for activities, appetite, food conversion efficiency), interspecies competition, disease, predation, and other subtle ecological factors (Fry 1951;[277] Brett 1971[256]). This complex limitation is evidenced by restricted southern and altitudinal distributions of many species. On the other hand, optimum temperatures (such as those producing fastest growth rates) are not generally necessary at all times to maintain thriving populations and are often exceeded in nature during summer months (Fry 1951;[277] Cooper 1953;[264] Beyerle and Cooper 1960;[246] Kramer and Smith 1960[297]). Moderate temperature fluctuations can generally be tolerated as long as a maximum upper limit is not exceeded for long periods.

A true temperature limit for exposures long enough to reflect metabolic acclimation and optimum ecological performance must lie somewhere between the physiological optimum and the ultimate upper incipient lethal temperatures. Brett (1960)[254] suggested that a provisional long-term exposure limit be the temperature greater than optimum that allowed 75 per cent of optimum performance. His suggestion has not been tested by definitive studies.

Examination of literature on performance, metabolic rate, temperature preference, growth, natural distribution, and tolerance of several species has yielded an apparently sound theoretical basis for estimating an upper temperature limit for long term exposure and a method for doing this with a minimum of additional research. New data will provide refinement, but this method forms a useful guide for the present time. The method is based on the general observations summarized here and in Figure III–4(a, b, c).

1. Performances of organisms over a range of temperatures are available in the scientific literature for a variety of functions. Figures III–4a and b show three characteristic types of responses numbered 1 through 3, of which types 1 and 2 have coinciding optimum peaks. These optimum temperatures are characteristic for a species (or life stage).

2. Degrees of impairment from optimum levels of various performance functions are not uniform with increasing temperature above the optimum for a single species. The most sensitive function appears to be growth rate, for which a temperature of zero growth (with abundant food) can be determined for important species and life stages. Growth rate of organisms appears to be an integrator of all factors acting on an organism. Growth rate should probably be expressed as net biomass gain or net growth (McCormick et al. 1971)[302] of the population, to account for deaths.

3. The maximum temperature at which several species are consistently found in nature (Fry 1951;[277] Narver 1970)[306] lies near the average of the optimum temperature and the temperature of zero net growth.

4. Comparison of patterns in Figures III–4a and among different species indicates that while the trends are similar, the optimum is closer to the lethal level in some species than it is in sockeye salmon. Invertebrates exhibit a pattern of temperature effects on growth rate that is very similar to that of fish (Figure III–4c).

The optimum temperature may be influenced by rate of feeding. Brett et al. (1969)[257] demonstrated a shift in optimum toward cooler temperatures for sockeye salmon when ration was restricted. In a similar experiment with channel catfish, Andrews and Stickney (1972)[242] could see no such shift. Lack of a general shift in optimum may be due to compensating changes in activity of the fish (Fry *personal observation*).[326]

These observations suggest that an average of the optimum temperature and the temperature of zero net growth [(opt. temp. + z.n.g. temp)/2] would be a useful estimate of a limiting weekly mean temperature for resident organisms, providing the peak temperatures do not exceed values recommended for short-term exposures. Optimum growth rate would generally be reduced to no lower than 80 per cent of the maximum if the limiting temperature is as averaged above (Table III–11). This range of reduction from optimum appears acceptable, although there are no quantitative studies available that would allow the criterion to be based upon a specific level of impairment.

The criteria for maximum upper temperature must all for seasonal changes, because different life stages of many species will have different thermal requirements for the average of their optimum and zero net growths. Thus a juvenile fish in May will be likely to have a lower maximum acceptable temperature than will the same fish in July, and this must be reflected in the thermal criteria for a waterbody.

TABLE III–11—Summary of Some Upper Limiting Temperatures in C, (for periods longer than one week) Based Upon Optimum Temperatures and Temperatures of Zero Net Growth.

Species	Optimum	Zero net growth	Reference	opt + z.n.g. / 2	% of optimum
Catostomus commersoni (white sucker)	27	29.6	*	28.3	86
Coregonus artedii (cisco or lake herring)	16	21.2	McCormick et al. 1971[302]	18.6	82
Ictalurus punctatus (channel catfish)	30	35.7	Strawn 1970[390]	32.8	94
"	30	35.7	Andrews and Stickney 1972[242]	32.8	88
Lepomis macrochirus (bluegill) (year II)	22	28.5	McComish 1971[301]	25.3	82
Micropterus salmoides (largemouth bass)	27.5	34	Strawn 1961[319]	30.8	83
Notropis atherinoides (emerald shiner)	27	33	*	30.5	83
Salvelinus fontinalis (brook trout)	15.4	18.8	*	17.1	80

*National Water Quality Laboratory, Duluth, Minn., unpublished data.[328]
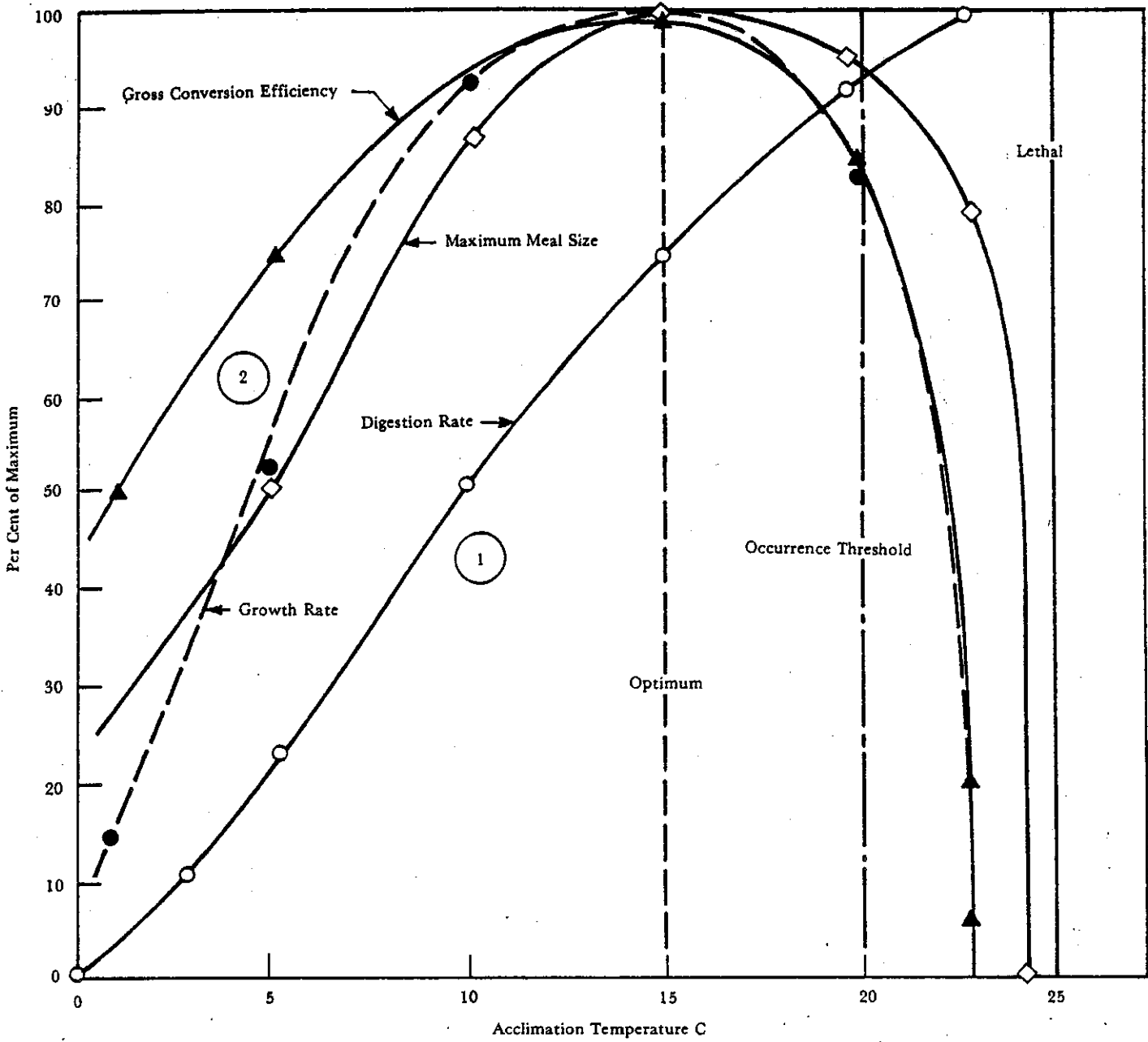
After Brett 1971[256]

FIGURE III-4a—Performance of Sockeye Salmon (Oncorhynchus nerka) *in Relation to Acclimation Temperature*

While this approach to developing the maximum sustained temperature appears justified on the basis of available knowledge, few limits can be derived from existing data in the literature on zero growth. On the other hand, there is a sizeable body of data on the ultimate incipient lethal temperature that could serve as a substitute for the data on temperature of zero net growth. A practical consideration in recommending criteria is the time required to cond:
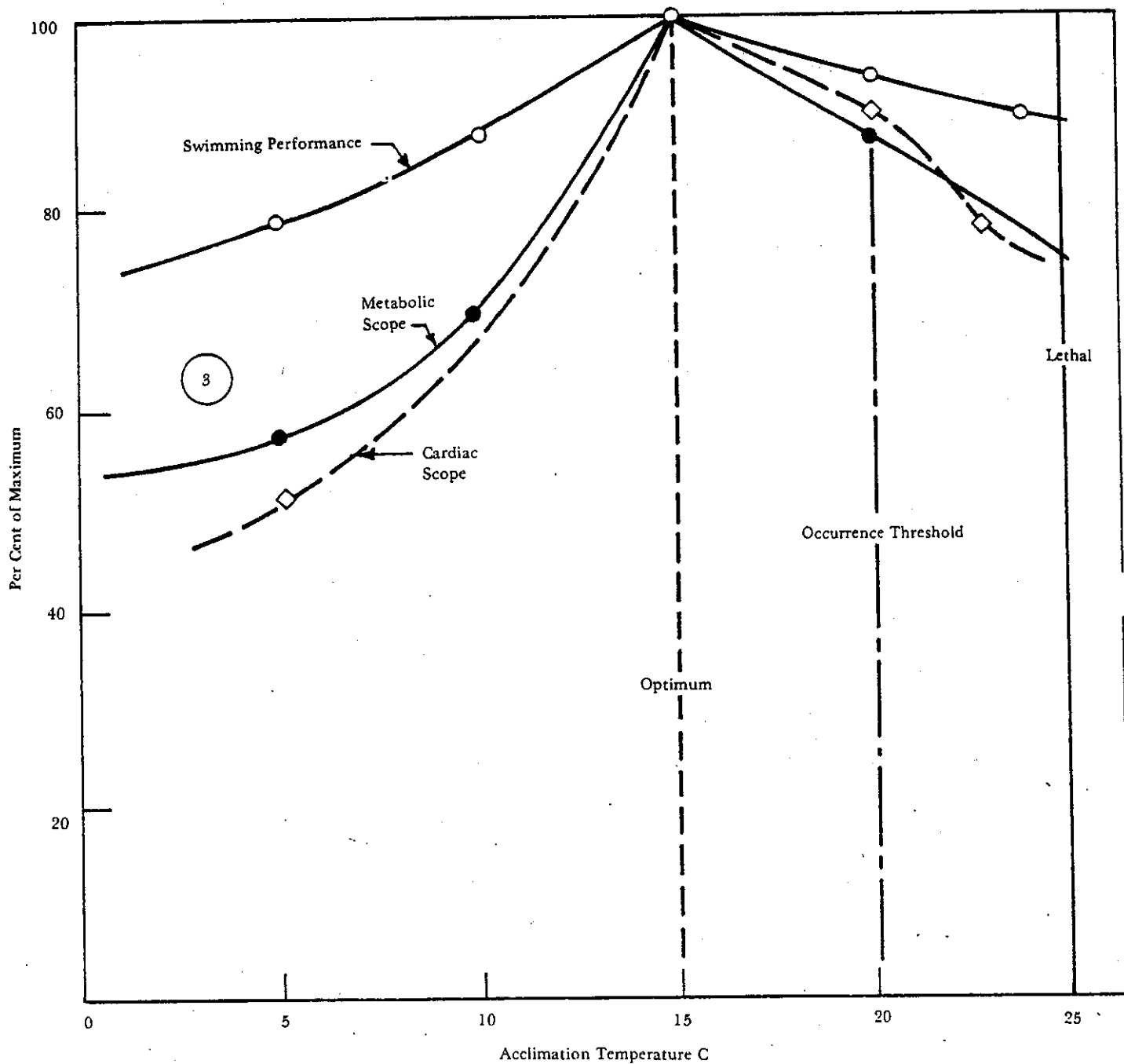

After Brett 1971[256]

FIGURE III-4b—Performance of Sockeye Salmon (Oncorhynchus nerka) in Relation to Acclimation Temperature
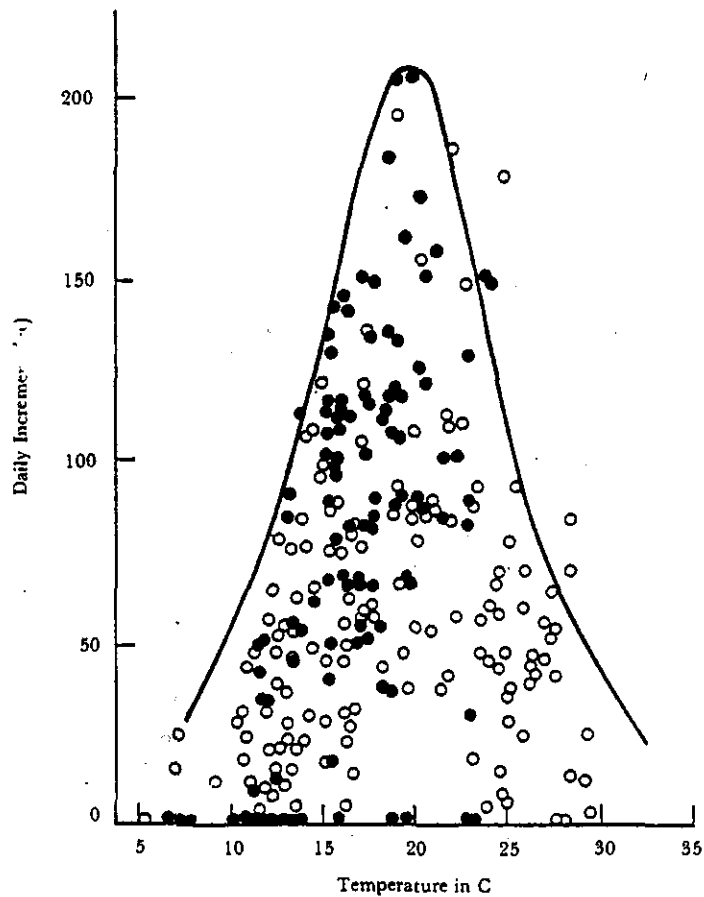
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research necessary to provide missing data. Techniques for determining incipient lethal temperatures are standardized (B- '+ 1952)[252] whereas those for zero growth are not.

.mperature that is one-third of the range between the ,ptimum temperature and the ultimate incipient lethal temperature that can be calculated by the formula

$$\text{optimum temp.} + \frac{\text{ultimate incipient lethal temp.} - \text{optimum temp.}}{3}$$

(Equation 1)

yields values that are very close to (optimum temp. + z.n.g. temp.)/2. For example, the values are, respectively, 32.7 and 32.8 C for channel catfish and 30.6 and 30.8 for largemouth bass (data from Table III-8 and Appendix II). This formula offers a practical method for obtaining allow-

able limits, while retaining as its scientific basis the requirements of preserving adequate rates of growth. Some limits obtained from data in the literature are given in Table III-12. A hypothetical example of the effect of this limit on growth of largemouth bass is illustrated in Figure III-5.

Figure III-5 shows a hypothetical example of the effects of the limit on maximum weekly average temperature on growth rates of juvenile largemouth bass. Growth data as a function of temperature are from Strawn 1961[319]; the ambient temperature is an averaged curve for Lake Norman, N. C., adapted from data supplied by Duke Power Company. A general temperature elevation of 10 F is used to provide an extreme example. Incremental growth rates (mm/wk) are plotted on the main figure, while annual accumulated growth is plotted in the inset. Simplifying assumptions were that growth rates and the relationship of growth rate to temperature were constant throughout the year, and that there would be sufficient food to sustain maximum attainable growth rates at all times.

The criterion for a specific location would be determined by the most sensitive life stage of an important species likely to be present in that location at that time. Since many fishes have restricted habitats (e.g., specific depth zones) at many life stages, the thermal criterion must be applied to the proper zone. There is field evidence that fish avoid localized areas of unfavorably warm water. This has been demonstrated both in lakes where coldwater fish normally evacuate warm shallows in summer (Smith 1964)[318] and at power station mixing zones (Gammon 1970;[282] Merriman et al. 1965).[304] In most large bodies of water there are both vertical and horizontal thermal gradients that mobile organisms can follow to avoid unfavorable high (or low) temperatures.

The summer maxima need not, therefore, apply to mixing zones that occupy a small percentage of the suitable habitat or necessarily to all zones where organisms have free egress to cooler water. The maxima must apply, however, to restricted local habitats, such as lake hypolimnia or thermoclines, that provide important summer sanctuary areas for cold-water species. Any avoidance of a warm area not part of the normal seasonal habitat of the species will mean that less area of the water body is available to support the population and that production may be reduced. Such reduction should not interfere with biological communities or populations of important species to a degree that is damaging to the ecosystem or other beneficial uses. Non-mobile organisms that must remain in the warm zone will probably be the limiting organisms for that location. Any recommendation for upper limiting temperatures must be applied carefully with understanding of the population dynamics of the species in question in order to establish both local and regional requirements.

Ansell 1968 [243]

FIGURE III-4c—M. mercenaria: *The general relationship between temperature and the rate of shell growth, based on field measurements of growth and temperature.*

●: *sites in Poole Harbor, England;* ○: *North American sites.*

Annual Accumulated Growth

Accumulated growth (mm)

Elevated (with limit)

Elevated (without limit)

Ambient

Weeks

Growth (mm/wk)

Ambient + 10 F

Average Ambient
(Lake Norman, N.C.)

Weekly Growth Rate
(Ambient + 10 F)

Weekly Growth Rate
(Ambient)

JAN.   FEB.   MAR.   APR.   MAY   JUNE

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FIGURE III-5—A hypothetical example of the effects of the limit on maximum weekly average temperature on growth rates of juvenile largemouth bass. Growth data as a function of temperature are from Strawn 1961; the ambient temperature is an averaged curve for Lake Norman, N.C., adapted from data supplied by Duke Power Company. A general temperature elevation of 10 F is used to provide an extreme example. Incremental growth rates (mm/wk) are plotted on the main figure, while annual accumulated growth is plotted in the inset. Simplifying assumptions were that growth rates and the relationship of growth rate to temperature were constant throughout the year, and that there would be sufficient food to sustain maximum attainable growth rates at all times.

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TABLE III-12—Summary of Some Upper Limiting Temperatures for Prolonged Exposures of Fishes Based on Optimum Temperatures and Ultimate Upper Incipient Lethal Temperatures (Equation 1).

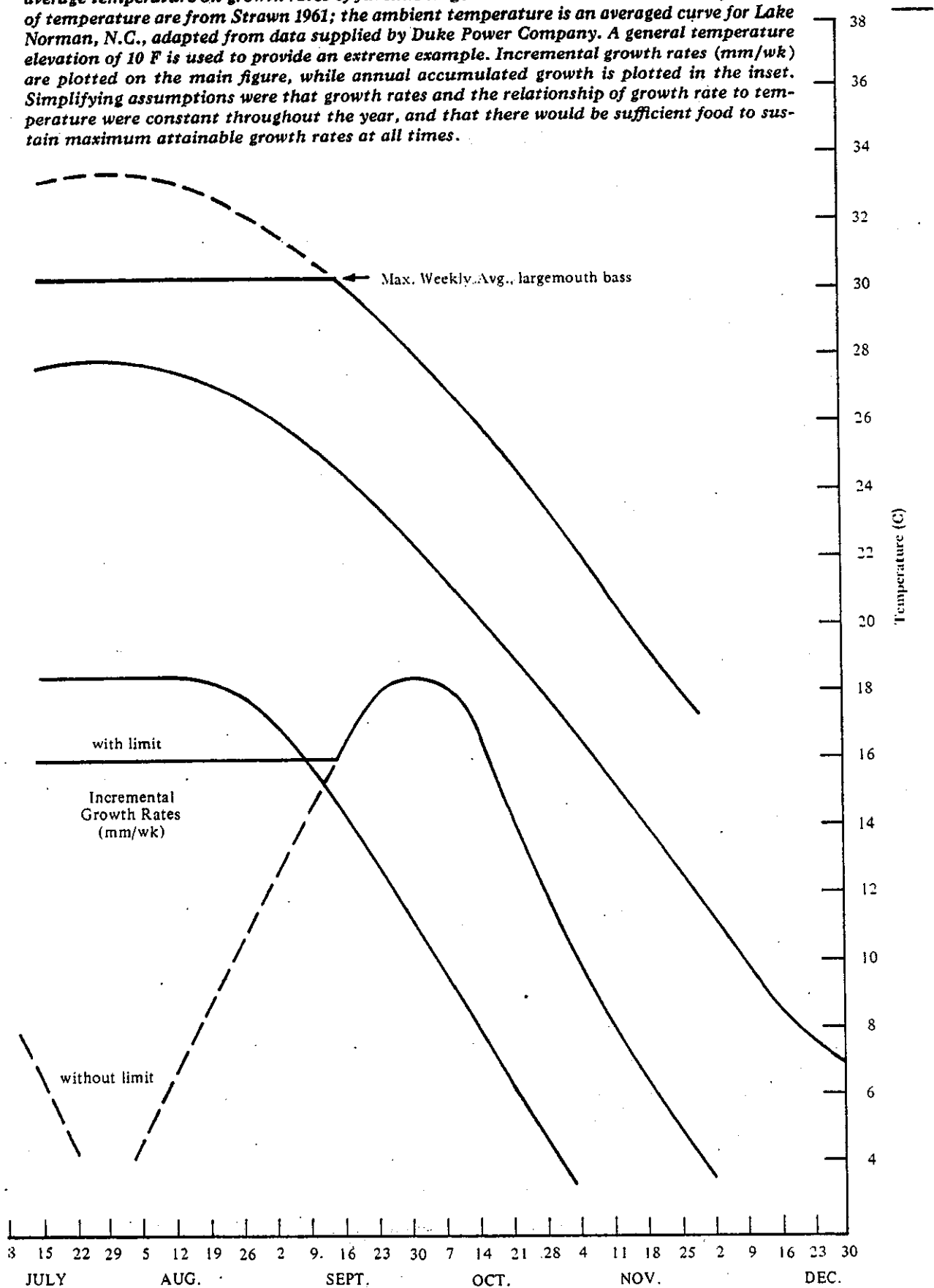| Species	Optimum		Function	Reference	Ultimate upper incipient lethal temperature		Reference	Maximum weekly average temperature (Eq. 1)	
	C	F			C	F		C	F
Catostomus commersoni (white sucker)......	27	80.6	growth	unpubl., NWQL[335]	29.3	84.7	Hart 1947[335]	27.8	82
Coregonus artedii (Cisco or lake herring).....	16	60.8	growth	McCormick et al. 1971[302]	25.7	78.3	Edsall and Colby 1970[274]	19.2	66.6
Ictalurus punctatus (channel catfish).........	30	86	growth	Strawn 1970;[320] Andrews and Stickney 1971[242]	38.0	100.4	Allen and Strawn 1968[240]	32.7	90.9
Lepomis macrochirus (bluegill) (yr II)........	22	71.6	growth	McComish 1971[301] Anderson 1959[241]	33.8	92.8	Hart 1952[286]	25.9	78.6
Micropterus dolomieu (smallmouth bass)....	26.3	83	growth	Horning and Pearson 1972[291]	35.0	95.0	Horning and Pearson 1972[291]	29.9	85.8
	28.3	83	growth	Peek 1965[309]					
	ave 27.3	81.1							
Micropterus salmoides (largemouth bass X fry).	27.5	81.5	growth	Strawn 1961[318]	36.4	97.5	Hart 1952[286]	30.5	86.7
Notropis atherinoides (emerald shiner).......	27	80.6	growth	unpubl., NWQL[325]	30.7	87.3	Hart 1952[286]	28.2	82.8
Oncorhynchus nerka (sockeye salmon).......	15.0	59.0	growth	Brett et al. 1969[257]	25.0	77.0	Brett 1952[253]	18.3	64.9
	15.0	59.0	other functions	Brett 1971[256]					
(juveniles).............................	15.0		max. swimming						
Pseudopleuronectes americanus (winter flounder).............................	18.0	64.4	growth	Brett 1970[255]	29.1	84.4	Hoff and Westman 1966[289]	21.8	71.2
Salmo trutta (brown trout).................	8 to 17	54.5	growth	Brett 1970[255]	23.5	74.3	Bishai 1960[247]	16.2	61.2
	ave 12.5								
Salvelinus fontinalis (brook trout)..........	15.4	59.7	growth	unpubl. NWQL[328]	25.5	77.9	Fry, Hart and Walker, 1946[281]	18.2	64.8
	13.0	55.4	growth	Baldwin 1957[244]					
	15	59	metabolic	Graham 1949[284]					
	ave 14.5	58.1	scope						
Salvelinus namaycush (lake trout)..........	16	60.8	scope for activity (2 metabolism)	Gibson and Fry 1954[283]	23.5		Gibson and Fry 1954[283]	18.8	65.8
	17	62.6	swimming speed						
	ave 16.5	61.7							

Heat added to upper reaches of some cold rivers can be retained throughout the river's remaining length (Jaske and Synoground 1970).[292] This factor adds to the natural trend of warming at distances from headwaters. Thermal additions in headwaters, therefore, may contribute substantially to reduction of cold-water species in downstream areas (Mount 1970).[305] Upstream thermal additions should be evaluated for their effects on summer maxima at downstream locations, as well as in the immediate vicinity of the heat source.

Recommendation

Growth of aquatic organisms would be maintained at levels necessary for sustaining actively growing and reproducing populations if the maximum weekly average temperature in the zone inhabited by the species at that time does not exceed one-third of the range between the optimum temperature and the ultimate upper incipient lethal temperature of the species (Equation 1, page 157), and the temperatures above the weekly average do not exceed the criterion for short-term exposures. This maximum need not apply to acceptable mixing zones (see proportional relationships of mixing zones to receiving systems, p. 114), and must be applied with adequate understanding of the normal seasonal distribution of the important species.

WINTER MAXIMA

Although artificially produced temperature elevations during winter months may actually bring the temperature closer to optimum or preferred temperature for important species and attract fish (Trembley 1965),[321] metabolic acclimation to these higher levels can preclude safe return of the organism to ambient temperatures should the artificial heating suddenly cease (Pennsylvania Fish Commission 1971;[310] Robinson 1970)[316] or the organism be driven from the heat area. For example, sockeye salmon (*Oncorhynchus nerka*) acclimated to 20 C suffered 50 percent mortality in the laboratory when their temperature was dropped suddenly to 5 C (Brett 1971;[256] see Figure III-3). The same population of fish withstood a drop to zero when acclimated to 5 C. The lower limit of the range of thermal tolerance of important species must, therefore, be maintained at the normal seasonal ambient temperatures throughout cold seasons, unless special provisions are made to assure that rapid temperature drop will not occur or that organisms cannot become acclimated to elevated temperatures. This can be accomplished by limitations on temperature elevations in such areas as discharge canals and mixing zones where organisms may reside, or by insuring that maximum temperatures occur only in areas not accessible to important aquatic life for lengths of time sufficient to allow metabolic acclimation. Such inaccessible areas wc include the high-velocity zones of diffusers or screened o...

large channels. This reduction of maximum temperatures ould not preclude use of slightly warmed areas as sites for :e inter fisheries.

T. onsideration may be important in some regions at nes other than in winter. The Great Lakes, for example, e susceptible to rapid changes in elevation of the thermo- ine in summer which may induce rapid decreases in oreline temperatures. Fish acclimated to exceptionally gh temperatures in discharge canals may be killed or verely stressed without changes in power plant opera- .ns (Robinson 1968).[314] Such regions should take special >te of this possibility.

Some numerical values for acclimation temperatures and wer limits of tolerance ranges (lower incipient lethal mperatures) are given in Appendix II–C. Other data must · provided by further research. There are no adequate ata available with which to estimate a safety factor for no ress from cold shocks. Experiments currently in progress, owever, suggest that channel catfish fingerlings are more isceptible to predation after being cooled more than 5 to C (Coutant, *unpublished data*).[324]

The effects of limiting ice formation in lakes and rivers ould be carefully observed. This aspect of maximum inter temperatures is apparent, although there is insuffi- ient evidence to estimate its importance.

ecommendation

J rtant species should be protected if the naximum weekly average temperature during win- er months in any area to which they have access oes not exceed the acclimation temperature minus a 2 C safety factor) that raises the lower ethal threshold temperature of such species above ne normal ambient water temperatures for that eason, and the criterion for short-term exposures s not exceeded. This recommendation applies es-)ecially to locations where organisms may be at- racted from the receiving water and subjected to apid thermal drop, as in the low velocity areas of vater diversions (intake or discharge), canals, and nixing zones.

HORT-TERM EXPOSURE TO EXTREME TEMPERATURE

To protect aquatic life and yet allow other uses of the vater, it is essential to know the lengths of time organisms an survive extreme temperatures (i.e., temperatures that xceed the 7-day incipient lethal temperature). Both iatural environments and power plant cooling systems can iriefly reach temperature extremes (both upper and lower) ithout apparent detrimental effect to the aquatic life Frv 1951;[277] Becker et al. 1971).[245]

ength of time that 50 per cent of a population will urvive temperature above the incipient lethal temperature can be calculated from a regression equation of experi- mental data (such as those in Figure III–3) as follows:

$$\log (\text{time}) = a + b (\text{temp.}) \quad (Equation\ 2)$$

where time is expressed in minutes, temperature in degrees centigrade and where a and b are intercept and slope, respectively, which are characteristics of each acclimation temperature for each species. In some cases the time- temperature relationship is more complex than the semi- logarithmic model given above. Equation 2, however, is the most applicable, and is generally accepted by the scientific community (Fry 1967).[279] Caution is recom- mended in extrapolating beyond the data limits of the original research (Appendix II–C). The rate of temperature change does not appear to alter this equation, as long as the change occurs more rapidly than over several days (Brett 1941;[251] Lemke 1970).[300] Thermal resistance may be diminished by the simultaneous presence of toxicants or other debilitating factors (Ebel et al. 1970,[273] and summary by Coutant 1970c).[269] The most accurate predictability can be derived from data collected using water from the site under evaluation.

Because the equations based on research on thermal tolerance predict 50 per cent mortality, a safety factor is needed to assure no mortality. Several studies have indi- cated that a 2 C reduction of an upper stress temperature results in no mortalities within an equivalent exposure duration (Fry et al. 1942;[280] Black 1953).[248] The validity of a two degree safety factor was strengthened by the results of Coutant (1970a).[267] He showed that about 15 to 20 per cent of the exposure time, for median mortality at a given high temperature, induced selective predation on thermally shocked salmon and trout. (This also amounted to reduction of the effective stress temperature by about 2 C.) Un- published data from subsequent predation experiments showed that this reduction of about 2 C also applied to the incipient lethal temperature. The level at which there is no increased vulnerability to predation is the best estimate of a no-stress exposure that is currently available. No similar safety factor has been explored for tolerance of low tem- peratures. Further research may determine that safety factors, as well as tolerance limits, have to be decided independently for each species, life stage, and water quality situation.

Information needed for predicting survival of a number of species of fish and invertebrates under short-term condi- tions of heat extremes is presented in Appendix II–C. This information includes (for each acclimation temperature) upper and lower incipient lethal temperatures: coefficients a and b for the thermal resistance equation; and information on size, life stage, and geographic source of the species. It is clear that adequate data are available for only a small percentage of aquatic species, and additional research is necessary. Thermal resistance information should be obtained locally for critical areas to account for simul-

taneous presence of toxicants or other debilitating factors, a consideration not reflected in Appendix II-C data. More data are available for upper lethal temperatures than for lower.

The resistance time equation, Equation 2, can be rearranged to incorporate the 2 C margin of safety and also to define conditions for survival (right side of the equation less than or equal to 1) as follows:

$$1 \geq \frac{time}{10^{[a+b(temp.+2)]}} \qquad (Equation\ 3)$$

Low levels of mortality of some aquatic organisms are not necessarily detrimental to ecosystems, because permissible mortality levels can be established. This is how fishing or shellfishing activities are managed. Many states and international agencies have established elaborate systems for setting an allowable rate of mortality (for sport and commercial fish) in order to assure needed reproduction and survival. (This should not imply, however, that a form of pollution should be allowed to take the entire harvestable yield.) Warm discharge water from a power plant may sufficiently stimulate reproduction of some organisms (e.g., zooplankton), such that those killed during passage through the maximally heated areas are replaced within a few hours, and no impact of the mortalities can be found in the open water (Churchill and Wojtalik 1969;[262] Heinle 1969).[288] On the other hand, Jensen (1971)[293] calculated that even five percent additional mortality of 0-age brook trout (*Salvelinus fontinalis*) decreased the yield of the trout fishery, and 50 per cent additional mortality would, theoretically. cause extinction of the population. Obviously, there can be no adequate generalization concerning the impact of short-term effects on entire ecosystems, for each case will be somewhat different. Future research must be directed toward determining the effects of local temperature stresses on population dynamics. A complete discussion will not be attempted here. Criteria for complete short-term protection may not always be necessary and should be applied with an adequate understanding of local conditions.

Recommendation

Unless there is justifiable reason to believe it unnecessary for maintenance of populations of a species, the right side of Equation 3 for that species should not be allowed to increase above unity when the temperature exceeds the incipient lethal temperature minus 2 C:

$$1 \geq \frac{time}{10^{[a+b(temp.+2)]}}$$

Values for *a* and *b* at the appropriate acclimation temperature for some species can be obtained from Appendix II-C or through additional research if necessary data are not available. This recommen- dation applies to all locations where organisms to be protected are exposed, including areas within mixing zones and water diversions such as power station cooling water.

REPRODUCTION AND DEVELOPMENT

The sequence of events relating to gonad growth and gamete maturation, spawning migration, release of gametes, development of the egg and embryo, and commencement of independent feeding represents one of the most complex phenomena in nature, both for fish (Brett 1970)[255] and invertebrates (Kinne 1970).[296] These events are generally the most thermally sensitive of all life stages. Other environmental factors, such as light and salinity, often seasonal in nature, can also profoundly affect the response to temperature (Wiebe 1968).[323] The general physiological state of the organisms (e.g., energy reserves), which is an integration of previous history, has a strong effect on reproductive potential (Kinne 1970).[296] The erratic sequence of failures and successes of different year classes of lake fish attests to the unreliability of natural conditions for providing optimum reproduction.

Abnormal, short-term temperature fluctuations appear to be of greatest significance in reduced production of juvenile fish and invertebrates (Kinne, 1963).[295] Such thermal fluctuations can be a prominent consequence of water use as in hydroelectric power (rapid changes in river flow rates), thermal electric power (thermal discharges at fluctua power levels), navigation (irregular lock releases), irrigation (irregular water diversions and wasteway releases). Jaske and Synoground (1970)[292] have documented such temperature changes due to interacting thermal and hydroelectric discharges on the Columbia River.

Tolerable limits or variations of temperature change throughout development, and particularly at the most sensitive life stages, differ among species. There is no adequate summary of data on such thermal requirements for successful reproduction. The data are scattered through many years of natural history observations (however, see Breder and Rosen 1966[250] for a recent compilation of some data; also see Table III-13). High priority must be assigned to summarizing existing information and obtaining that which is lacking.

Uniform elevations of temperature by a few degrees during the spawning period, while maintaining short-term temperature cycles and seasonal thermal patterns, appear to have little overall effect on the reproductive cycle of resident aquatic species, other than to advance the timing for spring spawners or delay it for fall spawners. Such shifts are often seen in nature, although no quantitative measurements of reproductive success have been made in this connection. For example, thriving populations of many fishes occur in diverse streams of the Tennessee Valle in which the date of the spawning temperature may var

TABLE III-13—Spawning Requirements of Some Fish, Arranged in Ascending Order of Spawning Temperatures
(Adapted from Wojtalik, T. A., unpublished manuscript)*

Fishes	Temp. (C)	Spawning site	Range in spawning depth	Daily spawning time	Egg site	Incubation period days (Temp. C)
...ger ...ostedion canadense	5.0	Shallow gravel bars	2-4 feet	Night	Bottom	25 (5.0)
...lleye ...itreum vitreum	7.0	Gravel, rubble, boulders on bar	3-10 feet	Day, night	Bottom	....
...gnose gar ...osteus osseus	10.8	Flooded shallows	Flooded shallows	Day	Weeds	8 (20.0)
...ite bass ...one chrysops	11.7	Sand & rock shores	2-12 feet	Day, long but esp. night	Surface	2 (15.6)
...l darter ...eostoma microperca	12.0					
...tted sucker ...ytrema melanops	12.8					
...ite sucker ...ostomus commersoni	12.0-13.0	Streams or bars		Day, night	Bottom	....
...ery minnow ...bognathus nuchalis	13.0	Coves		Day	Bottom	....
...ded pygmo sunfish ...ssoma zonatum	13.9-16.7					
...ite crappie ...moxis annularis	14.0-16.0	Submerged materials in shallows		Day	Bottom	1 (21.1-23.2)
...head minnow	14.4					
...ephales promelas	25.0	Shallows	Nr. surface	Day	Underside floating objects	....
...mouth buffalo ...obus cyprinellus	15.6-16.3	Shallows		Day	Bottom	9-10 (16.7)
...gemouth bass ...ropterus salmoides	15.6	Shallows near bank	30 inches	Day	Bottom	5 (16.9)
...mmon shiner ...tropis cornutus	15.6-16.3	Small gravel streams		Day	Bottom	
...lden shiner ...emigonus crysoleucas	15.6	Bays & shoals, weeds		Day	Weeds	4 (15.6+)
...en sunfish ...omis cyanellus	15.6	Bank, shallows	Inches to 1½ feet	Day	Bottom	....
...dlefish ...yodor ...ula	16.0	Over gravel bars	Nr. surface	Night, day	Bottom	....
...cki... ...cin... a.	16.5					
...zar... shad ...rosoma cepedianum	16.7					
...allmouth bass ...cropterus dolomieui	16.7	Gravel rock shore	3-20 feet	Day	Bottom	7 (15.6)
...tted bass ...cropterus punctulatus	17.8	Small streams, bar		Day	Bottom	4-5 (20.0)
...nny darter ...eostoma nigrum	18.0					
...nge spotted sunfish ...omis humilis	18.3					
...allmouth buffalo ...obus bubalus	18.9					
...ck buffalo ...iger	18.9					
...rp ...rinus carpio	19.0	Flooded shallows	Nr. surface	Day, night	Bottom	4-8 (16.7)
...egill ...pomis macrochirus	19.4	Weeds, shallows	2-6 feet	Day	Bottom	1½-3 (22.2)
...dbreast sunfish ...auritis	20.0					
...annel catfish	20.0					
...alurus punctatus	20.7	Bank cavity	<10 feet	Day, night	Bottom	9-10 (15.0)
...hite catfish ...catus	20.0	Sand gravel bar	<10 feet	Day	Bottom	6-7 (23.9-29.4)
...mpkinseed ...pomis gibbosus	20.0	Bank shallows	<5 feet	Day	Bottom	3 (27.8)
...ck crappie ...moxis nigromaculatus	20.0					
...ook silverside ...bidesthes sicculus	20.0	Over gravel	Surface	Day	Weeds, bottom	....
...own bullhead						
...talurus nebulosus	21.1	Shallows, weeds	Inches to 6 feet		Weeds, bottom	5 (25.0)
...readfin shad ...osoma petenense	21.1	Shallow and open water	Surface	Day	Bottom	3 (26.7)
...armouth ...pom... s	21.0	Bank shallows	<5 feet	Day	Bottom	1½ (25.0-26.7)
...ver ...oxos... _inatum	21.7-24.4	Riffles, streams		Day	Bottom	

TABLE III-13—Spawning Requirements of Some Fish, Arranged in Ascending Order of Spawning Temperatures—Continued

Fishes	Temp. (C)	Spawning site	Range in spawning depth	Daily spawning time	Egg site	Incubation period days (Temp
Blue catfish						
Ictalurus furcatus	22.2					
Flathead catfish						
Pylodictis olivaris	22.2					
Redear sunfish						
Lepomis microlophus	23.0	Quiet, various	inches to 10 feet	....	....	....
Longear sunfish						
L. megalotis	23.3					
Freshwater drum						
Aplodinotus grunniens	23.0					
River carpsucker						
Carpoides carpio	23.9					
Spotted bullhead						
Ictalurus serracanthus	26.7					
Yellow bullhead						
I. natalis	....	Quiet, shallows	1½–4 feet	....	Bottom	5–10 (18.9)

* T. A. Wojtalik, Tennessee Valley Authority, Muscle Shoals, Alabama.[329]

given year by 22 to 65 days. Examination of the literature shows that shifts in spawning dates by nearly one month are common in natural waters throughout the U.S. Populations of some species at the southern limits of their distribution are exceptions, e.g., the lake whitefish (Coregonus clupeaformis) in Lake Erie that require a prolonged, cold incubation period (Lawler 1965)[299] and species such as yellow perch (Perca flavescens) that require a long chill period for egg maturation prior to spawning (Jones, unpublished data).[327]

This biological plasticity suggests that the annual spring rise, or fall drop, in temperature might safely be advanced (or delayed) by nearly one month in many regions, as long as the thermal requirements that are necessary for migration, spawning, and other activities are not eliminated and the necessary chill periods, maturation times, or incubation periods are preserved for important species. Production of food organisms may advance in a similar way, with little disruption of food chains, although there is little evidence to support this assumption (but see Coutant 1968;[265] Coutant and Steele 1968;[271] and Nebeker 1971).[307] The process is similar to the latitudinal differences within the range of a given species.

Highly mobile species that depend upon temperature synchrony among widely different regions or environments for various phases of the reproductive or rearing cycle (e.g., anadromous salmonids or aquatic insects) could be faced with dangers of dis-synchrony if one area is warmed, but another is not. Poor long-term success of one year class of Fraser River (British Columbia) sockeye salmon (Oncorhynchus nerka) was attributed to early (and highly successful) fry production and emigration during an abnormally warm summer followed by unsuccessful, premature feeding activity in the cold and still unproductive estuary (Vernon 1958).[322] Anadromous species are able, in some cases, (see studies of eulachon (Thaleichthys pacificus) by Smith and

Saalfeld 1955)[317] to modify their migrations and spawning to coincide with the proper temperatures whenever and wherever they occur.

Rates of embryonic development that could lead to premature hatching are determined by temperatures of the microhabitat of the embryo. Temperatures of the microhabitat may be quite different from those of the remainder of the waterbody. For example, a thermal effluent at the temperature of maximum water density (approximately 4 C) can sink in a lake whose surface water temper· is colder (Hoglund and Spigarelli, 1972).[290] Incubₐ ₅ eggs of such species as lake trout (Salvelinus namaycush) and various coregonids on the lake bottom may be intermittently exposed to temperatures warmer than normal. Hatching may be advanced to dates that are too early for survival of the fry in their nursery areas. Hoglund and Spigarelli 1972,[290] using temperature data from a sinking plume in Lake Michigan, theorized that if lake herring (Coregonus artedii) eggs had been incubated at the location of one of their temperature sensors, the fry would have hatched seven days early. Thermal limitations must, therefore, apply at the proper location for the particular species or life stage to be protected.

Recommendations

After their specific limiting temperatures and exposure times have been determined by studies tailored to local conditions, the reproductive activity of selected species will be protected in areas where:

- periods required for gonad growth and gamete maturation are preserved;
- no temperature differentials are created that block spawning migrations, although some delay or advancement of timing based upon local · ᵥ- ditions may be tolerated;

temperatures are not raised to a level at which necessary spawning or incubation temperatures of winter-spawning species cannot occur;

( ) temperature changes are not induced in spawning areas, either in mixing zones or in mixed water bodies (the thermal and geographic limits to such changes will be dependent upon local requirements of species, including the spawning microhabitat, e.g., bottom gravels, littoral zone, and surface strata);

timing of reproductive events is not altered to the extent that synchrony is broken where reproduction or rearing of certain life stages is shown to be dependent upon cyclic food sources or other factors at remote locations.

normal patterns of gradual temperature changes throughout the year are maintained.

These requirements should supersede all others during times when they apply.

CHANGES IN STRUCTURE OF AQUATIC COMMUNITIES

Significant change in temperature or in thermal patterns over a period of time may cause some change in the composition of aquatic communities (i.e., the species represented and the numbers of individuals in each species). This has been documented by field studies at power plants (Trembley 95? 1960)[321] and by laboratory investigations (McIntyre 9( )[3] Allowing temperature changes to alter significantly the community structure in natural waters may be detrimental, even though species of direct importance to man are not eliminated.

The limits of allowable change in species diversity due to temperature changes should not differ from those applicable to any other pollutant. This general topic is treated in detail in reviews by others (Brookhaven National Lab. 1969)[258] and is discussed in Appendix II–B, Community Structure and Diversity Indices, p. 408.

NUISANCE ORGANISMS

Alteration of aquatic communities by the addition of heat may occasionally result in growths of nuisance organisms provided that other environmental conditions essential to such growths (e.g., nutrients) exist. Poltoracka (1968)[311] documented the growth stimulation of plankton in an artificially heated small lake; Trembley (1965[321]) reported dense growths of attached algae in the discharge canal and shallow discharge plume of a power station (where the algae broke loose periodically releasing decomposing organic matter to the receiving water). Other instances of algal growths in effluent channels of power stations were reviewed by Coutant (1970c).[269]

Changed thermal patterns (e.g., in stratified lakes) may growth alter the seasonal appearances of nuisance algal

growths even though the temperature changes are induced by altered circulation patterns (e.g., artificial destratification). Dense growths of plankton have been retarded in some instances and stimulated in others (Fast 1968;[275] and *unpublished data* 1971).[325]

Data on temperature limits or thermal distributions in which nuisance growths will be produced are not presently available due in part to the complex interactions with other growth stimulants. There is not sufficient evidence to say that any temperature increase will necessarily result in increased nuisance organisms. Careful evaluation of local conditions is required for any reasonable prediction of effect.

Recommendation

Nuisance growths of organisms may develop where there are increases in temperature or alterations of the temporal or spatial distribution of heat in water. There should be careful evaluation of all factors contributing to nuisance growths at any site before establishment of thermal limits based upon this response, and temperature limits should be set in conjunction with restrictions on other factors (see the discussion of Eutrophication and Nutrients in Section I).

CONCLUSIONS

Recommendations for temperature limits to protect aquatic life consist of the following two upper limits for any time of the year (Figure III–6).

1. One limit consists of a maximum weekly average temperature that:

(a) in the warmer months (e.g., April through October in the North, and March through November in the South) is one third of the range between the optimum temperature and the ultimate upper incipient lethal temperature for the most sensitive important species (or appropriate life stage) that is normally found at that location at that time; or

(b) in the cooler months (e.g., mid-October to mid-April in the North, and December to February in the South) is that elevated temperature from which important species die when that elevated temperature is suddenly dropped to the normal ambient temperature, with the limit being the acclimation temperature (minus a 2 C safety factor), when the lower incipient lethal temperature equals the normal ambient water temperature (in some regions this limit may also be applicable in summer); or

(c) during reproduction seasons (generally April-June and September-October in the North, and March-May and October-November in the South) is that

temperature that meets specific site requirements for successful migration, spawning, egg incubation, fry rearing, and other reproductive functions of important species; or

(d) at a specific site is found necessary to preserve normal species diversity or prevent undesirable growths of nuisance organisms.

2. The second limit is the time-dependent maximum temperature for short exposures as given by the species-specific equation:

$$1 \geq \frac{time}{10^{[a+b(temp.+2)]}}$$

Local requirements for reproduction should supersede all other requirements when they are applicable. Detailed ecological analysis of both natural and man-modified aquatic environments is necessary to ascertain when these requirements should apply.

USE OF TEMPERATURE CRITERIA

A hypothetical electric power station using lake water for cooling is illustrated as a typical example in Figure III. This discussion concerns the application of thermal criteria to this typical situation.

The size of the power station is 1,000 megawatts electric (MW$_e$) if nuclear, or 1,700 MW$_e$ if fossil-fueled (oil, coal, gas); and it releases 6.8 billion British Thermal Units (BTU) per hour to the aquatic environment. This size is representative of power stations currently being installed. Temperature rise at the condensers would be 20 F with cooling water flowing at the rate of 1,520 cubic feet/second (ft^3/sec) or 682,000 gallons/minute. Flow could be increased to reduce temperature rise.

The schematic Figure III–7 is drawn with two alternative discharge arrangements to illustrate the extent to which design features affect thermal impacts upon aquatic life
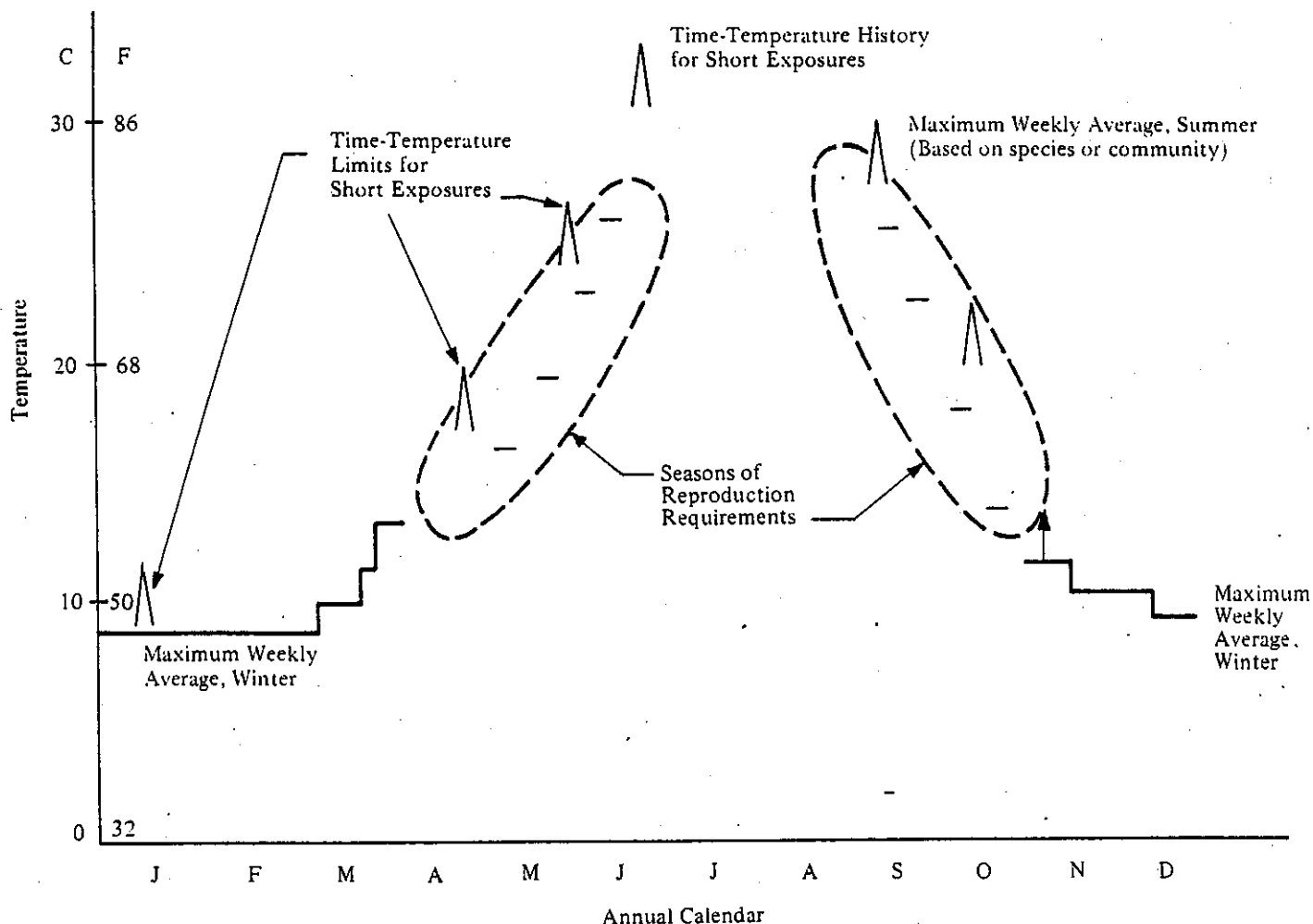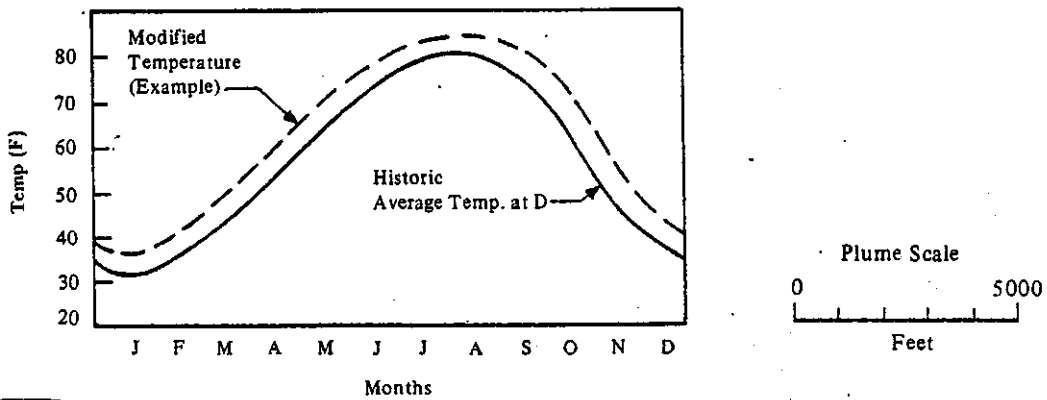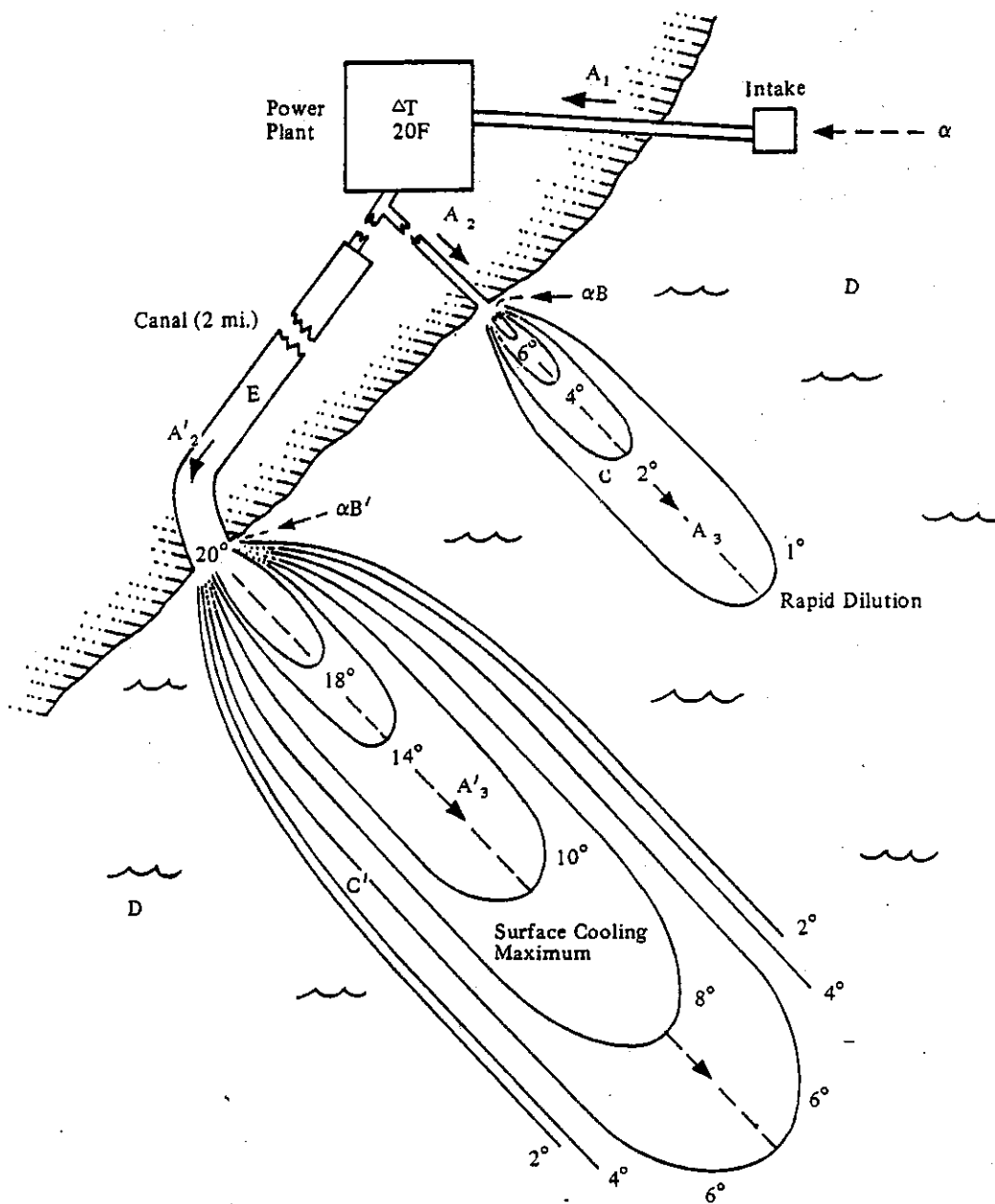

FIGURE III-6—Schematic Summary of Thermal Criteria

FIGURE III-7—Hypothetical Power Plant Site For Application of Water Temperature Criteria

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Warm condenser water can be carried from the station to the lake by (a) a pipe carrying water at a high flow velocity or (b) a canal in which the warm water flows slowly. There is little cooling in a canal, as measurements at several existing power stations have shown. Water can be released to the lake by using any of several combinations of water velocity and volume (i.e., number of outlets) or outlet dimensions and locations. These design features largely determine the configuration of the thermal plumes illustrated in Figure III–7 resulting from either rapid dilution with lake water or from slow release as a surface layer. The isotherms were placed according to computer simulation of thermal discharges (Pritchard 1971)[312] and represent a condition without lake currents to aid mixing.

Exact configuration of an actual plume depends upon many factors (some of which change seasonally or even hourly) such as local patterns of currents, wind, and bottom and shore topography.

Analytical Steps

Perspective of the organisms in the water body and of the pertinent non-biological considerations (chemical, hydrological, hydraulic) is an essential beginning. This perspective requires a certain amount of literature survey or on site study if the information is not well known. Two steps are particularly important:

1. identification of the important species and community (primary production, species diversity, etc.) that are relevant to this site; and
2. determination of life patterns of the important species (seasonal distribution, migrations, spawning areas, nursery and rearing areas, sites of commercial or sport fisheries). This information should include as much specific information on thermal requirements as it is possible to obtain from the literature.

Other steps relate the life patterns and environmental requirements of the biota to the sources of potential thermal damage from the power plant. These steps can be identified with specific areas in Figure III–7.

Aquatic Areas Sensitive to Temperature Change

Five principal areas offer potential for biological damage from thermal changes, labeled A–E on Figure III–7. (There are other areas associated with mechanical or chemical effects that cannot be treated here; see the index.)

Area A The cooling water as it passes through the intake, intake piping (A_1), condensers, discharge piping (A_2) or canal (A'_2), and thermal plume (A_3 or A'_3), carrying with it small organisms (such as phytoplankton, zooplankton, invertebrate larvae, and fish eggs or larvae). Organisms receive a thermal shock to the full 20 F above ambient

temperature with a duration that depends upon the rate of water flow and the temperature drop in the plume.

Area B Water of the plume alone that entrains t small and larger organisms (including small fish) as it is diluted (B or B′). Organisms receive thermal shocks from temperatures ranging from the discharge to the ambient temperature, depending upon where they are entrained.

Area C Benthic environment where bottom organisms (including fish eggs) can be heated chronically or periodically by the thermal plume (C or C′).

Area D The slightly warmed mixed water body (or large segment of it) where all organisms experience a slightly warmer average temperature (D).

Area E The discharge canal in which resident or seasonal populations reside at abnormally high temperatures (E).

Cooling Water Entrainment

It is not adequate to consider only thermal criteria for water bodies alone when large numbers of aquatic organisms may be pumped through a power plant. The probability of an organism being pumped through will depend upon the ratio of the volume of cooling water in the plant to the volume in the lake (or to the volume passing the plant in a river or tidal fresh water). Tidal environments (both freshwater and saline) offer greater potential for entrainment than is apparent, since the same water mass move back and forth past the plant many times during the lifetime of pelagic residence time of most organisms. Thermal shocks that could be experienced by organisms entrained at the hypothetical power station are shown in Figure III–8.

Detrimental effects of thermal exposures received during entrainment can be judged by using the following equation for short-term exposures to extreme temperatures:

$$\text{General criterion: } 1 \geq \frac{\text{time}}{10^{[a+b(\text{temp.}+2)]}}$$

Values for a and b in the equation for the species of aquatic organisms that are likely to be pumped with cooling water may be obtained from Appendix II, or the data may be obtained using the methods of Brett (1952).[252] The prevailing intake temperature would determine the acclimation temperature to be selected from the table.

For example, juvenile largemouth bass may frequent the near-shore waters of this lake and be drawn into the intake. To determine whether the hypothetical thermal discharges (Figure III–7) would be detrimental for juvenile bass, the following analysis can be made (assuming, for example, that the lake is in Wisconsin where these basic data for bass are available):

Criterion for juvenile bass (Wisconsin) when i.
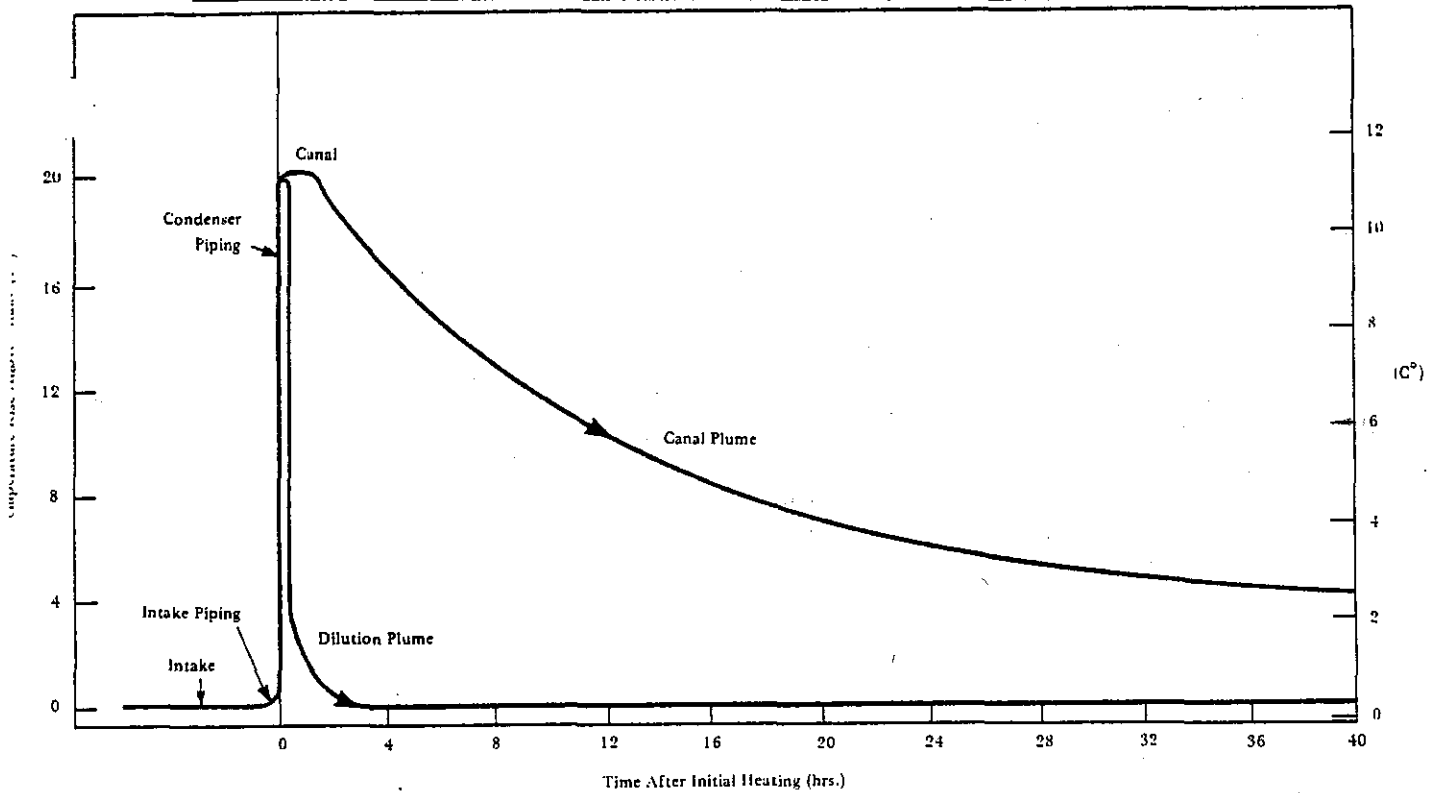
Modified after Coutant 1970c[269]

FIGURE III-8—Time Course of Temperature Change in Cooling Water Passing Through the Example Power Station with Two Alternate Discharges. The Canal Is Assumed to Flow at a Rate of 3 Ft. Per Sec.

temperature (acclimation) is 70 F (21.11 C). (Data from Appendix II-C).

$$1 \geq \frac{time}{10^{[34.3649-0.9789(temp.+2)]}}$$

Canal

Criterion applied to entrainment to end of discharge canal (discharge temperature is 70 F plus the 20 degree rise in the condensers or 90 F (32.22 C). The thermal plume would provide additional exposure above the lethal threshold, minus 2 C (29.5 C or 85.1 F) of more than four hours.

$$1 \geq \frac{60}{10^{[34.3649-0.9789(32.22+2)]}}$$

$$1 \geq 8.15$$

Conclusion:

Juvenile bass would not survive to the end of the discharge canal.

Dilution

Criterion applied to entrainment in the system em-

ploying rapid dilution.

$$1 \geq \frac{1.2}{10^{[34.3649-0.9789(32.22+2.0)]}}$$

$$1 \geq \frac{1.2}{7.36}$$

Travel time in piping to discharge is assumed to be 1 min., and temperature drop to below the lethal threshold minus 2 C (29.5 C or 85.1 F) is about 10 sec. (Pritchard, 1971).[312]

Conclusion

Juvenile bass would survive this thermal exposure:

$$1 \geq 0.1630$$

By using the equation in the following form,

$$\log (time) = a + b \ (temp.+2)$$

the length of time that bass could barely survive the expected temperature rise could be calculated, thus allowing selection of an appropriate discharge system. For example:

$$\log (time) = 34.3649 - 0.9789 \ (34.22)$$
$$\log (time) = 0.8669$$
$$time = 7.36$$

This would be about 1,325 feet of canal flowing at 3 ft/sec.

It is apparent that a long discharge canal, a nonrecirculating cooling pond, a very long offshore pipe, or delayed dilution in a mixing zone (such as the one promoting surface cooling) could prolong the duration of exposure of pumped organisms and thereby increase the likelihood of damage to them. Precise information on the travel times of the cooling water in the discharge system is needed to conduct this analysis.

The calculations have ignored changing temperatures in the thermal plume, because the canal alone was lethal, and cooling in the plume with rapid dilution was so rapid that the additional exposure was only for 10 seconds (assumed to be at the discharge temperature the whole time). There may be other circumstances under which the effect of decreasing exposure temperature in the plume may be of interest.

Effects of changing temperatures in the plume can be estimated by summing the effects of incremental exposures for short time periods (Fry et al. 1946[281]). For example, the surface cooling plume of Figures III–7 and III–8 could be considered to be composed of several short time spans, each with an average temperature, until the temperature had dropped to the upper lethal threshold minus 2 C for the juvenile bass. Each time period would be calculated as if it were a single exposure, and the calculated values for all time periods would be summed and compared with unity, as follows:

$$\frac{time_1}{10^{[a+b(temp._1+2)]}} + \frac{time_2}{10^{[a+b(temp._2+2)]}} + \cdots \frac{time_n}{10^{[a+b(temp._n+2)]}}$$

The surface cooling plume of Figure III–6 (exclusive of the canal) could be considered to consist of 15 min at 89.7 F (32.06 C), 15 min at 89.2 F (31.78 C), 15 min at 88.7 F (31.4 C), 15 min at 88.2 F (31.22 C), 15 min at 87.8 F (31.00 C), until the lethal threshold for 70 F acclimation minus 2 C (85.1 F) was reached. The calculation would proceed as follows:

$$1 \geq \frac{15}{10^{[34.3649-0.9789(32.06+2)]}}$$

$$+ \frac{15}{10^{[34.3649-0.9789(31.78+2)]}} + \cdots$$

In this case, the bass would not survive through the first 15-minute period. In other such calculations, several steps would have to be summed before unity was reached (if not reached, the plume would not be detrimental).

Entrainment in the Plume

Organisms mixed with the thermal plume during dilution will also receive thermal shocks, although the maximum temperatures will generally be less than the discharge temperature. The number of organisms affected to some degree may be significantly greater than the numbers actually pumped through the plant. The route of maximum thermal exposure for each plume is indicated in Figu III–7 by a dashed line. This route should be analyzed to determine the maximum reproducible effect.

Detrimental effects of these exposures can also be judged by using the criterion for short-term exposures to extreme temperatures. The analytical steps were outlined above for estimating the effects on organisms that pass through the thermal plume portions of the entrainment thermal pattern. There would have been no mortalities of the largemouth bass from entrainment in the plume with rapid dilution, due to the short duration of exposure (about 10 seconds). Any bass that were entrained in the near-shore portions of the larger plume, and remained in it, would have died in less than 15 minutes.

Bottom Organisms Impacted by the Plume

Bottom communities of invertebrates, algae, rooted aquatic plants, and many incubating fish eggs can be exposed to warm plume water, particularly in shallow environments. In some circumstances the warming can be continuous, in others it can be intermittent due to changes in plume configuration with changes in currents, winds, or other factors. Clearly a thermal plume that stratifies and occupies only the upper part of the water column will have least effect on bottom biota.

Several approaches are useful in evaluating effects on community. Some have predictive capability, while oth.. are suitable largely for identifying effects after they have occurred. The criterion for short-term exposures identified relatively brief periods of detrimental high temperatures. Instead of the organism passing through zones of elevated temperatures, as in the previous examples, the organism is sedentary, and the thermal pulse passes over it. Developing fish eggs may be very sensitive to such changes. A brief pulse of high temperature that kills large numbers of organisms may affect a bottom area for time periods far longer than the immediate exposure time. Repeated sublethal exposures may also be detrimental, although the process is more complex than straight-forward summation. Analysis of single exposures proceeds exactly as described for plume entrainment.

The criterion for prolonged exposures is more generally applicable. The maximum tolerable weekly average temperature may be determined by the organisms present and the phase of their life cycle. In May, for example, the maximum heat tolerance temperature for the community may be determined by incubating fish eggs or fish fry on the bottom. In July it may be determined by the important resident invertebrate species. A well-designed thermal discharge should not require an extensive mixing zone where these criteria are exempted. Special criteria for reproduc processes may have to be applied, although thermal

:harges should be located so that zones important for :eproduction—migration, spawning, incubation—are not ıse¬¹

¬ria for species diversity provide a useful tool for dentrfying effects of thermal changes after they have ɔccurred, particularly the effects of subtle changes that are ı result of community interactions rather than physiological responses by one or more major species. Further research may identify critical temperatures or sequences of temperature changes that cannot be exceeded and may thereby provide a predictive capability as well. (See Appendix II-B.)

Mixed Water Body (or major region thereof)

This is the region most commonly considered in establishing water quality standards, for it generally includes the major area of the water body. Here the results of thermal additions are observed as small temperature increases over a large area (instead of high temperatures locally at the discharge point), and all heat sources become integrated into the normal annual temperature cycle (Figure III-6 and Figure III-7 insert).

Detrimental high temperatures in this area (or parts of it) are defined by the criteria for maximum temperatures for prolonged exposure (warm and cool months) for the most sensitive species or life stage occurring there, at each time of year, and by the criteria for reproduction.

For example, in the lake with the hypothetical power st   , there may be 40 principal fish species, of which half are considered important. These species have spawning temperatures ranging from 5 to 6 C for the sauger (*Stizostedion canadense*) to 26.7 C for the spotted bullhead (*Ictalurus serracanthus*). They also have a similar range of temperatures required for egg incubation, and a range of maximum temperatures for prolonged exposures of juveniles and adults. The requirements, however, may be met any time within normal time spans, such as January 1 to 24 for sauger spawning, and March 25 to April 29 for smallmouth bass spawning. Maximum temperatures for prolonged exposures

may increase steadily throughout a spring period. To predict effects of thermal discharges the pertinent temperatures for reproductive activities and maximum temperatures for each life stage can be plotted over a 12-month period such as shown in Fig. III-6. A maximum annual temperature curve can become apparent when sufficient biological data are available. Mount (1970)[305] gives an example of this type of analysis.

Discharge Canal

Canals or embayments that carry nearly undiluted condenser cooling water can develop biological communities that are atypical of normal seasonal communities. Interest in these areas does not generally derive from concern for a balanced ecosystem, but rather from effects that the altered communities can have on the entire aquatic ecosystem.

The general criteria for nuisance organisms may be applicable. In the discharge canals of some existing power stations, extensive mats of temperature-tolerant blue-green algae grow and periodically break away, adding a decomposing organic matter to the nearby shorelines.

The winter criterion for maximum temperatures for prolonged exposures identifies the potential for fish kills due to rapid decreases in temperature. During cold seasons particularly, fish are attracted to warmer water of an enclosed area, such as a discharge canal. Large numbers may reside there for sufficiently long periods to become metabolically acclimated to the warm water. For any acclimation temperature there is a minimum temperature to which the species can be cooled rapidly and still survive (lower incipient lethal temperature). These numerical combinations, where data are available, are found in Appendix II-C. There would be 50 per cent mortality, for example, if largemouth bass acclimated in a discharge canal to 20 C, were cooled to 5.5 C or below. If normal winter ambient temperature is less than 5.5 C, then the winter maximum should be below 20 C, perhaps nearer 15 C. If it is difficult to maintain the lower temperatures, fish should be excluded from the area.

ORGANIC MERCURY

Until recently, mercury most commonly entered the aquatic environment by leaching from geological formations and by water transport to streams and lakes. Since the industrial revolution, however, increasing amounts of mercury have been added to the aquatic environment with waste products from manufacturing processes or through improper disposal of industrial and consumer products. In addition, large quantities of mercury enter the environment when ores are smelted to recover such metals as copper, lead, and zinc (Klein 1971),[343] and when fossil fuels are burned. Whereas the maximum amount of mercury released by weathering processes is approximately 230 metric tons per year worldwide, the amount released by the burning of coal is on the order of 3000 tons per year; and a further quantity, probably comparable to 3000 tons, is emitted from industrial processes (Joensuu 1971).[341]

In urban and industrial areas consumer products containing mercury are often disposed of in sewer systems. These mercury discharges, though individually small, cannot be considered insignificant, because cumulatively they add large quantities of mercury to the water courses that receive these effluents. On the average, the mercury concentration in sewage effluent is one order of magnitude greater than its concentration in the water course that receives it (D'Itri *unpublished data* 1971).[359] Based on Klein and Goldberg's 1970[344] report of mercury concentrations in samples of ocean sediments near municipal sewer out-falls, it can be calculated that in an urban area from 400 to 500 pounds of mercury per million population are discharged to receiving waters every year. The uses of mercury are varied, and its consumption is fairly large. The National Academy of Sciences (1969)[347] reported the consumption of mercury by user category.

World attention focused on the environmental mercury problem when human beings were poisoned by eating contaminated fish and shell fish during the middle and late 1950's in Minamata, Japan. Since the first occurrence of "Minamata disease" in 1953, 121 cases resulting in 46 deaths have been confirmed in the Minamata area with an additional 47 confirmed cases and 6 deaths in nearby Niigata (Takeuchi 1970).[352]

In Sweden in the 1950's, conservationists charged that the abundance of methylmercury in the environment was causing severe poisoning in seed-eating birds and their predators (Johnels et al. 1967).[342] These poisonings could be related to the use of methylmercury in seed dressings. When these seed dressings were prohibited, levels of mercury declined substantially in seed-eating animals. At about the same time, investigators found high levels of mercury in fish in waters off Sweden, practically all of it in the form of methylmercury.

Biological Methylation

Some microbes are capable of biologically synthesiz methylmercury from mercury ions (Jensen and Jernelöv 1969;[339] Wood et al. 1969;[358] Dunlap 1971;[333] Fagerström and Jernelöv 1971).[334] At low concentrations, the formation of dimethylmercury is favored in the methyl transfer reaction but at higher concentrations of mercury, the major product appears to be monomethylmercury. In any particular ecosystem, the amounts of mono- and dimethylmercury compounds are determined by the presence of microbial species, the amount of organic pollution loading, the mercury concentration, temperature, and pH (Wood et al. 1969).[358]

Biological Magnification

Aquatic organisms concentrate methylmercury in their bodies either directly from the water or through the food chain (Johnels et al. 1967;[342] Hannerz 1968;[336] Hasselrot 1968,[333] Miettinen et al. 1970[346]). Northern pike (*Esox lucius*) and rainbow trout (*Salmo gairdneri*) are able to assimilate and concentrate methylmercury directly into their muscle tissues from ingested food (Miettinen et al. 1970).[346] In general, mercury in organisms eaten by fish increases at each trophic level of the food chain (Hamilton 1971).[335] The magnitude of the bioaccumulation of mercury is determined by the species, its exposure, feeding habits, metabolic rate, age and size, quality of the water, and degree of mercury pollution in the water. Rucker

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Amend (1969)[349] established that rainbow trout contained mercury levels of 4.0 and 17.3 µg/g in their muscle and kidney tissue after being exposed to 60 µg/l of ethylmercury for hour a day over 10 days. Fresh water phytoplankton, macrophytes, and fish are capable of biologically magnifying mercury concentrations from water 1000 times (Chapman et al. 1968).[330] Johnels et al. (1967)[342] reported a mercury concentration factor from water to pike of 5000 or more. Johnels et al. (1967)[342] had previously shown that when mercury levels in pike muscle were below 0.2 µg/g, the level was relatively constant irrespective of weight, but above 0.2 µg/g, the concentration of mercury tended to increase with increasing age and weight.

Experiments in progress at the National Water Quality Laboratory in Duluth, Minnesota, (Mount *unpublished data* 1971)[361] indicate that when brook trout (*Salvelinus fontinalis*) are held in water containing 0.05 µg/l of methylmercury for 2 months they can accumulate more than 0.5 µg/g of mercury. This is a magnification of 10,000 times. In the same experiments, exposure to 0.03 µg/l for 5 months resulted in continuing accumulation in fish tissue with no indication of a plateau. In a group of fish held at one µg/l, some organs contained 30 µg/g. Some fresh water invertebrates have also been reported to have a 10,000 magnification (Hannerz 1968).[336]

Although the mechanisms by which mercury accumulates and concentrates have not been fully explained, at least three factors are involved: the metabolic rate of individual fish; differences in the selection of food as fish mature; and the epithelial surface of the fish (Wobeser et al. 1970;[357] Hannerz 1968).[338] The rate at which fish lose methylmercury also has considerable effect on magnification of mercury in the tissues. Miettinen et al. have shown in a series of papers (1970)[346] that the loss of methylmercury is both fast and slow in fishes. The fast loss occurs early, while mercury is being redistributed through the body, and lasts only a few weeks. The subsequent loss from established binding sites follows slowly; a half-life is estimated to be on the order of 2 years. These rates mean that fishes, and perhaps other lower vertebrates, reduce their content of methylmercury many times more slowly than do the higher terrestrial vertebrates. Man, for example, is usually considered to excrete half of any given mercury residue in about 80 days. Extremely low rates of loss have also been shown in different species of aquatic mollusks and crayfish (*Cambarus*) (Nelson 1971).[348]

Excessive mercury residues in the sediments are dissipated only slowly. Löfroth (1970)[345] estimated that aquatic habitats polluted with mercury continue to contaminate fish for as long as 10 to 100 years after pollution has stopped.

Mercury in Fresh Waters

Mercury measured in the water of selected rivers of the United States ranged from less than 0.1 µg/l to 17 µg/l. Two thirds of the rivers contained 0.1 µg/l or less (Wallace

et al. 1971).[355] The value of 0.1 µg/l is also reported as the earliest reliable estimate of mercury levels in uncontaminated fresh water (Swedish National Institute of Public Health 1971).[351] Some rivers tested by the Swedish Institute were as low as 0.05 µg/l, which was also the average mercury level in some salt waters.

Toxicity of Organic Mercury in Water

The chemical form of methylmercury administered to fish makes little difference in its toxic effect (Miettinen et al. 1970).[346] The methylmercury bound to sulfhydryl groups of proteins, as it would be in nature, is just as toxic as the free unbound ionic form.

Fish are able to survive relatively high concentrations of organomercurials for a short time with few ill effects. For example, fry of steel head trout (*Salmo gairdneri*) and fingerlings of sockeye salmon (*Oncorhynchus nerka*) are able to survive in 10 mg/l of pyridyl mercuric acetate for one hour with no toxic effects (Rucker and Whipple 1951).[350] The LC50 of pyridyl mercuric acetate for some freshwater fish ranges from 390 µg/l to 26,000 µg/l for exposures between 24 and 72 hours (Willford 1966;[356] Clemmens and Sneed 1958,[331] 1959).[332]

As the exposure times lengthen, lower concentrations of mercury are lethal. On the basis of 120-hour bioassay tests of three species of minnows, Van Horn and Balch (1955)[354] determined that the minimum lethal concentrations of pyridyl mercuric acetate, pyridyl mercuric chloride, phenyl mercuric acetate, and ethyl mercuric phosphate averaged 250 µg/l.

Recent experiments at the National Water Quality Laboratory (Mount, *personal communication* 1971)[360] indicated that 0.2 µg/l of methylmercury killed fathead minnows (*Pimephales promelas*) within 6 to 8 weeks. Toxicity data from this same laboratory on several other species including *Gammarus*, *Daphnia*, top minnow (*Fundulus* sp.) and brook trout (*Salvelinus fontinalis*) indicated that none was more sensitive than the fathead minnow.

Northern pike seem to be more sensitive. When they were reared in water containing 0.1 µg/l of methylmercury for a season and then placed in clean water, they underwent continuing mortality. Scattered mortality from this source could ordinarily not be detected in nature, because the affected fish became uncoordinated and probably would have been eaten by predators (Hannerz 1968,[336] quoted by Nelson 1971[348]).

Some species of plankton are particularly sensitive. Studies of the effect of mercury on phytoplankton species confirmed that concentrations as low as 0.1 µg/l of selected organomercurial fungicides decreased both the photosynthesis and the growth of laboratory cultures of the marine alga *Nitzschia delicatissum*, as well as of some fresh water phytoplankton species (Harriss et al. 1970).[337] Ethylmercury phosphate is lethal to marine phytoplankton at 60 µg/l, and levels as low as 0.5 µg/l drastically limit their

growth (Ukeles 1962).[353] There is insufficient information about the thresholds for chronic toxicity.

Tissue Levels and Toxicity

There is almost no information on the concentrations of mercury in the tissues of aquatic organisms that are likely to cause mortality of the organisms themselves. Fish and shellfish found dead in Minamata contained 9 to 24 μg/g of mercury on the usual wet-weight basis; presumably some of these levels were lethal (Nelson 1971).[348] Miettinen et al. (1970)[346] showed that pike which had been experimentally killed by methylmercury contained from 5 to 9.1 μg/g and averaged 6.4 and 7.4 micrograms of methylmercury per gram of muscle tissue.

Discussion of Proposed Recommendations

At the present time there are not sufficient data available to determine the levels of mercury in water that are safe for aquatic organisms under chronic exposure. There have not been, for example, any experiments on the effects of chronic exposure to mercury on reproduction and growth of fish in the laboratory. Since experiments on sublethal effects are lacking, the next most useful information is on lethal effects following moderately long exposures of weeks or months. The lowest concentration shown to be lethal to fish is 0.2 μg/l of methylmercury which is lethal to fathead minnows (*Pimephales promelas*) in six weeks. Because 0.2 μg/l of methylmercury has been shown to be lethal, it is suggested that this concentration of mercury not be exceeded at any time or place in natural waters. Since phytoplankton are more sensitive, the average concentration of methylmercury in water probably should not exceed 0.05 μg/l for their protection. This recommended average is approximately equal to the supposed natural concentrations of mercury in water; hence little mercury can be added to the aquatic environment. The National Water Quality Laboratory (Mount, *unpublished data* 1971)[361] found that exposure of trout to 0.05 μg/l of methylmercury for 3 months resulted in concentrations of 0.5 μg/g, the Food and Drug Administration guideline for the maximum level for edible portions of fish flesh.

These concentrations of mercury or methylmercury in water are very low and difficult to measure or differentiate without special equipment and preparation. These low concentrations can also only be measured as total mercury. Since sediments may contain 10,000 times the amount of mercury in water, suspended solids in water can seriously affect the values found in analyses of water for mercury (Jernelöv 1972).[340] Because of these difficulties and because the real danger of mercury pollution results from a biological magnification, recommendations for mercury residues in tissues of aquatic organisms should be developed. This would make monitoring and control not only more effective and certain but also more feasible technically. Unfortunately, data are not yet available on the residue levels that

are safe for the aquatic organisms themselves and for organisms higher in the food chain, such as predatory fish or fish-eating birds. It is known that concentrations of 5 to 10 μg/g are found in some fish that died of methylmercury poisoning, and that 0.01 to 0.2 μg/g is apparently a usual background level in freshwater fish. Because data are lacking for safe residue levels in aquatic food chains, it is suggested that the Food & Drug Administration guideline level of 0.5 μg/g of total mercury in edible portions of freshwater fish used as human food be the guideline to protect predators in aquatic food chains.

Hence, mercury residues should not exceed 0.5 μg/g in any aquatic organisms. If levels approaching this are found, there should be total elimination of all possible sources of mercury pollution.

No distinction has been drawn between organic and inorganic forms of mercury in these discussions because of the possibility of biological transformation to the organic phase in aquatic habitats. Since the form of mercury in water cannot be readily determined, the recommendations are primarily based upon methylmercury but expressed as total mercury.

Recommendations

Selected species of fish and predatory aquatic organisms should be protected when the following conditions are fulfilled: (1) the concentration of total mercury does not exceed a total body burden of 0.5 μg/g wet weight in any aquatic organism (2) the total mercury concentrations in unfilter water do not exceed 0.2 μg/l at any time or place; and (3) the average total mercury concentration in unfiltered water does not exceed 0.05 μg/l.

PHTHALATE ESTERS

The occurrence of dialkyl phthalate residues has been established in various segments of the aquatic environment of North America. Phthalate ester residues occur principally in samples of water, sediment, and aquatic organisms in industrial and heavily populated areas (Stalling 1972).[366] In fish di-*n*-butyl phthalate residues ranged from 0 to 500 μg/kg, and di-2-ethylhexyl phthalate residues were as high as 3,200 μg/kg. No well-documented information exists on the fate of phthalate compounds in aquatic environments.

Phthalate esters are widely used as plasticizers, particularly in polyvinyl chloride (PVC) plastics. The most common phthalate ester plasticizer is di-2-ethylhexyl phthalate. Di-*n*-butyl phthalate has been used as an insect repellent (Frear 1969)[362] and in pesticide formulations to retard volatilization (Schoof et al. 1963).[365] Production of dioctyl phthalate ester placticizers was estimated to be 4.10×10^8 lbs in 1970 (Neely1 970).[363] Total phthalate ester production was reported to be 8.40×10^8 lbs in 1968, of which 4.40×10^8 lbs were dioctyl phthalate esters (Nematollahi et al. 1967) Production of phthalic anhydride was estimated to

7.60×10^8 lbs in 1970 (Neely 1970).[363] PVC plastic formula-
tions may contain 30 to 60 parts per hundred of phthalate
est lasticizer (Nematollahi et al. 1967).[364]

Toxicity

Studies to determine the acute or chronic toxicity effects
of phthalate esters or other plasticizers on aquatic organisms
have only recently been undertaken (Stalling 1972).[366] For
example, the acute toxicity of di-*n*-butyl phthalate to fish
is extremely low compared to pesticides (Table III-14).

Daphnia magna were exposed to 0.1 µg/l of ^{14}C di-*n*-butyl
phthalate and the organisms accumulated chemical residues
of 600 µg/kg within 10 days, or a 6,000-fold magnification
(Saunders, *unpublished data* 1971).[367] However, after transfer
of the *Daphnia* to uncontaminated water, approximately
50 per cent of the di-*n*-butyl phthalate was excreted in three
days. It was recently found that a concentration of 3 µg/l
of di-2-ethylhexyl phthalate significantly reduced the growth
and reproduction of *Daphnia magna* (Sanders *unpublished
data* 1971).[367]

The acute toxicity of phthalate esters appears to be rela-
tively insignificant, but these compounds may be detri-
mental to aquatic organisms at low chronic concentrations.

Recommendation

**Until a more detailed evaluation is made of toxi-
cological effects of phthalate esters on aquatic eco-
y   ns, a safety factor of 0.1 has been applied to
d   or *Daphnia magna* toxicity, and a level not
to exceed 0.3 µg/l should protect fish and their
food supply.**

POLYCHLORINATED BIPHENYLS

Polychlorinated biphenyls (PCB) have been found in fish
and wildlife in many parts of the world and at levels that
may adversely affect aquatic organisms (Jensen et al.
1969;[376] Holmes et al. 1967;[375] Koeman et al. 1969;[378]

*TABLE III-14—Acute Toxicity of Di-n-butyl Phthalate to
Four Species of Fish and Daphnia Magna.*

Species	Temperature	LC50 in µg/l		
		24 hr	48 hr	96 hr
Fathead minnow (Pimephales promelas)....	....		1490	1300 (Stalling)[366]
Bluegill (Lepomis macrochirus)...........	1230		731	731 (Stalling)[366]
Channel catfish (Ictalurus punctatus).......	3720		2910	2910 (Stalling)[366]
Rainbow trout (Salmo gairdneri)...........	....		....	8470 (Sanders)[367]
Daphnia magna.........................	....		....	>5000 (Sanders)[367]

Risebrough et al. 1968).[386] The environmental occurrence,
uses, and present toxicological aspects of PCB were recently
reviewed by Peakall and Lincer (1970),[384] Gustafson
(1970),[372] Risebrough (1970),[387] and Reynolds (1971).[385]

Biphenyls may have 1 to 10 attached chlorine atoms,
making possible over 200 compounds (Gustafson 1970).[372]
PCB occur as residues in fish, and presumably also in water,
as mixtures of chlorinated biphenyl isomers as shown in
Table III-15 (Stalling and Johnson, *unpublished data* 1970,[396]
Stalling *in press*[392]).

Analysis of PCB has been accomplished by gas chromatog-
raphy after separation of PCB from pesticides. A separation
method has been described by Armour and Burke (1970)[369]
and modified by Stalling and Huckins (1971).[391] A method
using separation on a charcoal column has shown good
reproducibility (Frank and Rees, *personal communication*).[395]
No standardized gas-liquid chromatography method has
been proposed for the analysis of mixtures of PCB in en-
vironmental samples. The solubility of these formulations
in water has not been precisely determined, but it is in the
range of 100 to 1,000 µg/l (Papageorge 1970).[383] Since
PCB have gas chromatographic characteristics similar to
many organochlorine pesticides, they can cause serious
interference in the gas chromatographic determination of
chlorinated insecticides (Risebrough et al. 1968).[386]

The Monsanto Company, the sole manufacturer of PCB

*TABLE III-15—Composition of PCB Residues in Selected Fish Samples from the 1970 National Pesticide Residue
Monitoring Program*

River	Location	Species	PCB Residue as Aroclor ® type (µg/g whole body)				
			1232	1248	1254	1260	Total
Ohio...............................	Cincinnati, O.	Carp Cyprinus carpio	10	75	42	6.0	133
Ohio...............................	Cincinnati, O.	White crappie Poxinus annularus	16	17	27	5.6	66
Ohio...............................	Marietta, O.	Channel catfish Ictalurus punctatus	38	23	11	4.9	77
Ohio...............................	Marietta, O.	Channel catfish	16	5.2	13	4.6	38
Yazoo.............................	Redwood, Miss.	Smallmouth buffalo Ictiobus bubalus	72	....	1.4	....	73
Hudson............................	Poughkeepsie, N.Y.	Goldfish Carassius auratus	9	173	32	....	213
Allegheny..........................	Natrona, Pa.	Walleye Stizostedion vitreum v.	....	5.2	25	4.6	35
Delaware...........................	Camden, N.J.	White perch Roccus americanus	....	8.0	6.8	3.9	19
Cape Fear.........................	Elizabeth Town, N.C.	Gizzard shad Porosoma cepadianum	19	....	2.6	1.1	23
Lake Ontario......................	Port Ontario, N.Y.	White perch	13	....	4.6	1.2	19
Mi	Memphis, Tenn.	Drum Aplodinotus grunniens	11	....	4.5	3.4	19
Mc	Lowell, Mass.	Drum	14	75	6.1	3.2	98

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in the United States (Gustafson 1970),[372] markets eight formulations of chlorinated biphenyls under the trademarks Aroclor® 1221, 1232, 1242, 1248, 1254, 1260, 1262, and 1268. The last two digits of each formulation designate the percent chlorine. Aroclor® 1248 and 1254 are produced in greatest quantities. They are used as dielectric fluids in capacitors and in closed-system heat exchangers (Papageorge 1970).[383] Aroclor® 1242 is used as a hydraulic fluid, and Aroclor® 1260 as a plasticizer. Chlorinated terphenyls are marketed under the trademark Aroclor® 5442 and 5460, and a mixture of bi- and terphenyls is designated Aroclor® 4465. The isomer composition and chromatographic characteristics of each formulation have been described by Stalling and Huckins (1971)[391] and Bagley et al. (1970).[370] A contaminant of some PCB, especially those manufactured in Europe, are chlorinated dibenzofurans (Brungs *personal communication* 1972).[393] Although these byproducts would appear to be extremely toxic, no data are available on their toxicity to aquatic life.

Direct Lethal Toxicity

Studies of toxicity of PCB to aquatic organisms are limited. They show considerable variation of toxicity to different species, as well as variation with the chlorine content of the PCB. Nevertheless, some trends in the toxic characteristics have become apparent, principally from the work of Mayer as described below:

- The higher the per cent chlorine, the lower the apparent toxicity of PCB to fish (Mayer, *in press*).[379] This was found in 15-day intermittent-flow bioassays using bluegills (*Lepomis macrochirus*) and channel catfish (*Ictalurus punctatus*) with Aroclor® 1242, 1248, 1254. All LC50 values were in the range 10 to 300 μg/l.
- The bluegill/channel catfish experiments also illustrated that all LC50 values decreased significantly when exposures continued from 15 to 20 days. The 96-hour LC50 of a PCB to fish cannot adequately measure its lethal toxicity.
- The same tests showed that the toxicity of Aroclor® 1248 doubled when the temperature was raised from 20 C to 27 C.

To invertebrates, Aroclor® 1242 has about the same acute toxicity that it has to fish. In 4- and 7-day tests (Saunders, *in press*),[389] it killed *Gammarus* at 42 μg/l and crayfish (*Cambarus*) at 30 μg/l, with values that were similar to the 15-day LC50 reported for bluegills. However, there is an extreme range in the reported short-term lethal levels of Aroclor® 1254 for invertebrates. Saunders (*in press*)[389] reported a 96-hour LC50 as 80 μg/l for crayfish and only 3 μg/l for glass shrimp (*Paleomonetes*) in 7-day tests; and Duke et al. (1970)[371] reported that as little as 0.94 μg/l killed immature pink shrimp (*Panaeus duorarum*). Part of this variation is related to exposure periods in the tests; part

is no doubt the variation in species response. Again this emphasizes the point that short-term tests of acute toxicities of PCB have serious limitations.

Marine animals may be more easily killed by PCB th freshwater ones (see Section IV). When two estuarine fishe (*Lagodon rhomboides* and *Leiostomus xanthurus*) were exposed for 14 to 45 days to Aroclor® 1254, mortalities were observed at 5 μg/l (Hansen, et al. 1971).[373] This indicated a toxicity about five times greater than summarized above for freshwater fish but about the same as the toxicity for the marine crustaceans mentioned above.

Feeding Studies

Dietary exposure to PCB seems to be less of a direct hazard to fish than exposure in water. Coho salmon (*Oncorhynchus kisutch*) fed Aroclor® 1254 in varying amounts up to 14,500 μg/kg body weight per day accumulated whole body residues which were only 0.9 to 0.5 of the level in the food after 240 days of dietary exposure. Growth rates were not affected. However, all fish exposed to the highest treatment died after 240 days exposure; and thyroid activity was stimulated in all except the group treated at the lowest concentration (Mehrle and Grant *unpublished data* 1971).[394]

At present, evaluation of data from laboratory experiments indicates that exposures to PCB in water represents a greater hazard to fish than dietary exposures. However, in the environment, residue accumulation from dietary sources could be more important, because PCB have a high affinity for sediments, and therefore, they readily er food chains (Duke et al. 1970;[371] Nimmo, et al. 1971).[3t]

Residues in Tissue

It is clear that widespread pollution of major waterways has occurred, and that appreciable PCB residues exist in fish. When analyses of 40 fish from the 1970 National Pesticide Monitoring Program were made, only one of the fish was found to contain less than 1 μg/g PCB (Stalling and Mayer 1972).[390] The 10 highest residue levels in the 40 selected fish ranged from 19 μg/g to 213 μg/g whole body weight.

By contrast, residues measured in ocean fish have been generally below 1 μg/g (Risebrough 1970;[387] Jensen, et al. 1969).[376] Between the ranges in freshwater fish and those in marine fish are the levels of PCB found in seals (Jensen et al. 1969;[376] Holden 1970),[374] and in the eggs of fish-eating birds in North America (Anderson et al. 1969;[368] Mulhern et al. 1971;[380] Reynolds 1971).[385]

In laboratory experiments, crustacea exposed to varying levels of Aroclor® 1254 in the water concentrated the PCB within their bodies more than 20,000 times. The tissue residues may sometimes reach an equilibrium, and in *Gammarus fasciatus* PCB did not concentrate beyond 27,000 times despite an additional 3-week exposure to 1.6 μg/l Aroclor® (Saunders 1972).[388] In contrast, PCB residue in crayfish did not reach equilibrium after a 28-day expo.

PCB concentration factors by two estuarine fishes, *Lagondon rhomboides* and *Leiostomus xanthurus*, were similar to that de ᵔ⁻ᵈed above for crustaceans, i.e., about 10,000 to 50,000 tii. .he exposure levels in water (Hansen et al. 1971).[373] It is important to note that these accumulations occurred at water concentrations of PCB that killed the fish in 15 to 45 days.

Also similar were the accumulation ratios of 26,000 to 56,000 for bluegills (*Lepomis macrochirus*) chronically exposed to 2 to 15 μg/l of Aroclor ® 1248 and 1254. Fathead minnows (*Pimephales promelas*) chronically exposed to Aroclor ® 1242 and 1254 for 8 weeks concentrated PCB 100,000 and 200,000 times the exposure levels, respectively. Residues of 50 μg/l (whole body) resulted from exposure for 8 weeks to 0.3 μg/l Aroclor ® 1254 (Nebeker et al. 1972).[381] These experiments with bluegills also indicated that the maximum levels of PCB were generally related to the concentration of PCB in the water (50,000–200,000 times higher) to which they were exposed (Stalling and Huckins *unpublished data* 1971).[397]

Effects on Reproduction

PCB residues in salmon eggs are apparently related to mortality of eggs. In preliminary investigations in Sweden, Jensen and his associates (1970)[377] reported that when residues in groups of eggs ranged from 0.4 to 1.9 μg/g on a whole-weight basis (7.7 to 34 μg/g on a fat basis), related mortalities ranged from 16 per cent up to 100 per cent.

concentrations in the range of 0.5 to 10 μg/l in water interfered with reproduction of several aquatic animals according to recent work of Nebeker et al. (1971).[381] About 5 μg/l of Aroclor ® 1248 was the highest concentration that did not affect reproduction of *Daphnia magna* and *Gammarus pseudolimnaeus*. In tests of reproduction by fathead minnows (*Pimephales promelas*) all died when exposed chronically to greater than 8.3 μg/l of either Aroclor ® 1242 or Aroclor ® 1254. Reproduction occurred at and below 5.4 μg/l Aroclor ® 1242, and at and below 1.8 μg/l of Aroclor ® 1254.

The association between residue levels and biological effects in aquatic animals is scarcely known, but the work of Jensen et al. (1970)[377] suggested that about 0.5 μg/g of PCB in whole salmon eggs might be the threshold for egg mortality. Such a level in eggs would be associated with levels in general body tissue (e.g., muscle) of 2.5 to 5.0 μg/g. The residue in muscle corresponded to the present Food and Drug Administration level for allowable levels of PCB in fish used as human food. Residues measured in the survey by the 1970 National Pesticide Monitoring Program were generally above 5 μg/g.

Applying a minimal safety factor of 10 for protection of the affected population, and for protection of other species higher in the food chain, would yield a maximum permissₛⁱ ˙ssue concentration of 0.5 μg/g in any aquatic organism in .y habitat affected by PCB.

General Considerations and Further Needs

Another means of control would be justified in view of the toxicity of PCB, the lack of knowledge about how it first enters natural ecosystems as a pollutant, and its apparent distribution in high concentrations in freshwater fish in the United States. This method would be to regulate the manufacture of PCB and maintain close control of its uses to avoid situations where PCB is lost to the environment. The Monsanto Company recently restricted the sale of PCB for uses in which disposal of the end products could not be controlled, as with plasticizers (Gustafson 1970).[372]

Basis for Recommendations

For PCB levels in water, the most sensitive reaction shown by aquatic organisms is to the lethal effects of low concentrations continually present in water for long periods (weeks or months). Concentrations in the range of 1 to 8 μg/l have been shown to be lethal to several animals.

The work of Hansen, et al. (1971)[373] and Stallings and Huckins (*unpublished data* 1971)[391] indicates that concentrations of 0.01 μg/l of PCB in water over periods of up to 36 weeks could lead to dangerous levels of PCB in the tissues of aquatic organisms. Accumulation by factors of 75,000 to 200,000 times is indicated by their work. If the higher ratio is taken, 0.01 μg/l in water might result in 2.0 μg/g in flesh on whole fish basis. This is comparable to the residue level in salmon eggs associated with complete mortality of embryos. Therefore, a concentration is recommended that is reduced by a factor of 5, or 0.002 μg/l. In addition, a control based on residue levels is required, as well as one based on PCB in the water.

Recommendations

**Aquatic life should be protected where the maximum concentration of total PCB in unfiltered water does not exceed 0.002 μg/l at any time or place, and the residues in the general body tissues of any aquatic organism do not exceed 0.5 μg/g.**

METALS

General Data

Several reviews of the toxicity of metals are available (e.g., Skidmore 1964;[428] McKee and Wolf 1963;[415] Doudoroff and Katz 1953).[406] Some of the most relevant research is currently in progress or only recently completed. Some deals with chronic effects of metals on survival, growth, and reproduction of fish and other organisms. The completed studies have estimated safe concentrations, and from these application factors have been derived as defined in the discussion of bioassays (pp. 118–123).

The important relation between water hardness and lethal toxicity is well documented for some metals (see Figure III–9). For copper, the difference in toxicity may
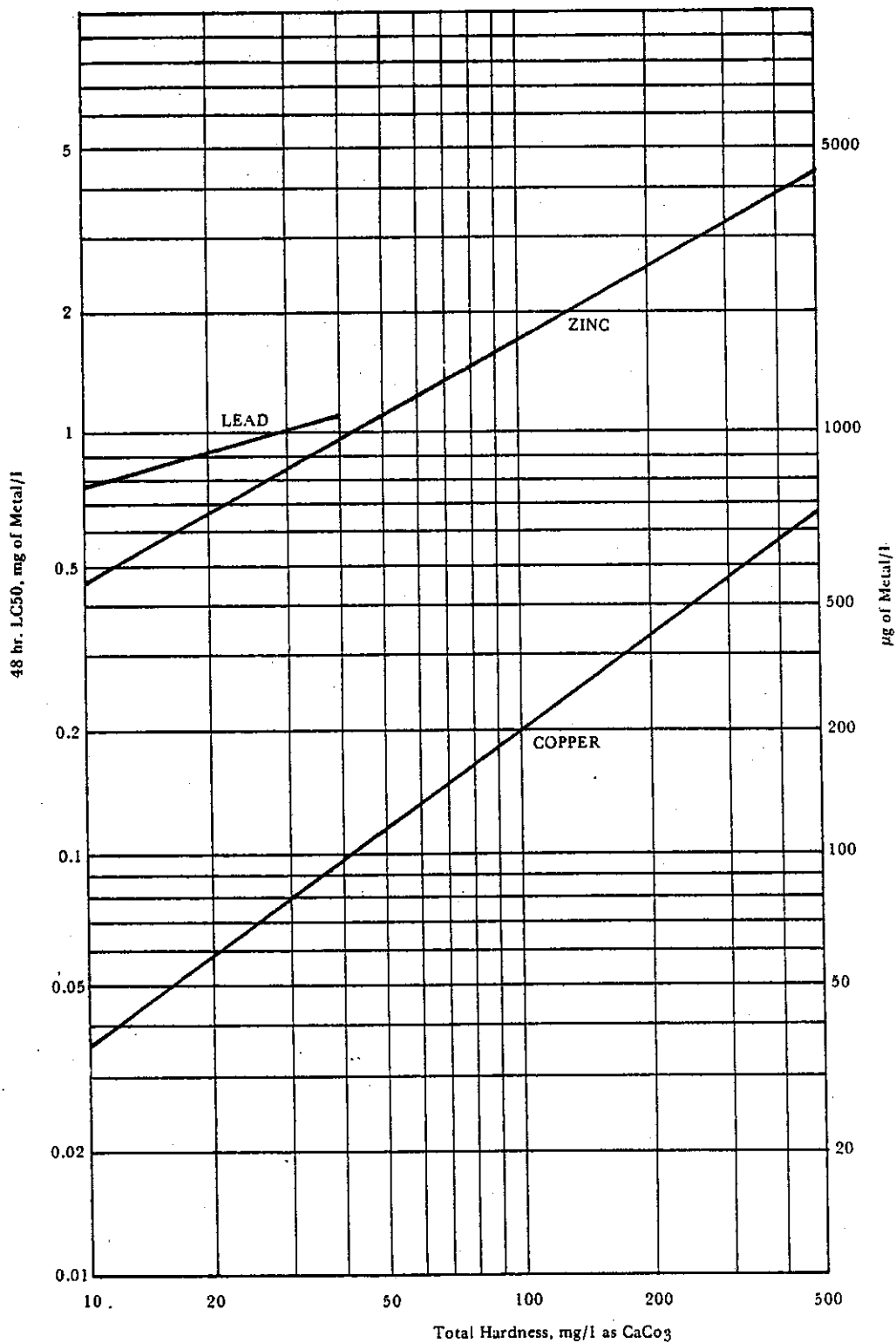
Brown 1968;[401] Lloyd and Herbert 1960 [414]

FIGURE III-9—*The 48-Hour Lethal Concentrations of Three Heavy Metals for Rainbow Trout* (Salmo gairdneri). (*Sin Relationships Exist for Other Species of Fish.*)

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not be related to the difference in hardness per se, but to the difference in alkalinity of the water that accompanies the change in hardness (Stiff 1971).[434] Nevertheless, the relation to hardness is a convenient and accepted one. The hardness classification developed by the U.S. Geological Survey is the following:

Soft	0– 60 mg/l (hardness as $CaCO_3$)
Moderately hard	61–120 mg/l
Hard	in excess of 120 mg/l

There are many chemical species of metals in water; some are toxic to aquatic life, others are not. Hydrogen ion concentration in water is extremely important in governing the species and solubility of metals and therefore the lethal toxicity. At high pH, many heavy metals form hydroxides or basic carbonates that are relatively insoluble and tend to precipitate. They may, however, remain suspended in the water as fine particles (O'Connor et al. 1964;[421] Stiff 1971).[434]

The toxicity of suspended hydroxides of metal depends on the particular situation. For example, suspended zinc has been found to be nontoxic (Sprague 1964a & b),[429,430] equally as toxic as dissolved zinc (Lloyd 1960)[412] and more toxic than dissolved zinc (Mount 1966).[417] This indicates that suspended zinc is at least potentially poisonous, and therefore the total metal measured in the water should be considered toxic. It is difficult to predict the effect of pH on toxicity. For example, low pH (about 5) as well as high pH (about 9) reduced toxicity of copper and zinc compared to that at neutral pH (Fisheries Research Board of Canada *unpublished data* 1971).[444] Therefore pH should be regulated in bioassays with metals in order to simulate local conditions and to explore any effect of local variation of pH.

In addition to hardness, numerous other factors influence the lethal toxicity of copper to fish. McKee and Wolf (1963)[415] and Doudoroff and Katz (1953)[406] included dissolved oxygen, temperature, turbidity, carbon dioxide, magnesium salts, and phosphates as factors affecting copper toxicity. Artificial chelating compounds such as nitrilotriacetic acid can reduce or eliminate toxic effects of zinc and other metals (Sprague 1968b)[432] and there may be natural chelating agents that would do the same thing. Certain organic ligands (Bender et al. 1970)[399] and amino acids from sewage treatment plant effluent (United Kingdom Ministry of Technology 1969)[435] also reduce the toxicity of copper by forming copper-organic complexes that do not contribute to lethal toxicity. It is safe to assume that some of these factors will influence the toxicity of other metals. In addition, the amount of metals found (at least temporarily) in living biological matter is included in most routine water analyses. At the present time, however, it is not possible to predict accurately the amount of total metal in any environment that may be lethal, biologically active, or contributory to toxicity. Consequently, the following recommendations are made.

Recommendations

Since forms or species of metals in water may change with shifts in the water quality, and since the toxicity to aquatic life may concurrently change in as yet unpredictable ways, it is recommended that water quality criteria for a given metal be based on the total amount of it in the water, regardless of the chemical state or form of the metal, except that settleable solids should be excluded from the analysis (Standard Methods 1971).[433] Additionally, hardness affects the toxicity of many metals (see Figure III–9).

Metals which have collected in the sediments can redissolve into the water, and such redissolved metals should meet the criteria for heavy metals. To protect aquatic life, amounts likely to be harmful should not occur in the sediments.

It is recommended that any metal species not specifically mentioned in this report but suspected of causing detrimental effects on aquatic life be examined as outlined in the section on Bioassays.

Aluminum

Current research by Freeman and Everhart (1971)[407] indicated that aluminum salts were slightly soluble at neutral pH; 0.05 mg/l dissolved and had no sublethal effects on fish. At pH 9, at least 5 mg/l of aluminum dissolved and this killed fingerling rainbow trout within 48 hours. However, the suspended precipitate of ionized aluminum is toxic. In most natural waters, the ionized or potentially ionizable aluminum would be in the form of anionic or neutral precipitates, and anything greater than 0.1 mg/l of this would be deleterious to growth and survival of fish.

Recommendation

Careful examination of toxicity problems should be made to protect aquatic life in situations where the presence of ionic aluminum is suspected. Aluminum may have considerably greater toxicity than has been assumed.

Cadmium

This metal is an extremely dangerous cumulative poison. In mammals (Nilsson 1970),[420] fish (Eaton *unpublished data* 1971),[442] and probably other animals, there is insidious, progressive, chronic poisoning because there is almost no excretion of the metal. In its acute lethal action on rainbow trout (*Salmo gairdneri*), Ball (1967)[398] found cadmium unusually slow. A lethal threshold of 0.01 mg/l was not discernible until seven days' exposure. Other investigators (Pickering and Gast, *in press*,[427] Eaton *unpublished data* 1971)[442] have determined lethal threshold concentrations in fathead minnows in 2 to 6 days and in bluegill in 96 hours. The chronically safe levels for both fathead minnows

(*Pimephales promelas*) (Pickering and Gast, *in press*)[427] and bluegill sunfish (*Lepomis macrochirus*) (Eaton *unpublished data* 1971)[442] in hard water (200 mg/l as CaCO₃) are between 0.06 and 0.03 mg/l. In these exposures, death of eggs or early larvae was one of the effects observed at the lowest unsafe concentrations tested. Recent exposures of eggs and larvae at the National Water Quality Laboratory (Duluth) in soft water (45 mg/l as CaCO₃) demonstrated that 0.01 mg/l was unsafe; 0.004 mg/l was safe for several warm- and coldwater fishes, including some salmonids; and the safe level for coho salmon fry (*Oncorhynchus kisutch*) was lower, i.e., between 0.004 mg/l and 0.001 mg/l (McKim and Eaton *unpublished data* 1971).[445]

Daphnia magna appeared to be very sensitive to cadmium. Concentrations of 0.0005 mg/l were found to reduce reproduction in one-generation exposures lasting three weeks (Biesinger and Christensen *unpublished data* 1971).[440] This sensitivity is probably representative of other crustaceans as well.

Recommendation

Aquatic life should be protected where levels of cadmium do not exceed 0.03 mg/l in water having total hardness above 100 mg/l as CaCO₃, or 0.004 mg/l in waters with a hardness of 100 mg/l or below at any time or place. Habitats should be safe for crustaceans or the eggs and larvae of salmon if the levels of cadmium do not exceed 0.003 mg/l in hard water or 0.0004 mg/l in soft water at any time or place.

Chromium

The chronic toxicity of hexavalent chromium to fish has been studied by Olson (1958),[422] and Olson and Foster (1956,[423] 1957).[424] Their data demonstrated a pronounced cumulative toxicity of chromium to rainbow trout and chinook salmon (*Oncorhynchus tshawytscha*). Duodoroff and Katz (1953)[406] found that bluegills (*Lepomis macrochirus*) tolerated a 45 mg/l level for 20 days in hard water. Cairns (1956),[403] using chromic oxide (CrO₃), found that a concentration of 104 mg/l was toxic to bluegills in 6 to 84 hours. Bioassays conducted with four species of fish gave 96-hour LC50's of hexavalent chromium that ranged from 17 to 118 mg/l, indicating little effect of hardness on toxicity (Pickering and Henderson 1966).[426]

Recently some tests of chronic effects on reproduction of fish have been carried out. The 96-hour LC50 and safe concentrations for hexavalent chromium were 33 and 1.0 mg/l for fathead minnows (*Pimephales promelas*) in hard water (Pickering *unpublished data* 1971),[446] 50 and 0.6 mg/l for brook trout (*Salvelinus fontinalis*) in soft water, and 69 and 0.3 mg/l for rainbow trout (*Salmo gairdneri*) in soft water (Benoit *unpublished data* 1971).[438] Equivalent values for trivalent chromium were little different: 27 mg/l for the 96-hour LC50, and 1.0 mg/l for a safe concentration

for fathead minnows in hard water (Pickering *unpublished data* 1971).[446]

For *Daphnia* the LC50 of hexavalent chromium was reported as 0.05 mg/l, and the chronic no-effect level trivalent chromium on reproduction was 0.33 mg/l (Biesinger and Christensen *unpublished data* 1971).[440] Some data are available concerning the toxicity of chromium to algae. The concentrations of chromium that inhibited growth for the test organisms are as follows (Hervey 1949):[410] Chlorococcales, 3.2 to 6.4 mg/l; Euglenoids, 0.32 to 1.6 mg/l; and diatoms, 0.032 to 0.32 mg/l. Patrick (*unpublished data* 1971)[447] found that 50 per cent growth reduction for two diatoms in hard and soft water occurred at 0.2 to 0.4 mg/l chromium.

Thus it is apparent that there is a great range of sensitivity to chromium among different species of organisms and in different waters. Those lethal levels reported above are 17 to 118 mg/l for fish, 0.05 mg/l for invertebrates, and 0.032 to 6.4 mg/l for algae, the highest value being 3,700 times the lowest one. The apparent "safe" concentration for fish is moderately high, but the recommended maximum concentration of 0.05 mg/l has been selected in order to protect other organisms, in particular *Daphnia* and certain diatoms which are affected at slightly below this concentration.

Recommendation

Mixed aquatic populations should be protected where the concentration of total chromium water does not exceed 0.05 mg/l at any time or place.

Copper

Copper is known to be particularly toxic to algae and mollusks, and the implications of this should be considered for any given body of water. Based on studies of effects on these organisms, it is known that the criteria for fish protect these other forms as well. Recent work (Biesinger et al. *unpublished data* 1971)[439] indicated that the safe level of copper for reproduction and growth of *Daphnia magna* in soft water (45 mg/l as CaCO₃) is 0.006 mg/l, which is similar to the concentrations described below as safe for fish. The relationship of LC50 to water hardness was shown in Figure III–7 for rainbow trout (*Salmo gairdneri*).

The safe concentration of copper for reproduction by fathead minnows (*Pimephales promelas*) in hard water (200 mg/l as CaCO₃) was between 0.015 and 0.033 mg/l (Mount 1968),[418] and in soft water (30 mg/l as CaCO₃) was between 0.011 and 0.018 mg/l (Mount and Stephan 1969).[419] More recent work with fathead minnows in hard water indicated that a concentration of 0.033 mg/l would probably be safe (Brungs *unpublished data* 1971).[441] Acceptable reproduction by brook trout (*Salvelinus fontinalis*) in soft water (45 mg/l as CaCO₃) occurred between 0 and 0.018 mg/l (McKim and Benoit 1971).[416] The safe

lethal ratios determined in these studies varied somewhat; but that for hard water is close to 0.1 and that for soft water is ~~oximately 0.1 to 0.2. In very soft water, typical of ~~northern and mountainous regions, 0.1 of the 96-hour LC50 for sensitive species would be close to what is considered a natural concentration in these waters.

Recent work indicated that avoidance reactions by fish may be as restrictive as reproductive requirements or even more so (Sprague 1964b).[430] It has been demonstrated that Atlantic salmon (*Salmo salar*) avoid a concentration of 0.004 mg/l in the laboratory.

Recommendation

Once a 96-hour LC50 has been determined using the receiving water in question and the most sensitive important species in the locality as the test organism, a concentration of copper safe to aquatic life in that water can be estimated by multiplying the 96-hour LC50 by an application factor of 0.1.

Lead

Lead has a low solubility of 0.5 mg/l in soft water and only 0.003 mg/l in hard water, although higher concentrations of suspended and colloidal lead may remain in the water. The extreme effects of water hardness on lead toxicity are demonstrated by the LC50 values in hard and soft w~~ ~~. The 96-hour LC50 values in soft water (20 to 45 n.~~ as CaCO$_3$) were 5 to 7 mg/l and 4 to 5 mg/l for the fathead minnow (*Pimephales promelas*) and the brook trout (*Salvelinus fontinalis*) respectively (Pickering and Henderson 1966,[426] Benoit *unpublished data* 1971).[438] Brown (1968)[401] reported a 96-hour LC50 of 1 mg/l for rainbow trout (*Salmo gairdneri*) in soft water (50 mg/l as CaCO$_3$). (See Figure III–9 for other values for this species.) The 96-hour LC50 values of lead in hard water were 482 mg/l and 442 mg/l for fathead minnow and brook trout (Pickering and Henderson 1966).[426]

There is not sufficient information on chronic toxicity of lead to fish to justify recommending values as application factors. However, preliminary information on long exposures (2 to 3 months) on rainbow trout and brook trout (Everhart *unpublished data* 1971,[443] Benoit *unpublished data* 1971)[438] indicated detrimental effects at 0.10 mg/l of lead in soft water (20 to 45 mg/l as CaCO$_3$), a safe-to-lethal ratio of less than 0.02.

Growth of guppies (*Lebistes*) was affected by 1.24 mg/l of lead (Crandall and Goodnight 1962).[405] Jones (1939)[411] and Hawksley (1967)[408] found chronic or sublethal effects on sticklebacks from lead concentrations of 0.1 and 0.3 mg/l. The conditioned behavior of goldfish (*Carassius auratus*) in a light-dark shuttlebox was adversely affected b~~ ~~.07 mg/l of lead in soft water (Weir and Hine 1970).[437] ~~ronic lead toxicity was recently investigated with *Daphnia magna* (Biesinger and Christensen *unpublished data*

1971)[440] and the effect on reproduction was observed at a level of 0.03 mg/l of lead. This concentration of 0.03 mg/l, the safe level for *Daphnia*, is recommended as the criterion for protection of aquatic life. It is probably also close to the safe level for fish, because the tests described above, although somewhat preliminary, indicated that concentrations about 2 or 3 times higher had detrimental effects.

Recommendation

The concentration of lead in water should not be higher than 0.03 mg/l at any time or place in order to protect aquatic life.

Mercury

Most data about mercury involve the organic compounds (see the discussion of Organic Mercury, p. 172.) Information is available, however, for inorganic mercury in the form of mercuric ions. Short-term 96-hour bioassay studies indicated that concentrations of 1 mg/l are fatal to fish (Boetius 1960,[400] Jones 1939,[411] Weir and Hine 1970).[437] For long-term exposures of 10 days or more, mercury levels as low as 10 to 20 mg/l have been shown to be fatal to fish (Uspenskaya 1946).[436]

Recommendation

In protecting aquatic life, the recommendations for organic mercury (p. 174) also pertain here.

Nickel

The 96-hour LC50 of nickel for fathead minnows (*Pimephales promelas*) ranges from 5 mg/l in soft water (20 mg/l as CaCO$_3$) to 43 mg/l in hard water (360 mg/l as CaCO$_3$) under static test conditions (Pickering and Henderson 1966).[426] In water of 200 mg/l hardness (as CaCO$_3$), the 96-hour LC50 for fathead minnows was 26 to 31 mg/l with a chronically safe concentration between 0.8 and 0.4 mg/l (Pickering *unpublished data* 1971).[446] On the basis of this work, an application factor of 0.02 appeared to be appropriate for the protection of fish. If this factor is used, the estimated safe concentration of nickel for fathead minnows in soft water would be about 0.1 mg/l. Using static test conditions and *Daphnia magna*, Biesinger and Christensen (*unpublished data* 1971)[440] determined that a nickel concentration of 0.095 mg/l reduced reproduction during a 3-week exposure in soft water (45 mg/l as CaCO$_3$), and a nickel concentration of 0.030 mg/l had no effect. This result indicated that the sensitivity of *Daphnia magna* is comparable to that of fish.

Recommendation

Once a 96-hour LC50 has been determined using the receiving water in question and the most sensitive important species in the locality as the test organism, a concentration of nickel safe to aquatic

life in that water can be estimated by multiplying the 96-hour LC50 by an application factor of 0.02.

Zinc

The acute lethal toxicity of zinc is greatly affected by water hardness (see Figure III-7). Pickering and Henderson (1966)[426] determined the 96-hour LC50 of zinc for fathead minnows (*Pimephales promelas*) and bluegills (*Lepomis macrochirus*) using static test conditions. For fathead minnows in soft water (20 mg/l as $CaCO_3$) the LC50 was 0.87 mg/l, and in hard water (360 mg/l as $CaCO_3$) it was 33 mg/l. Bluegills were more resistant in both waters. Similarly the lethal threshold concentration was 3 or 4 times as high for coarse fish as for trout (*Salvelinus fontinalis*) (Ball 1967).[398]

The 24-hour LC50 of zinc for rainbow trout (*Salmo gairdneri*) was reduced only 20 per cent when the fish were forced to swim at 85 per cent of their maximum sustained swimming speed (Herbert and Shurben 1964).[409] The maximum effect of a reduction in dissolved oxygen from 6 to 7 mg/l to 2 mg/l on the acute toxicity of zinc was a 50 per cent increase (Lloyd 1961,[413] Cairns and Scheier 1958,[404] Pickering 1968).[425] The effects are small in comparison to the difference between acutely toxic and safe concentrations. The recommended application factor recognizes these effects.

A chronic test in hard water (200 mg/l as $CaCO_3$), involving fathead minnow reproduction, determined the safe concentration of zinc to be between 0.03 mg/l, which had no effect, and 0.18 mg/l, which caused 83 per cent reduction in fecundity (Brungs 1969).[402] Using the 96-hour LC50 of 9.2 mg/l, the ratio of the above no-effect concentration to the LC50 is 0.0034. Interpolation suggests that about 0.005 of the LC50 would cause 20 per cent reduction of fecundity, making the best estimate of a valid application factor close to 0.005.

There was a reduction in reproduction of *Daphnia magna* at a zinc concentration of 0.10 mg/l using soft water (45 mg/l as $CaCO_3$) (Biesinger and Christensen *unpublished data* 1971).[440] No effect was observed at 0.07 mg/l, which indicated that *Daphnia magna* was more resistant to zinc than the fathead minnow.

Avoidance reactions by rainbow trout in the laboratory have been caused by 0.01 of the LC50 of zinc (Sprague 1968a).[431]

Recommendation

Once a 96-hour LC50 has been determined using the receiving water in question and the most sensitive important species in the locality as the test organism, a concentration of zinc safe to aquatic life in that water can be estimated by multiplying the 96-hour LC50 by an application factor of 0.005.

PESTICIDES

Pesticides are chemicals, natural and synthetic, used to control or destroy plant and animal life considered adver to human society. Since the 1940's a large number o synthetic organic compounds have been developed for pesticide purposes. Presently there are thousands of registered formulations incorporating nearly 900 different chemicals. Trends in production and use of pesticides indicate an annual increase of about 15 per cent, and there are predictions of increased demand during the next decade (Mrak 1969).[477] The subject of pesticides and their environmental significance has been carefully evaluated in the Report of the Secretary's Commission on Pesticides and their Relationship to Environmental Health (Mrak 1969).[477]

Methods, Rate, and Frequency of Application

Pesticides are used for a wide variety of purposes in a multitude of environmental situations. Often they are categorized according to their use or intended target (e.g., insecticide, herbicide, fungicide), but their release in the environment presents an inherent hazard to many non-target organisms. Some degree of contamination and risk is assumed with nearly all pesticide use. The risk to aquatic ecosystems depends upon the chemical and physical properties of the pesticide, type of formulation, frequency, rate and methods of application, and the nature of the receiving system.

The pesticides of greatest concern are those that a persistent for long periods and accumulate in the enviro ment; those that are highly toxic to man, fish, and wildlife; and those that are used in large volumes over broad areas. A list of such chemicals recommended for monitoring in the environment appears in Appendix II–F. The majority of these compounds are either insecticides or herbicides used extensively in agriculture, public health, and for household or garden purposes. In the absence of definitive data on their individual behavior and their individual effect on the environment, some generalization about pesticides is required to serve as a guideline for establishing water quality criteria to protect aquatic life. In specific instances, however, each compound must be considered individually on the basis of information about its reaction in the environment and its effect on aquatic organisms.

Sources and Distribution

The major sources of pesticides in water are runoff from treated lands, industrial discharges, and domestic sewage. Significant contributions may also occur in fallout from atmospheric drift and in precipitation (Tarrant and Tatton 1968).[485] Applications to water surfaces, intentional or otherwise, will result in rapid and extensive contamination. The persistent organochlorine pesticides have received the greatest attention in monitoring programs (Lichtenb et al. 1970,[471] Henderson et al. 1969).[461] Their extens

distribution in aquatic systems is indicative of environmental loading from both point and nonpoint sources.

ny pesticides have a low water solubility that favors tl. apid sorption on suspended or sedimented materials and their affinity to plant and animal lipids. Soluble or dispersed fractions of pesticides in the water rapidly decline after initial contamination, resulting in increased concentrations in the sediments (Yule and Tomlin 1971).[489] In streams, much of the residue is in continuous transport on suspended particulate material or in sediments (Zabik 1969).[490] The distribution within the stream flow is nonuniform because of unequal velocity and unequal distribution of suspended materials within the stream bed (Feltz et al. 1971).[454] Seasonal fluctuations in runoff and use pattern cause major changes in concentration during the year, but the continuous downstream transport tends to reduce levels in the upper reaches of streams while increasing them in the downstream areas and eventually in major receiving basins (i.e., lakes, reservoirs, or estuaries). If applications in a watershed cease entirely, residues in the stream will gradually and continuously decline (Sprague et al. 1971).[484] A similar decline would be expected in the receiving basins but at a slower rate.

In lakes the sediments apparently act as a reservoir from which the pesticide is partitioned into the water phase according to the solubility of the compound, the concentration in the sediment, and the type of sediment (Hamelink et ~l 1971).[458] Dissolved natural organic materials in the v may greatly enhance the water solubility of some pesticides (Wershaw et al. 1969).[487] *Some investigations indicated pesticides may be less available to the water in eutrophic systems where the higher organic content in the sediments has a greater capacity to hold pesticide residues (Lotse et al. 1968,[472] Hartung 1970[460]). This in part explained the difference in time required for some waters to "detoxify," as observed in lakes treated with toxaphene to eradicate undesirable fish species (Terriere et al. 1966).[486]*

Herbicides applied to aquatic systems to control plant growths are removed from the water by absorption in the plants or sorption to the hydrosoil. The rate of disappearance from the water may be dependent upon the availability of suitable sorption sites. Frank and Comes (1967)[455] found residues of dichlobenil in soil and water up to 160 days after application. They also found that diquat and paraquat residues were persistent in hydrosoils for approximately 3 to 6 months after application. Granular herbicide treatments made on a volume basis deposit greater quantities on the hydrosoil in deep water areas than in water of less depth. The granules may supply herbicide to the water over a period of time depending upon solubility of the herbicide, concentrations in the granule, and other conditions.

Because the distribution of pesticides is nonuniform, sampling methods and frequency, as well as selection of s ing sites, must be scientifically determined (Feltz e. 1971).[454] Pesticides found in the water in suspended particulate material and in sediments may be toxic to aquatic organisms or contribute to residue accumulation in them.

Persistence and Biological Accumulation

All organic pesticides are subject to metabolic and nonmetabolic degradation in the environment. Specific compounds vary widely in their rate of degradation, and some form degradation products that may be both persistent and toxic. Most pesticides are readily degraded to nontoxic or elementary materials within a few days to a few months; these compounds may be absorbed by aquatic organisms, but the residues do not necessarily accumulate or persist for long periods. Concentrations in the organism may be higher than ambient water levels, but they rapidly decline as water concentrations are diminished. Examples of such dynamic exchange have been demonstrated with malathion (Bender 1969),[448] methoxychlor (Burdick et al. 1968),[449] and various herbicides (Mullison 1970).[478] If degradation in water is completed within sufficient time to prevent toxic or adverse physiological effects, these nonpersistent compounds do not pose a long-term hazard to aquatic life. However, degradation rates of specific pesticides are often dependent upon environmental conditions. Considerable variation in persistence may be observed in waters of different types. Gakstatter and Weiss (1965),[456] for example, have shown that wide variations in the stability of organic phosphorous insecticides in water solutions is dependent upon the pH of the water. The half-life of malathion was *reduced from about six months at pH 6 to only one to two weeks at pH 8.* Repeated applications and slow degradation rates may maintain elevated environmental concentrations, but there is no indication that these compounds can be accumulated through the food chain.

Some pesticides, primarily the organochlorine compounds, are extremely stable, degrading only slowly or forming persistent degradation products. Aquatic organisms may accumulate these compounds directly by absorption from water and by eating contaminated food organisms. In waters containing very low concentrations of pesticides, fish probably obtain the greatest amount of residue from contaminated foods; but the amount retained in the tissue appears to be a function of the pesticide concentration in the water and its rate of elimination from the organism (Hamelink et al. 1971).[458] The transfer of residues from prey to predator in the food chain ultimately results in residues in the higher trophic levels many thousand times higher than ambient water levels. Examples of trophic accumulation have been described in several locations including Clear Lake, California (Hunt and Bischoff 1960),[463] and Lake Poinsett, South Dakota (Hannon et al. 1970).[459]

Residues

Samples of wild fish have often contained pesticide residues in greater concentrations than are tolerated in any

commercially produced agricultural products. The highest concentrations are often found in the most highly prized fish. Coho salmon (*Oncorhyncus kisutch*) from Lake Michigan are not considered acceptable for sale in interstate commerce on the basis of an interim guideline for DDT and its metabolites set for fish by the U.S. Food and Drug Administration (Mount 1968).[476] Lake trout (*Salvelinus namaycush*) and some catches of chubs (*Coregonus kiyi* and *Coregonus hoyi*) and lake herring (*Coregonus artedi*) from Lake Michigan also exceed the guideline limits and are thus not considered acceptable for interstate commerce (Reinert 1970;[481] Michigan Department of Agriculture *personal communication*).[492] Pesticide residues in fish or fish products may enter the human food chain indirectly in other ways, as in fish oil and meal used in domestic animal feeds.

Fish may survive relatively high residue concentrations in their body fats, but residues concentrated in the eggs of mature fish may be lethal to the developing fry. Up to 100 per cent loss of lake trout (*Salvelinus namaycush*) fry occurred when residues of DDT–DDD in the eggs exceeded 4.75 mg/kg (Burdick et al. 1964).[460] A similar mortality was reported in coho salmon fry from Lake Michigan where eggs contained significant quantities of DDT, dieldrin, and polychlorinated biphenyls (Johnson and Pecor 1969;[468] Johnson 1968).[466] Johnson (1967)[467] reported that adult fish not harmed by low concentrations of endrin in water accumulated levels in the eggs that were lethal to the developing fry. Residues in fish may be directly harmful under stress conditions or at different temperature regimes. Brook trout (*Salvelinus fontinalis*) fed DDT at 3.0 mg/kg body weight per week for 26 weeks suffered 96.2 per cent mortality during a period of reduced feeding and declining water temperature. Mortality of untreated control fish during the same period was 1.2 per cent (Macek 1968).[473] Declining water temperature during the fall was believed to cause delayed mortality of salmon parr in streams contaminated with DDT (Elson 1967).[453]

In addition to the problem of pesticide residues in aquatic systems, other problems suggest themselves and remain to be investigated, including the potential of resistant fish species to accumulate levels hazardous to other species (Rosato and Ferguson 1968);[482] the potential for enhanced residue storage when fish are exposed to more than one compound (Mayer et al. 1970);[474] and the potential effect of metabolites not presently identified. The adverse effects of DDT on the reproductive performance of fish-eating birds has been well documented. (See the discussion of Wildlife, pp. 194–198.)

Levels of persistent pesticides in water that will not result in undesirable effects cannot be determined on the basis of present knowledge. Water concentrations below the practical limits of detection have resulted in unacceptable residues in fish for human consumption and have affected reproduction and survival of aquatic life. Criteria based upon residue concentrations in the tissues of selected species may offer some guidance. Tolerance levels for pesticides in wild fish have not been established, but action levels have been suggested by the U.S. Food and Drug Administration (Mour 1968).[476] However, acceptable concentrations of persistent pesticides that offer protection to aquatic life and human health are unknown.

It should also be recognized that residue criteria are probably unacceptable except on a total ecosystem basis. Residues in stream fish may meet some guidelines, but pesticides from that stream may eventually create excessive residues in fish in the downstream receiving basins. Until more is known of the effects of persistent pesticide residues, any accumulation must be considered undesirable.

Toxicity

Concentrations of pesticides that are lethal to aquatic life have often occurred in local areas where applications overlap streams or lakes, in streams receiving runoff from recently treated areas, and where misuse or spillage has occurred. Applications of pesticides to water to control noxious plants, fish, or insects have also killed desirable species. Fish populations, however, usually recovered within a few months to a year (Elson 1967).[453] The recovery of aquatic invertebrates in areas that have been heavily contaminated may require a longer period, with some species requiring several years to regain precontamination numbers (Cope 1961,[451] Ide 1967).[465] Undesirable species of insects may be the first to repopulate the area (Hynes 1961),[464] and some instances the species composition has been completer, changed (Hopkins et al. 1966).[462] Areas that are contaminated by pesticide application are subject to loss of fish populations and reduced food for fish growth (Schoenthal 1964,[483] Kerswill and Edwards 1967).[469] Where residues are persistent in bottom sediments for long periods, benthic organisms may be damaged even though water concentrations remain low (Wilson and Bond 1969).[488]

Pesticides are toxic to aquatic life over wide ranges. Great differences in susceptibility to different compounds exist between species and within species. For example, 96-hour LC50 values of 5 to 610,000 µg/l were reported for various fish species exposed to organophosphate pesticides (Pickering et al. 1962).[479] In addition to species' differences, the toxicity may be modified by differences in formulation, environmental conditions, animal size and age, and physiological condition. The effect of combinations of pesticides on aquatic organisms has not received sufficient attention. Macek (*unpublished data* 1971)[491] reported that combinations of various common pesticides were synergistic in their action on bluegill (*Lepomis macrochirus*) and rainbow trout (*Salmo gairdneri*), while others had additive effects. Several of the combinations that were found to be synergistic are recommended for insect pest control (Table III–16).

TABLE III-16—Acute Toxic Interaction of Pesticide Combinations to Rainbow Trout and Bluegills.

Pesticide Combination		
Compound A	Compound B	Toxic interaction
DDT	Vapona	Additive
...."	Endrin	Additive
...."	Dieldrin	Additive
...."	Azinphosmethyl	Additive
...."	Toxaphene	Additive[a]
...."	Zectran	Additive
...."	BHC	Synergistic[a]
Parathion	Copper sulfate	Synergistic
...."	Diazinon	Synergistic
...."	DDT	Additive[a]
...."	Endosulfan	Additive
...."	Methoxychlor	Synergistic[a]
Malathion	Baytex	Synergistic
...."	Copper sulfate	Antagonistic
...."	DDT	Additive
...."	EPN	Synergistic
...."	Parathion	Synergistic
...."	Perthane	Synergistic[a]
...."	Carbaryl	Synergistic[a]
...."	Toxaphene	Additive[a]
Carbaryl	Copper sulfate	Synergistic
...."	DDT	Additive
...."	Azinphosmethyl	Additive[a]
...."	Methoxychlor	Additive
...."	Parathion	Additive[a]
Methyl parathion	DDT	Additive
...."	Endosulfan	Additive[a]
...."	Carbaryl	Additive[c]
Bidrin	Sumithion	Additive

[a] This combination recommended for control of insect pests by the U.S. Department of Agriculture.
Not mention of trade names does not constitute endorsement.

Most data on pesticide effects on aquatic life are limited to a few species and concentrations that are lethal in short-term tests. The few chronic tests conducted with aquatic species indicated that toxic effects occurred at much lower concentrations. Mount and Stephan (1967)[475] found the 96-hour LC50 for fathead minnows (*Pimephales promelas*) in malathion was 9,000 $\mu g/l$, but spinal deformities in adult fish occurred during a 10-month exposure to 580 $\mu g/l$. Eaton (1970)[452] found that bluegill suffered the same crippling effects after chronic exposure to 7.4 $\mu g/l$ malathion and the 96-hour LC50 was 108 $\mu g/l$.

Where chronic toxicity data are available, they may be used to develop application factors to estimate safe levels. Mount and Stephan (1967)[475] have suggested using an application factor consisting of the laboratory-determined maximum concentration that has no effect on chronic exposure divided by the 96-hour LC50. Using this method, Eaton (1970)[452] showed that application factors for bluegill and fathead minnow exposed to malathion were similar despite a greater than 50-fold difference in species sensitivity. Application factors derived for one compound may be appropriate for closely related compounds that have a similar mode of action, but additional research is necessary to verify this concept. In the absence of chronic toxicity

data, the application factors for many compounds must be arbitrary values set with the intention of providing some margin of safety for sensitive species, prolonged exposure, and potential effects of interaction with other compounds.

Basis for Criteria

The reported acute toxicity values and subacute effects of pesticides for aquatic life are listed in Appendix II-D. The acute toxicity values multiplied by the appropriate application factor provided the recommended criteria. The 96-hour LC50 should be multiplied by an application factor of 0.01 in most cases. The value derived from multiplying the 96-hour LC50 by a factor of 0.01 can be used as the 24-hour average concentration.

Recommended concentrations of pesticides may be below those presently detectable without additional extraction and concentration techniques. However, concentrations below those detectable by routine techniques are known to cause detrimental effects to aquatic organisms and to man. Therefore, recommendations are based on bioassay procedures and the use of an appropriate application factor.

The recommendations are based upon the most sensitive species. Permissible concentrations in water have been suggested only where several animal species have been tested. Where toxicity data are not available, acute toxicity bioassays should be conducted with locally important sensitive aquatic species, and safe levels should be estimated by using an application factor of 0.01.

Some organochlorine pesticides (i.e., DDT including DDD and DDE, aldrin, dieldrin, endrin, chlordane, heptachlor, toxaphene, lindane, endosulfan, and benzene hexachloride) are considered especially hazardous because of their persistence and accumulation in aquatic organisms. These compounds, including some of their metabolites, are directly toxic to various aquatic species at concentrations of less than one $\mu g/l$. Their accumulation in aquatic systems presents a hazard, both real and potential, to animals in the higher trophic levels, including man (Pimentel 1971,[480] Mrak 1969,[477] Kraybill 1969,[470] Gillett 1969).[457] Present knowledge is not yet sufficient to predict or estimate safe concentrations of these compounds in aquatic systems. However, residue concentrations in aquatic organisms provide a measure of environmental contamination. Therefore, specific maximum tissue concentrations have been recommended as a guideline for water quality control.

Recommendations

Organochlorine Insecticides The recommendations for selected organochlorine insecticides are based upon levels in water and residue concentrations in whole fish on a wet weight basis. Aquatic life should be protected where the maximum con-

centration of the organochlorine pesticide in the water does not exceed the values listed in Table III–17.

For the protection of predators, the following values are suggested for residues in whole fish (wet weight): DDT (including DDD and DDE)—1.0 mg/kg; aldrin, dieldrin, endrin, heptachlor (including heptachlor epoxide), chlordane, lindane, benzene hexachloride, toxaphene, and endosulfan—0.1 mg/kg, either singly or in combination. For further discussion, see the section on Wildlife (p. 197).

If fish and wildlife are to be protected, and where residues exceed the recommended concentrations, pesticide use should be restricted until the recommended concentrations are reached (except where a substitute pesticide will not protect human health).

Other pesticides The recommended maximum concentrations of pesticides in freshwater are listed in Table III–18 except that where pesticides are applied to water to kill undesirable aquatic life, the values will be higher. In the latter instances, care should be taken to avoid indiscriminate use and to insure that application of the pesticide follows the prescribed methods.

OTHER TOXICANTS

Ammonia

Ammonia is discharged from a wide variety of industrial processes and cleaning operations that use ammonia or ammonia salts. Ammonia also results from the decomposition of organic matter.

Ammonia gas is soluble in water in the form of ammonium hydroxide to the extent of 100,000 mg/1 at 20 C. Ammonium hydroxide dissociates readily into ammonium

TABLE III–17—Recommended Maximum Concentrations of Organochlorine Pesticides in Whole (Unfiltered) Water, Sampled at Any Time and Any Place.[a]

Organochlorine pesticides	Recommended maximum concentration (μg/l)
Aldrin	0.01
DDT	0.002
TDE	0.006
Dieldrin	0.005
Chlordane	0.04
Endosulfan	0.003
Endrin	0.002
Heptachlor	0.01
Lindane	0.02
Methoxychlor	0.005
Toxaphene	0.01

[a] Concentrations were determined by multiplying the acute toxicity values for the more sensitive species (Appendix II-D) by an application factor of 0.01 except where an experimentally derived application factor is indicated.

TABLE III–18—Recommended Maximum Concentrations of Other Pesticides in Whole (Unfiltered) Water, Sampled at Any Time and Any Place.[a]

Organophosphate insecticides	Recommended maximum concentration (μg/l)
Abate	(b)
Azinphosmethyl	0.001
Azinphosethyl	(b)
Carbophenothion	(b)
Chlorothion	(b)
Ciodrin	0.1
Coumaphos	0.001
Demeton	(b)
Diazinon	0.009
Dichlorvos	0.001
Dioxathion	0.09
Disulfoton	0.05
Dursban	0.001
Ethion	0.02
EPN	0.06
Fenthion	0.006
Malathion	0.008
Methyl Parathion	(b)
Mevinphos	0.002
Naled	0.004
Oxydemeton methyl	0.4
Parathion	0.0004
Phorate	(b)
Phosphamidon	0.03
Ronnel	(b)
TEPP	0.4
Trichlorophon	0.002

Carbamate insecticides	Recommended maximum concentrations (μg/l)
Aminocarb	(b)
Bayer	(b)
Baygon	(b)
Carbaryl	0.02
Zectran	0.1

Herbicides, fungicides and defoliants	Recommended maximum concentrations (μg/l)
Acrolein	(b)
Aminotriazole	300.0
Balan	(b)
Bensulide	(b)
Choroxuron	(b)
CIPC	(b)
Dacthal	(b)
Dalapon	110.0
DEF	(b)
Dexon	(b)
Dicamba	200
Dichlobenil	37.0
Dichlone	0.2
Diquat	0.5
Diuron	1.6
Difolitan	(b)
Dinitrobutyl phenol	(b)
Diphenamid	(b)
2,4-D (PGBE)	(b)
2,4-D (BEE)	4.0
2,4-D (IOE)	(b)
2,4-D (Diethylamine salts)	(b)
Endothal (Disodium salt)	(b)
Endothal (Dipotassium salt)	(b)
Eptam	(b)
Fenac (Sodium salt)	45.0
Hyamine-1622	(b)
Hyamine-2389	(b)
Hydrothal-47	(b)
Hydrothal-191	(b)
Hydrothal plus	(b)
IPC	(b)
MCPA	(b)
Molinate	(b)
Monuron	(b)
Paraquat	(b)

TABLE III-18—Continued

Herbicides, fungicide and defoliants	Recommended maximum concentration (µ/l)
abulate	(b)
aloram	(b)
roanii	(b)
ilvex (BEE)	2.5
ilvex (PGBE)	2.0
ilvex (IOE)	(b)
ilvex (Potassium salt)	(b)
imazine	10.0
rifluaralin	(b)
ernolate	(b)

Botanicals	Recommended maximum concentrations (µg/l)
llethrin	0.002
yrethrum	0.01
lotanone	10.0

[a] Concentrations were determined by multiplying the acute toxicity values for the more sensitive species (Appendix II-D) by an application factor of 0.01 except where an experimentally derived application factor is indicated.
[b] Insufficient data to determine safe concentrations.

TABLE III-19—Sublethal and Acutely Toxic Concentrations of Un-Ionized Ammonia for Various Fish Species[a]

Species	Acute mortality LC50 (mg/l)	No sublethal effect (mg/l)	Author
Stickleback	1.8-2.1		Hazel et al. (1971)[500]
Striped bass (Marone saxatalis)	1.9-2.8		"
Rainbow trout	0.39	0.046	Lloyd and Orr (1969)[503]
Perch (Perca)	0.29		Ball (1967)[493]
Roach (Hesperoleucus)	0.35		"
Rudd (Scardinius)	0.36		"
Bream (Lepomis)	0.41		"
Rainbow trout	0.41		"
Rainbow trout	0.42-0.89		Lloyd and Herbert (1960)[504]
Atlantic salmon (Salmo salar)	0.38		Herbert and Shurben (1965)[501]
Rainbow trout	0.88		"
Trout		<0.27	Reichenbach-Klinke (1967)[506]
Chinook salmon (Oncorhynchus tshawytscha)		<0.006	Burrows (1964)[495]

[a] To insure a high level of protection, the mean of the 96-hour LC50's was used as a base, and an application factor of 0.05 applied to arrive at an acceptable level for most species in fresh water. Two apparently resistant species were omitted because they were far out of line with the others. After application of the factor, the resultant level is approximately half that projected from the data of Lloyd and Orr (1969).[503]

and hydroxyl ions as follows:

$$NH_3 + H_2O \rightarrow HN_4^+ + OH^-$$
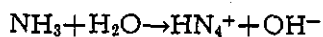
The equilibrium of the reaction is dependent upon pH, and within the pH range of most natural waters ammonium ions predominate (Figure III-10). Since the toxic component of ammonia solutions is the un-ionized ammonia, toxicity of ammonia solutions increases with increased pH (1   1937,[497] Wuhrmann et al. 1947,[508] Wuhrmann and Woker 1948,[509] Downing and Merkens 1955[496]).

Wuhrmann (1952),[507] Downing and Merkens (1955),[496] and Merkens and Downing (1957)[505] found that a decrease in dissolved oxygen concentration increased the toxicity of un-ionized ammonia to several species of freshwater fishes. Lloyd (1961)[502] showed that the increase in toxicity of un-ionized ammonia to rainbow trout (*Salmo gairdneri*) with decreased oxygen was considerably more severe than for zinc, copper, lead, or phenol.

Much of the data on ammonia toxicity is not useable, because reporting of chemical conditions or experimental control was unsatisfactory. Ellis (1937)[497] reported that total ammonia nitrogen concentrations of 2.5 mg/l in the pH range of 7.4 to 8.5 were harmful to several fish species, but concentrations of 1.5 mg/l were not. Most streams without a source of pollution contained considerably less than 1 mg/l total ammonia. The sublethal and acutely toxic concentrations of un-ionized ammonia for various fish species are given in Table III-19.

Brockway (1950)[494] found impairment of oxygen-carrying capacity of the blood of trout at a total ammonia nitrogen concentration of 0.3 mg/l. Fromm (1970)[499] found that at total ammonia nitrogen concentrations of 5 mg/l, ammonia excretion by rainbow trout (*Salmo gairdneri*) was inhibited; ε   ıg/l the trout became hyperexcitable; and at 8 mg/l (approximately 1 mg/l un-ionized ammonia) 50 per cent

were dead in 24 hours (Fromm 1970).[499] Goldfish (*Carassius auratus*) were more tolerant; at 40 mg/l of total ammonia nitrogen, 10 per cent were dead in 24 hours.

Burrows (1964)[495] found progressive gill hyperplasia in fingerling chinook salmon (*Oncorhynchus tshawytscha*) during a six-week exposure to the lowest concentration applied, 0.006 mg/l un-ionized ammonia. Reichenbach-Klinke (1967)[506] also noted gill hyperplasia, as well as pathology of the liver and blood, of various species at un-ionized ammonia concentrations of 0.27 mg/l. Exposure of carp (*Cyprinus carpio*) to sublethal un-ionized ammonia concentrations in the range of 0.11 to 0.34 mg/l resulted in extensive necrotic changes and tissue disintegration in various organs (Flis 1968).[498]

Lloyd and Orr (1969)[503] found that volume of urine production increased with exposure to increasing ammonia concentrations, but that an ammonia concentration of 12 per cent of the lethal threshold concentration resulted in no increased production of urine. This concentration of un-ionized ammonia was 0.046 mg/l for the rainbow trout used in the experiments.

Recommendation·

Once a 96-hour LC50 has been determined using the receiving water in question and the most sensitive important species in the locality as the test organism, a concentration of un-ionized ammonia (NH₃) safe to aquatic life in that water can be estimated by multiplying the 96-hr LC50 by an application factor of 0.05; but no concentration greater than 0.02 mg/l is recommended at any time or place.
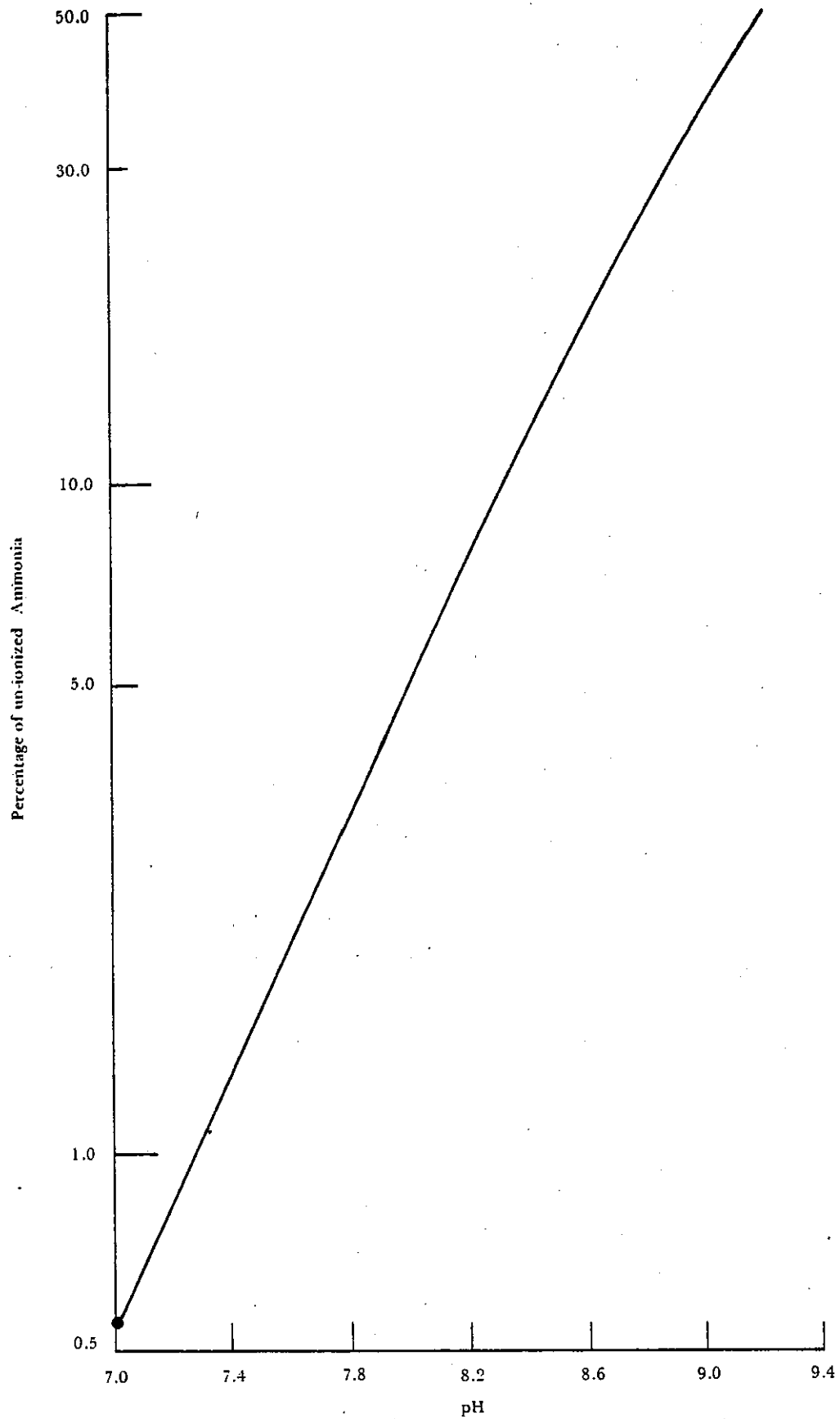
FIGURE III-10—Percentage of Un-ionized Ammonia in Ammonium Hydroxide Solutions at 20 C and Various Levels of pH

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Chlorine

 'rine and chloramines are widely used in treatment of
ro. .e water supplies and sewage-treatment-plant effluents,
and in power plants, textile and paper mills, and certain
other industries. Field tests conducted on caged fish in
streams below a sewage outfall where chlorinated and non-
chlorinated effluents were discharged showed that toxic
conditions occurred for rainbow trout *(Salmo gairdneri)* 0.8
miles below the plant discharge point when chlorinated
effluents were discharged (Basch et al. 1971).[511] It has also
been shown that total numbers of fish and numbers of
species were drastically reduced below industrial plants
discharging chlorinated sewage effluents (Tsai 1968,[517]
1970).[518]

The toxicity to aquatic life of chlorine in water will
depend upon the concentration of residual chlorine re-
maining and the relative amounts of free chlorine and chlor-
amines. Since addition of chlorine or hypochlorites to water
containing nitrogenous materials rapidly forms chloramines,
problems of toxicity in most receiving waters are related to
chloramine concentrations. Merkens (1958)[515] stated that
toxicities of free chlorine and chloramines were best esti-
mated from total chlorine residuals. In monitoring pro-
grams, evaluation of chlorine content of water is usually
stated in terms of total chlorine residuals. Because the
chlorine concentrations of concern are below the level of
de   ion by the orthotolidine method, a more sensitive
a   .cal technique is recommended.

The literature summarized by McKee and Wolf (1963)[514]
showed a wide range of acute chlorine toxicity to various
aquatic organisms, but the conditions of the tests varied so
widely that estimation of generally applicable acute or
safe levels cannot be derived from the combined data. It
has also been demonstrated that small amounts of chlorine
can greatly increase the toxicity of various industrial
effluents.

Merkens (1958)[515] found that at pH 7.0, 0.008 mg/l
residual chlorine killed half the test fish in seven days. The
test results were obtained using the amperometric titration
and the diethyl-*p*-phenylene diamine methods of chlorine
analysis. Zillich (1972),[519] working with chlorinated sewage
effluent, determined that threshold toxicity for fathead
minnows *(Pimephales promelas)* was 0.04–0.05 mg/l residual
chlorine. In two series of 96-hour LC50 tests an average of
0.05–0.19 mg/l residual chlorine was noted. Basch et al.
(1971)[511] found 96-hour LC50 for rainbow trout *(Salmo
gairdneri)* to be 0.23 mg/l. Arthur and Eaton (1971),[510]
working with fathead minnows and *Gammarus pseudolimnaeus*,
found that the 96-hour LC50 total residual chlorine
(as chloramine) for *Gammarus* was 0.22 mg/l, and that
all minnows were dead after 72 hours at 0.15 mg/l.
After seven days exposure to 0.09 mg/l, the first fish died.
T   C50 for minnows was therefore between these levels.
In chronic tests extending for 15 weeks, survival of *Gammarus*

was reduced at 0.04 mg/l, and reproduction was reduced at
0.0034 mg/l. Growth and survival of fathead minnows after
21 weeks was not affected by continuous exposure to 0.043
mg/l total chloramines, but fecundity of females was re-
duced. The highest level showing no significant effect was
0.016 mg/l. Merkens (1958)[515] postulated by extrapolation
that a concentration of 0.004 mg/l residual chlorine would
permit one half the test fish to survive one year. Sprague
and Drury (1969)[516] have shown an avoidance response of
rainbow trout to free chlorine at 0.001 mg/l.

Aquatic organisms will tolerate longer short-term ex-
posures to much higher levels of chlorine than the concen-
trations which have adverse chronic effects. Brungs (1972)[512]
in a review has noted that 1-hour LC50's of fish vary from
0.74 to 0.88 mg/l, and that longer short-term exposures
have LC50's lower but still substantially higher than ac-
ceptable for long-term exposure. Available information,
however, does not show what effect repeated exposure to
these, or lower levels, will have on aquatic life.

Because *Gammarus*, an essential food for fish, is affected
at 0.0034 mg/l, and a safe level is judged to be one that
will not permit adverse effect on any element of the biota,
the following recommendation has been made.

Recommendation

**Aquatic life should be protected where the con-
centration of residual chlorine in the receiving
system does not exceed 0.003 mg/l at any time or
place. Aquatic organisms will tolerate short-term
exposure to high levels of chlorine. Until more is
known about the short-term effects, it is recom-
mended that total residual chlorine should not
exceed 0.05 mg/l for a period up to 30-minutes in
any 24-hour period.**

Cyanides

The cyanide radical is a constituent of many compounds
or complex ions that may be present in industrial wastes.
Cyanide-bearing wastes may derive from gas works, coke
ovens, scrubbing of gases in steel plants, metal plating
operations, and chemical industries. The toxicity of cyanides
varies widely with pH, temperature, and dissolved oxygen
concentration. The pH is especially important, since the
toxicity of some cyanide complexes changes manyfold over
the range commonly found in receiving waters.

"Free cyanide" (CN^- ion and HCN) occurs mostly as
molecular hydrogen cyanide, the more toxic form, at pH lev-
els of natural waters as well as in unusually acid waters. Fifty
per cent ionization of the acid occurs at pH near 9.3. Free
cyanide concentrations from 0.05 to 0.01 mg/l as CN have
proved fatal to many sensitive fishes (Jones 1964),[527] and
levels much above 0.2 mg/l are rapidly fatal for most
species of fish. A level as low as 0.01 mg/l is known to have
a pronounced, rapid, and lasting effect on the swimming
ability of salmonid fishes.

The work of Doudoroff et al. (1966)[524] has demonstrated that the effective toxicant to fish in nearly all solutions of complex metallocyanides tested was molecular HCN, the complex ions being relatively harmless. The total cyanide content of such solutions is not a reliable index of their toxicity. The HCN derives from dissociation of the complex ions, which can be greatly influenced by pH changes. Doudoroff (1956)[523] demonstrated a more than thousand-fold increase of the toxicity of the nickelocyanide complex associated with a decrease of pH from 8.0 to 6.5. A change in pH from 7.8 to 7.5 increased the toxicity more than tenfold.

Burdick and Lipschuetz (1948)[521] have shown that solutions containing the ferro and ferricyanide complexes become highly toxic to fish through photodecomposition upon exposure to sunlight. Numerous investigations have shown that toxicity of free cyanide increased at reduced oxygen concentrations (Downing 1954,[525] Wuhrmann and Woker 1955,[528] Burdick et al. 1958,[520] Cairns and Scheier 1963).[522] The toxic action is known to be accelerated markedly by increased temperature (Wuhrmann and Woker 1955,[528] Cairns and Scheier 1963),[522] but the influence of temperature during long exposure has not been demonstrated. The toxicity of the nitriles (organic cyanides) to fish varied greatly. Henderson et al. (1960)[526] found marked cumulative toxicity of acrylonitrile. Lactonitrile decomposed rapidly in water yielding free cyanide, and its high toxicity evidently was due to the HCN formed.

The toxicity of cyanide to diatoms varied little with change of temperature and was a little greater in soft water than in hard water (Patrick *unpublished data* 1971).[529] For *Nitzchia linearis*, concentrations found to cause a 50 per cent reduction in growth of the population in soft water (44 mg/l Ca-Mg as $CaCO_3$) were 0.92 mg/l (CN) at 72 F, 0.30 mg/l at 82 F, and 0.28 mg/l at 86 F. For *Navicula seminulum var. Hustedtil*, the concentrations reducing growth of the population by 50 per cent in hard water (170 mg/l Ca-Mg as $CaCO_3$) were found to be 0.36 mg/l at 72 F, 0.49 mg/l at 82 F, and 0.42 mg/l at 86 F. Cyanide appeared to be more toxic to animals than to algae.

Recommended maximum concentrations of cyanide-bearing wastes of unknown composition and properties should be determined by static and flow-through bioassays. The bioassays should be performed with dissolved oxygen, temperature, and pH held at the local water quality conditions under which cyanides are most toxic. Because the partial dissociation of some complex metallocyanide ions may be slow, static bioassays may reveal much greater toxicity than that demonstrable by the flow-through methods. On the other hand, standing test solutions of simple and some complex cyanides exposed to the atmosphere gradually lose their toxicity, because the volatile HCN escapes.

Chemical determination of the concentration of undissociated, molecular HCN alone may be the best way to evaluate the danger of free cyanide to fish in waters receiving cyanide bearing wastes. Such tests may reveal the occurrence of harmful concentrations of HCN not predictable through bioassay of the wastes. Because an acceptable concentration of HCN or fraction of a LC50 of cyanic and cyanide-bearing effluents has not yet been positively determined, a conservative estimate must be made; and because levels as low as 0.01 mg/l have proved harmful under some conditions, a factor of 0.05 should be applied to LC50 levels.

Recommendation

Once a 96-hour LC50 has been determined using the receiving water in question and the most sensitive important species in the locality as the test organism, a concentration of free cyanide (CN⁻) safe to aquatic life in that water can be estimated by multiplying the 96-hour LC50 by an application factor of 0.05; but no concentration greater than 0.005 mg/l is recommended at any time or place.

Detergents

Detergents are a common component of sewage and industrial effluents derived in largest amounts from household cleaning agents. In 1965 a shift from tetrapropylene-derived alkylbenzene sulfonates (ABS) to the more biodegradable linear alkylate sulfonates (LAS) was made by the detergent industry. In current detergent formulas, LAS is the primary toxic active compound, two to four times more toxic than ABS (Pickering 1966).[534] However, toxicity of LAS appears along with the methylene blue active substance (MBAS) response upon biodegradation (Swisher 1967).[537] Retrieval of MBAS data from the National Surveillance Stations throughout the U.S. from 1966 to the present showed that the mean of 3,608 samples was less than 0.1 mg/l. There has been a downward trend in MBAS concentrations. Only four stations reported mean concentrations greater than 0.2 mg/l.

The MBAS determination has been the routine analytical method for measurement of surfactant concentrations. Positive errors are more common than negative ones in the determination of anionic surfactants in water (Standard Methods 1971).[536] An infrared determination or a carbon absorption cleanup procedure is recommended when high MBAS concentrations are found.

Marchetti (1965)[533] critically reviewed the effects of detergents on aquatic life. Most available information on LAS toxicity relates to fish. Short term studies by a number of investigators have shown that lethal concentrations to selected fish species vary from 0.2 to 10.0 mg/l (Hokanson and Smith 1971).[532] Bardach et al. (1965)[531] reported that 10 mg/l is lethal to bullheads (*Ictalurus* sp.), and that 0.5 mg/l eroded 50 per cent of their taste buds within 24 days. Thatcher and Santner (1966)[538] found 96-hour LC50 values from 3.3 to 6.4 mg/l for five species of fish.

Pickering and Thatcher (1970)[535] found in their stud

chronic toxicity that a concentration of 0.63 mg/l had no measurable effect on the life cycle of the fathead minnow (*F ales promelas*), while a concentration of 1.2 mg/l was le   to the newly hatched fry. A safe level should be between 14 and 28 per cent of the 96-hour LC50. Hokanson and Smith (1971)[532] reported that a concentration of 1 mg/l was an approximate safe concentration for bluegills in Mississippi River water of good quality. Arthur (1970)[530] found that the no-effect level of LAS on *Gammarus pseudo-limnaeus* was 0.2 to 0.4 mg/l. This investigator also subjected opculate and pulmonate snails to 60-week exposures of LAS and showed the toxicity levels to be 0.4 to 1.0 mg/l and greater than 4.4 mg/l, respectively.

Detergent Builders

Phosphates have been included in household detergents to increase their effectiveness, although this use has been seriously questioned recently. Nitrilotriacetate (NTA) and other builders have been tried, but most are either less effective or have been barred for reasons of potential health hazard. Available builders do not have serious direct effects on fish or aquatic organisms at concentrations likely to be encountered in receiving waters. In view of the uncertain legal status of present commercial detergents and the extensive search for adequate substitutes now in progress, recommendations for builders are not practical at this time. However, it can be stated that a satisfactory builder should be ologically degradable and nontoxic to aquatic or   sms and humans, and that it should not cause aesthetic problems in the receiving water.

Recommendation

Once a 96-hour LC50 has been determined using the receiving water in question and the most sensitive important species in the locality as the test organism, a concentration of LAS safe to aquatic life in that water can be estimated by multiplying the 96-hour LC50 by an application factor of 0.05; but no concentration greater than 0.2 mg/l is recommended at any time or place.

Phenolics

Phenols and phenolic wastes are derived from petroleum, coke, and chemical industries; wood distillation; and domestic and animal wastes. Many phenolic compounds are more toxic than pure phenol: their toxicity varies with the combinations and general nature of total wastes. Acute toxicity of pure phenol varies between 0.079 mg/l in 30 minutes to minnows, and 56.0 mg/l in 96 hours to mosquito fish (*Gambusia affinis*). Mitrovic et al. (1968)[541] found a 48-hour LC50 of 7.5 mg/l to trout; they noted that exposure to 6 5 mg/l caused damage to epithelial cells in 2 hours, a   tensive damage to reproductive systems in 7 days. Ellis (1937)[539] reported 1.0 mg/l safe to trout; and 0.10

mg/l was found nonlethal to bluegill (*Lepomis macrochirus*) in 48 hours (Turnbull et al. 1954).[542] These studies illustrated the wide range of phenol toxicity. There is not yet adequate documentation about chronic effects and toxicity of mixed wastes on which to base recommendations of safe levels for fish.

Phenolics affect the taste of fish at levels that do not appear to affect fish physiology adversely. Mixed wastes often have more objectionable effects than pure materials. For example, 2,4-dicholorphenol affects taste at 0.001 to 0.005 mg/l; *p*-chlorophenol at 0.01 to 0.06 mg/l; and 2-methyl, 6-chlorophenol at 0.003 mg/l. (See the discussion of Tainting Substances, p. 147.) Pure phenol did not affect taste until levels of 1 to 10 mg/l were reached (Fetterolf 1964).[540] The taste of fish in most polluted situations is adversely affected by phenolics before acute toxic effects are observed.

Recommendations

In view of the wide range of concentrations of phenolics which produce toxic effects in fish and the generally lower levels which taint fish flesh, it is recommended that taste and odor criteria be used to determine suitability of waste receiving waters to support usable fish populations. Where problems of fish kills occur or fish are subjected to occasional short-term exposure to phenolic compounds, a 96-hour LC50 should be determined using the receiving water in question and the most sensitive important fish in the locality as the test animal. Concentrations of phenolic compounds safe to fish in that water can then be estimated by multiplying the 96-hour LC50 by an application factor of 0.05; but no concentration greater than 0.1 mg/l is recommended at any time or place. Tests of other species will be necessary to protect other trophic levels.

Sulfides

Sulfides are constituents of many industrial wastes, such as those from tanneries, paper mills, chemical plants, and gas works. Hydrogen sulfide may be generated by the anaerobic decomposition of sewage and other organic matter in the water, and in sludge beds. Natural production of H_2S may also result from deposits of organic material.

When soluble sulfides are added to water, they react with hydrogen ions to form HS^- or H_2S, the proportion of each depending on the pH values. The toxicity of sulfides derives primarily from H_2S rather than the sulfide ion. The rapid combination of H_2S with other materials, including oxygen, has frequently caused investigators to overlook the importance of H_2S as it affects aquatic life, especially when it originates from sludge beds. Because water samples usually are not taken at the mud/water interface, the importance of H_2S in this habitat for fish eggs, fish fry, and
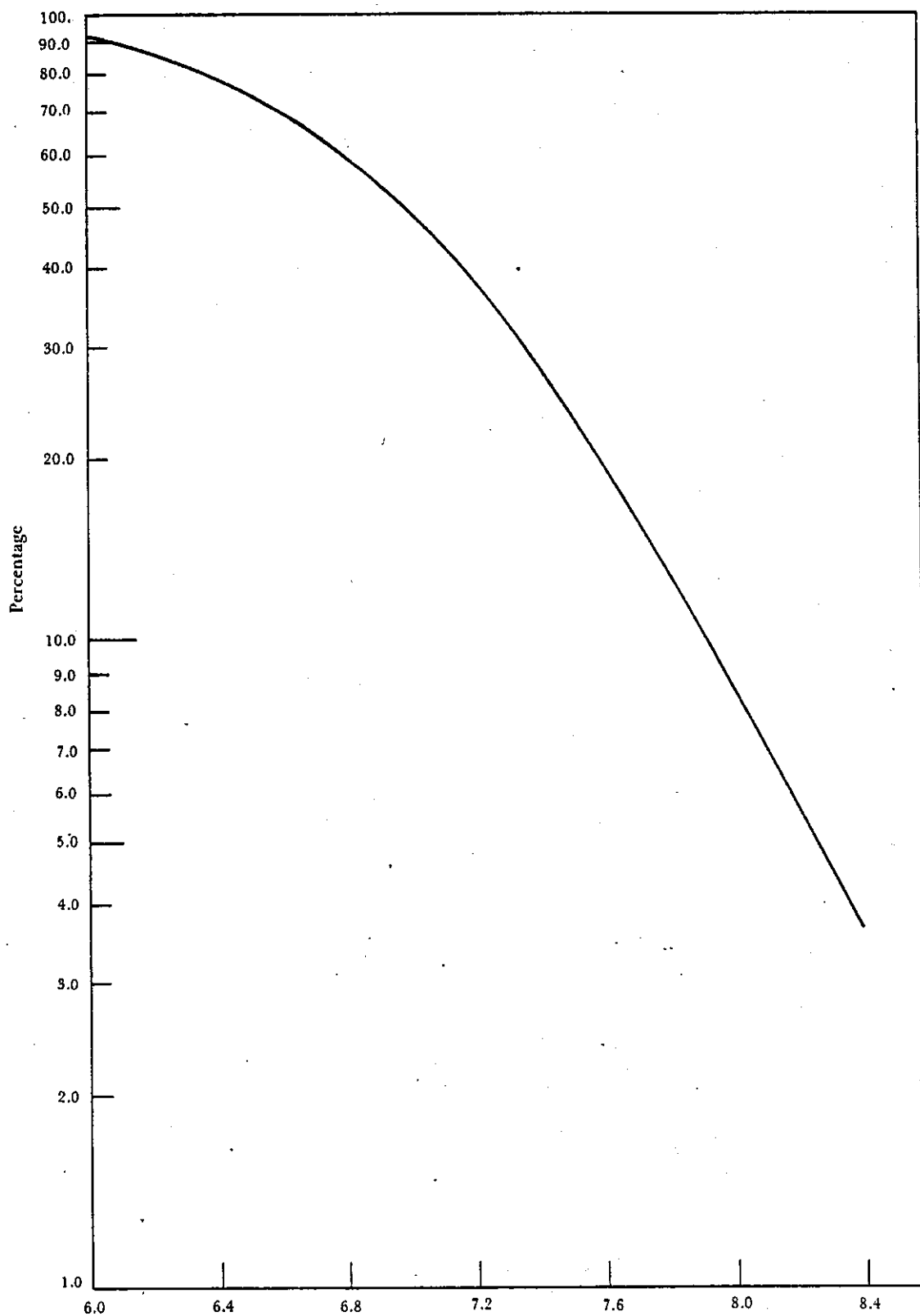
FIGURE III-11—Percentage of Hydrogen Sulfide in the Form of Undissociated H₂S at Various pH Levels (Temperatu 20 C; ionic strength μ = 0.01)

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sh food organisms is often overlooked (Colby and Smith 967).[545]

Γ ᷦogen sulfide is a poisonous gas, soluble in water to heᷦ .nt of about 4,000 mg/l at 20 C and one atmosphere ᷦ pressure (Figure III–11). Upon solution, it dissociates ᷦcording to the reaction $H_2S \rightarrow HS^- + H^+$ and $HS^- \rightarrow -- + H^+$. At pH 9, about 99 per cent of the sulfide is in 1e form of HS^-; at pH 7 it is about equally divided between 1S$^-$ and H_2S; and at pH 5 about 99 per cent is present s H_2S.

Consequently, the toxicity of sulfides increases at lower H because a greater proportion is in the form of undissociated H_2S. Only at pH 10 and above is the sulfide ion resent in appreciable amounts. In polluted situations, ᷦhere the pH may be neutral or below 7.0, or where oxygen ᷦvels are low but not lethal, problems arising from sulfides r from hydrogen sulfide generated in sludge deposits will e increased.

Much available data on the toxicity of hydrogen sulfide ᷦ fish and aquatic life have been based on extremely short xposure periods and have failed to give adequate information on water quality, oxygen, and pH. Consequently, arly data have suggested that concentrations between 0.3 nd 4.0 mg/l permit fish to survive (Schaut 1939,[546] ᷦanHorn 1958,[550] Bonn and Follis 1967,[544] Theede et al. 969).[549] Recent data both in field situations and under ᷦntrolled laboratory conditions demonstrated hydrogen ᷦlfiᷦᷦ toxicity at lower concentrations. Colby and Smith ᷦᷦ ᷦ found that concentrations as high as 0.7 mg/l ᷦre tound within 20 mm of the bottom on sludge beds, nd that levels of 0.1 to 0.02 mg/l were common within the rst 20 mm of water above this layer. Walleye (*Stizostedion ᷦitreum v.*) eggs held in trays in this zone did not hatch. ᷦdelman and Smith (1970)[543] reported that hatching of ᷦorthern pike (*Esox lucius*) eggs was substantially reduced t 0.025 mg/l of H_2S, and at 0.047 mg/l mortality was lmost complete. Northern pike fry had 96-hour LC50 alues that varied from 0.017 to 0.032 mg/l at normal xygen levels (6.0 mg/l). The highest concentration of ᷦvdrogen sulfide at which no short-term effects on eggs or ᷦy were observed was 0.814 mg/l. Smith and Oseid (*in ress* 1971),[548] working on eggs, fry, and juveniles of walleyes nd white suckers (*Catostomus commersonni*), and Smith 1971),[547] working on walleyes and fathead minnows *Pimephales promelas*), found that safe levels varied from 0029 to 0.012 mg/l with eggs being the least sensitive and

TABLE III–20—96-Hour LC50 and Safe Levels Based on No Adverse Effect on Critical Life History Stages

Species		96-Hr. LC (mg/l)	Safe levels[a] (mg/l)
Northern Pike	eggs	0.037	0.014
	fry	0.026	0.004
Walleye	eggs	0.071	0.012
	fry	0.007	0.007
	juvenile	0.017	0.0037
White Sucker	eggs		0.015
	fry	0.0018	0.002
	juvenile	0.0185	0.002
Fathead minnows	juvenile	0.032 (at 20 C)	0.003
	adult	0.032	0.003
Bluegill	juvenile	0.032	0.002
	adult	0.032	0.002
Gammarus pseudolimnaeus		0.042 (10-day)	0.0033
Hexagenia limbata		0.350	

[a] Safe levels are construed to mean no demonstrable deleterious effect on survival or growth after long-term chronic exposure.

juveniles being the most sensitive in short-term tests (Table III–20). In 96-hour bioassays fathead minnows and goldfish (*Carassius auratus*) varied greatly in tolerance to hydrogen sulfide with changes in temperature. They were more tolerant at low temperatures (6 to 10 C).

On the basis of chronic tests evaluating growth and survival, the safe level for bluegill (*Lepomis macrochirus*) juveniles and adults was 0.002 mg/l. White sucker eggs all hatched at 0.015 mg/l, but juveniles showed a negligible growth reduction at 0.002 mg/l. Safe levels for fathead minnows were between 0.002 and 0.003 mg/l. Studies on various arthropods (*Gammarus pseudolimnaeus* and *Hexagenia limbata*), useful as fish food, indicated that safe levels were between 0.002 and 0.003 mg/l (Smith 1971).[547] Some species typical of normally stressed habitats were much more resistant (*Asellus* sp.).

Recommendation

On the basis of available data, a level of undissociated hydrogen sulfide assumed to be safe for all aquatic organisms including fish is 0.002 mg/l. At a pH of 6.0 and a temperature of 13.0 C, approximately 99 per cent of the total sulfide is present as undissociated hydrogen sulfide. Therefore, to protect aquatic organisms within the acceptable limits of pH and temperature, it is recommended that the concentration of total sulfides not exceed 0.002 mg/l at any time or place.

WILDLIFE

In this report, wildlife is defined as all species of vertebrates other than fish and man. To assure the short-term and long-term survival of wildlife, the water of the aquatic ecosystem must be of the quality and quantity to furnish the necessary life support throughout the life-cycle of the species involved. In addition to the quantity, the quality of food substances produced by the aquatic environment must be adequate to support the long-term survival of the wildlife species.

Many species of wildlife require the existence of specific, complex, and relatively undisturbed ecosystems for their continued existence. Aquatic ecosystems, such as bogs, muskegs, seepages, swamps, and marshes, can exhibit marked fragility under the influence of changing water levels, various pollutants, fire, or human activity. Changes in the abundance of animal populations living in such aquatic communities can result in reactions and altered abundance of plant life, which in turn will have repercussions of other species of animal life. In general, these transitional ecosystems between land and water are characterized by very high productivity and importance for wildlife, and they should thus be maintained in that state to the greatest possible extent.

In many instances, criteria to protect fish and invertebrates or to provide water suitable for consumption by man or domestic animals will also provide the minimal requisites for some species of wildlife. This would be true for species that use water only for direct consumption or that feed on aquatic organisms to only a minor extent. For many species of wildlife, however, the setting of water quality criteria is complicated by their ecological position at the apex of complex food webs, and also by the extreme mobility of some wildlife, especially birds.

Those substances which are concentrated via food chains, such as many chlorinated hydrocarbons, present special problems for those species that occupy the apex of long food chains. In those instances, environmental levels which are safe for fish, do not necessarily convey safety to predators or even to scavengers that consume fish.

PROTECTION OF FOOD AND SHELTER FOR WILDLIFE

A number of factors can be identified that can affect specific components of the ecosystem and cause reduced food and shelter for wildlife. These factors also affect fish and other aquatic life and therefore are discussed in greater detail in appropriate related subtopics.

pH

In bioassays with aquatic plants, Sincock (1968)[593] found that when the pH of the water in test vessels dropped to 4.5, reedhead-grass (*Potamogeton perfoliatus*), a valuable waterfowl food plant, died within a few days. Similarly, in F Bay, Virginia, between August and November, 1963, ⌐ ⌐ aquatic plant production declined from 164 to 13 pounds per acre. This atypical decline was immediately preceded by a decline in pH to 6.5 compared to previous midsummer readings of 7.7 to 9.2. (U.S. Bureau of Sport Fisheries and Wildlife).[601]

Recommendation

Aquatic plants of greatest value as food for waterfowl thrive best in waters with a summer pH range of 7.0 to 9.2.

ALKALINITY

Generally, waters with reasonably high bicarbonate alkalinity are more productive of valuable waterfowl food plants than are waters with low bicarbonate alkalinity. Few waters with less than 25 mg/l bicarbonate alkalinity can be classed among the better waterfowl habitats. Many waterfowl habitats productive of valuable foods, such as sago pondweed (*Potamogeton pectinatus*), widgeongrass (*Rappia maritima* and *R. occidentalis*), banana waterlily (*Castalia flava*), wild celery, (*Vallisneria americana*), and others have a bicarbonate alkalinity range of 35 to 200 mg/l.

Definitive submerged aquatic plant communities de⌐ in waters with different concentrations of bicarb⌐

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alkalinity. It is logical to assume that excessive and prolonged fluctuation in alkalinity would not be conducive to the ation of any one plant community type. Sufficient experimental evidence is not available to define the effects of various degrees and rates of change in alkalinity on aquatic plant communities. Fluctuations of 50 mg/1 probably would contribute to unstable plant communities. Fluctuations of this magnitude may be due to canals connecting watersheds, diversion of irrigation water, or flood diversion canals (Federal Water Pollution Control Administration 1968, hereafter referred to as FWPCA 1968).[562]

Recommendation

Waterfowl habitats should have a bicarbonate alkalinity between 30 and 130 mg/1 to be productive. Fluctuations should be less than 50 mg/1 from natural conditions.

SALINITY

Salinity can also affect plant communities. All saline water communities, from slightly brackish to marine, produce valuable waterfowl foods, and the most important consideration is the degree of fluctuation of salinity. The germination of seeds and the growth of seedlings are critical stages in the plant-salinity relationship; plants become more tolerant to salinity with age.

Salinities from 0.35 to 0.9 per cent NaCl in drinking water have been shown to be toxic to many members of the order Galliformes (chickens, pheasant, quail) (Krista et al. 1961,[585] Scrivner 1946,[592] Field and Evans 1946[561]).

Young ducklings were killed or retarded in growth as a result of salt poisoning by solutions equal to those found on the Suisun Marsh, California, during the summer months. Salinity maxima varied from 0.55 to 1.74 per cent, and the means varied from 0.07 to 1.26 per cent during July from 1956 to 1960 (Griffith 1962-63).[565]

Recommendation

Salinity should be kept as close to natural conditions as possible. Rapid fluctuations should be minimized.

LIGHT PENETRATION

Criteria for light penetration established in the discussions of Color (p. 130) and Settleable Solids (p. 129) should also be adequate to provide for the production of aquatic plants for freshwater wildlife.

SETTLEABLE SUBSTANCES

Accumulation of silt deposits are destructive to aquatic plants due especially to the creation of a soft, semi-liquid substratum inadequate for the anchoring of roots. Back Bay, Virginia, and Currituck Sound, North Carolina, serve as examples of the destructive nature of silt deposition. Approximately 40 square miles of bottom are covered with soft, semi-liquid silts up to 5 inches deep; these areas, constituting one-fifth of the total area, produce only 1 per cent of the total aquatic plant production (FWPCA 1968).[562]

Recommendation

Setteable substances can destroy the usefulness of aquatic bottoms to waterfowl, and for that reason, settleable substances should be minimized in areas expected to support waterfowl.

PRODUCTION OF WILDLIFE FOODS OTHER THAN PLANTS

The production of protozoans, crustaceans, aquatic insects, other invertebrates, and fish is dependent on water quality. The water quality requirements for the production of fish are dealt with elsewhere in this Section, and a normal level of productivity of invertebrates is also required for the normal production of fish that feed upon them.

While it is well known that many species of invertebrates are easily affected by low concentrations of pollutants, such as insecticides, in water (Gaufin et al. 1965,[563] Burdick et al. 1968,[555] Kennedy et al. 1970[584]), most of the field studies do not supply reliable exposure data, and most laboratory studies are of too short a duration or are performed under static conditions, allowing no reliable extrapolations to natural conditions. The general impression to be gained from these studies is that insects and crustaceans tend to be as sensitive as or more sensitive than fish to various insecticides, and that many molluscs and oligochetes tend to be less sensitive.

TEMPERATURE

The increasing discharge of warmed industrial and domestic effluents into northern streams and lakes has changed the duration and extent of normal ice cover in these northern regions. This has prompted changes in the normal overwintering pattern of some species of waterfowl. Thus, Hunt (1957)[576] details the increasing use since 1930 of the Detroit River as a wintering area for black duck (*Anas rubripes*), canvasback (*Aythya valisneria*), lesser scaup (*Aythya affines*), and redhead (*Athya americana*). In this process, waterfowl may become crowded into areas near industrial complexes with a shrinking supply of winter food. The proximity of sources of pollutants, food shortages, and low air temperatures often interact to produce unusually high waterfowl mortalities.

Recommendation

Changes in natural freezing patterns and dates should be avoided as far as possible in order to minimize abnormal concentrations of wintering waterfowl.

SPECIFIC POTENTIALLY HARMFUL SUBSTANCES

Direct Acting Substances

Oils Waterbirds and aquatic mammals, such as muskrat and otter, require water that is free from surface oil. Catastrophic losses of waterbirds have resulted from the contamination of plumages by oils. Diving birds appear to be more susceptible to oiling than other species (Hawkes 1961).[571] Heavy contamination of the plumage results in loss of buoyancy and drowning. Lower levels of contamination cause excessive heat loss resulting in an energy deficit which expresses itself in an accelerated starvation (Hartung 1967a).[567] Less than 5 mg of oil per bird can produce significant increases in heat loss. The ingestion of oils may contribute to mortalities, and this is especially true for some manufactured oils (Hartung and Hunt 1966).[569] When small quantities of oil are coated onto eggs by incubating mallards (*Anas platyrhynchos*), the likelihood of those eggs to hatch is greatly reduced (Hartung 1965).[566] Rittinghaus (1956)[591] reported an incident in which numerous Cabot's Terns (*Thalasseus sandvicensis*) and other shorebirds became contaminated with oil that had been washed on shore. Eggs which were subsequently oiled by the plumage of oiled female terns did not hatch even after 50 days of incubation. The absence of visible surface oils should protect wildlife from direct effect.

Oils can be sedimented by coating particulates on the surface and then sinking to the bottom. Sedimented oils have been associated with changes in benthic communities (Hunt 1957)[576] and have been shown to act as concentrators for chlorinated hydrocarbon pesticides (Hartung and Klingler 1970[570]).

Recommendation

To protect waterfowl, there should be no visible floating oil (see p. 146 of this Section and pp. 263–264 of Section IV).

Lead Waterfowl often mistake spent lead shot for seed or grit and ingest it. See Section IV, pp. 227–228, for a discussion of this problem.

Recommendation

The recommendation of the Marine Aquatic Life and Wildlife Panel, Section IV, (p. 228) to protect waterfowl also applies to the freshwater environment.

Botulism Poisoning Botulism is a food poisoning caused by the ingestion of the toxin of *Clostridium botulinum* of any six immunologically distinct types, designated A through F. The disease, as it occurs in epizootic proportions in wild birds, is most commonly of the C type, although outbreaks of type E botulism have been observed on the Great Lakes (Kaufman and Fay 1964[582], Fay 1966[560]).

Cl. botulinum, a widely distributed anaerobic bacterium, is capable of existing for many years in its dormant spore form, even under chemically and physically adverse environmental conditions. Its toxins are produced in the course of its metabolic activity as the vegetative form grows and reproduces in suitable media. Outbreaks occur when aquatic birds consume this preformed toxin.

The highest morbidity and mortality rates from botulism in aquatic birds have been recorded in shallow, alkaline lakes or marshes in the western United States, and outbreaks have most commonly occurred from July through September and, in some years, October. The optimum temperatures for growth of the bacterium or the toxin production, or both, have been reported as low as 25 C (Hunter et al. 1970)[577] and as high as 37 C (Quortrup and Sudheimer 1942[588]). The discrepancies are probably the result of differences in the experimental conditions under which the measurements were made and the strains of *Cl. botulinum* type C used.

The popular belief that avian botulism epizootics are associated with low water levels and consequent stagnation is not necessarily supported by facts. In three of the years of heaviest bird losses in the history of the Bear River Migratory Bird Refuge (1965, 1967, and 1971), the water supply was considerably more abundant than normal (Hunter, California Department of Fish and Game, *personal communication*; unpublished Bureau of Sport Fisheries and Wildlife reports[600]). The high water levels caused flooding of mud flats not normally under water in the summer months. Similar inundations of soil that had been dry for several years have been associated previously with outbreaks on the Bear River Refuge and in other epizootic areas. A partial explanation for these associations may be that flooding of dry ground is commonly followed by a proliferation of many species of aquatic invertebrates (McKnight 1970[587]), the carcasses of which may be utilized by *Cl. botulinum*.

Bell et al. (1955)[552] provided experimental support for an idea expressed earlier by Kalmbach (1934).[581] According to their "microenvironment concept," the bodies of invertebrate animals provide the nutrients and the anaerobic environment required by *C. botulinum* type C for growth and toxin production. These bodies would presumably also offer some protection to the bacterium and its toxin from a chemically unfavorable ambient medium. Jensen and Allen (1960)[578] presented evidence of a possible relationship between die-offs of certain invertebrate species and subsequent botulism outbreaks.

The relationship between alkalinity or salinity of the marsh and the occurrence of botulism outbreaks is not clear. Invertebrate carcasses suspended in distilled water support high levels of toxin (Bell et al. 1955).[552] Laboratory media are commonly composed of ingredients such as peptones, yeast extract, and glucose, without added salts. The medium used routinely at the Bear River Research Station for the culture of *Cl. botulinum* type C has a pH of 6.8 to 7.0 after heat sterilization. McKee et al. (1958)[586] showed that pH was automatically maintained at a particular level in

laboratory cultures of *Cl. botulinum* type C throughout the growth period, the largest amount of toxin was produced at p⁰ 7, the lowest level tested. Decomposing carcasses of b. .ead of botulism commonly contain very high concentrations of type C toxin, and in these cases production is ordinarily independent of the chemical composition of the marsh.

Kalmbach (1934)[581] tabulated the salt concentrations of water samples collected from 10 known botulism epizootic areas. The values ranged from 261 to 102,658 ppm (omitting the highest, which was taken from a lake where the bird losses were possibly from a cause other than botulism).

Christiansen and Low (1970)[556] recorded conductance measurements on water in the management units of the Bear River Migratory Bird Refuge and the Farmington Bay Waterfowl Management Area, both sites of botulism outbreaks varying in severity from year to year. The average conductance of water flowing into the five units of the Bear River Refuge in five summers (1959–1963) ranged from 3.7 to 4.9 millimhos per centimeter at 25 C. The readings on outflowing water from the five units ranged from 4.4 to 8.3 mmhos. Comparable figures for the three Farmington Bay units were 1.8 to 3.2 (inflow) and 3.2 to 4.8 mmhos (outflow). Thus the salinity range of the inflowing water at Bear River was comparable to that of the outflowing water at Farmington.

These data suggest that salt concentration of the water in an ¬nizootic area is not one of the critical factors influencing tl :urrence of outbreaks. If high salinity does favor their . ccurrence, it is probably not because of its effect on *Cl. uotulinum* itself. Other possible explanations for the higher incidence of botulism in shallow, alkaline marshes are:

- Saline waters may support higher invertebrate population levels than do relatively fresh waters. (Comparisons, as they relate to avian botulism, have not been made.)
- High salinity may inhibit some of the microorganisms that compete with *Cl. botulinum* for nutrients or those that cause deterioration of the toxin.
- Salinity may have no significant effect on the invertebrates or the bacteria, but it increases the susceptibility of the birds. Cooch (1964)[557] has shown that type C botulinum toxin decreases the activity of the salt gland in ducks, reducing its capacity to eliminate salt. Birds so affected succumb to smaller doses of toxin than do those provided with fresh water.
- Outbreaks of botulism poisoning tend to be associated with or affected by insect die-offs, water temperatures above 70 F, fluctuations in water levels and elevated concentrations of dissolved solids.

Recommendation

tbreaks of botulism poisoning tend to be as-sᵥ ᵤted with, or affected by insect die-offs, water temperature above 70 F, fluctuating water levels, and elevated concentrations of dissolved solids. Management of these factors may reduce outbreaks of botulism poisoning.

Substances Acting After Magnification in Food Chains

Chlorinated Hydrocarbon Pesticides

DDT and Derivatives DDT and its abundant derivatives DDE and TDE have high lipid solubility and low water solubility, and thus tend to concentrate in the lipid, i.e., living fraction of the aquatic environment (Hartung 1967b).[568] DDE is the most stable of the DDT compounds and has been especially implicated in producing thinning of egg shells, increased breakage of eggs, reproductive failure in species occupying the apex of aquatic food chains in areas with long histories of DDT usage.

Reproductive failures and local extirpation associated with egg shell thinning have been reported for several North American bird species. The phenomenon was first described and is most wide-spread for the peregrine falcon (*Falco peregrinus*) (Hickey and Anderson 1968).[374] Since then similar phenomena have been described in Brown Pelicans (*Pelecanus occidentalis*) (Anderson and Hickey 1970)[551] and species of several other families of predatory birds. Further increases of DDE in large receiving basins, such as the Great Lakes, would be expected to increase the extent of repro--ductive failure among predatory aquatic bird populations. Concentrations as low as 2.8 ppm p,p'DDE on a wet-weight basis produced experimental thinning of egg shells in the American Kestrel (*Falco sparvarius*) (Wiemeyer and Porter 1970).[599] Heath et al. (1969)[572] induced significant levels of eggshell thinning in mallards after feeding them similarly low levels of DDE. Concentrations of DDT compounds in the water of Lake Michigan have been estimated to be 1 to 3 parts per trillion (Reinert 1970)[589] (Table III-21). Concentrations that would permit the assured survival of sensitive predatory bird species are evidently much lower than that. Because such low concentrations cannot be reliably measured by present technologies and because the concentrating factor for the food chains appears to be variable or is not known, or both, a biological monitoring system should be chosen. If it is desired to protect a number of fish-eating and raptorial birds, it is essential to reduce the levels of DDE contamination, especially in large receiving basins (see Section IV).

The available data indicate that there should not be concentrations greater than 1 mg/kg of total DDT in any aquatic plants or animals in order to protect most species of aquatic wildlife. Present unpublished data indicate effects for even lower levels of DDE to some species of predatory birds (Stickel *unpublished data*).[601]

Present environmental levels vastly exceed the recommended levels in many locations, and continued direct or

TABLE III-21—Relationship of DDT and Metabolites to Eggshell Thinning

Species	Dosage* wet-weight basis	Pesticide level in eggs	Thinning Percent	Reference
Mallard	1000 mg/kg single dose	N.D.†	25	Tucker & Haegele, 1970[696]
Prairie falcon (Falco mexicanus)	N.D.†	0-10 ppm DDE	ca. 5	Enderson & Berger, 1970[569]
		10-20 ppm DDE	ca. 13	
		20-30 ppm DDE	ca. 18	
		30 ppm DDE	ca. 25	
Japanese quail (Coturnix)	100 ppm o,pDDT	23.6 ppm o,pDDT	4	Bitman et al., 1969[552]
		0.52 ppm DDE		
	100 ppm p,p'DDT	48.0 ppm p,p'DDE	6	
Herring gull (Larus argentatus)	ca. 3.3 ppm total DDT	227 ppm total DDT	N.D.†	Keith, 1966[583]
American kestrel (Falco sparvarius)	2.8 ppm p,p'DDE	32.4 ppm DDE	10	Wiemeyer & Porter, 1970[649]
Mallard	**2.8 ppm DDE	N.D.†	11	Heath et al., 1969[572]
	**11.2 ppm DDE	N.D.†	14	

* All tests except the first one are chronic, spanning at least several months.
** Converted from dry-basis.
† Not determined.

indirect inputs of DDT would make these recommendations unattainable.

Recommendation

In order to protect most species of aquatic wild-life, the total DDT concentration on a wet-weight basis should be less than 1 mg/kg in any aquatic plants or animals. (Also see Recommendations for Pesticides, p. 185-186.)

Polychlorinated Biphenyls (PCB) Polychlorinated biphenyls are chlorinated hydrocarbons which are highly resistant to chemical or biological degradation. They have been widespread environmental contaminants (Jensen et al. 1969,[580] Risebrough et al. 1968[590]). Their biological effects at present environmental concentrations are not known. PCB's can elevate microsomal enzyme activity (Risebrough et al. 1968,[590] Street et al. 1968[594]), but the environmental significance of that finding is not clear. The toxicity of PCB is influenced by the presence of small amounts of con-taminated chlorinated dibenzofurans (Vos and Koeman 1970,[596] Vos et al. 1970[597]) which are highly toxic to de-veloping embryos.

Recommendation

Because of the persistence of PCB and their susceptibility to biological magnification, it is recommended that the body burdens of PCB in birds and mammals not be permitted to increase and that monitoring programs be instituted (see Section IV).

Mercury

Westoo (1966)[598] reported that almost all of the mercury found in fish is methyl mercury. Jensen and Jernelöv (1969)[579] showed that natural sediments can methylate ionic mercury. Mercury levels in fish in Lake St. Clair ranged between 0.4 and 3 ppm, averaging near 1.5 ppm (Greig and Seagram 1970).[564] Residues in fish-eating birds from Lake St. Clair ranged up to 7.5 ppm in a tern, and up to 23 ppm in a great blue heron (Dustman et al. 1970).[568] These residues are comparable to those found in Swedish birds that died after experimental dosing with methyl-mercury, and in birds that died with signs of mercury poi-soning under field conditions in Scandinavian countres (Henriksson et al. 1966,[573] Borg et al. 1969,[554] Holt 1969[575]). To date, no bird mortalities due to mercury contamination have been demonstrated in the Lake St. Clair area, but body burdens of fish-eating birds are obviously close to demonstrated toxic levels. It is therefore concluded that mercury levels in fish flesh should be kept below 0.5 ppm to assure the long-term survival of fish-eating birds. Since this level incorporates little or no safety margin for fish-eating wildlife, it is suggested that the safety of a 0.5 ppm level be reevaluated as soon as possible.

Recommendation

Fish-eating birds should be protected if mercury levels in fish do not exceed 0.5 μg/g.

Since the recommendation of 0.5 μg/g mercury in fish provides little or no safety margin for fish-eating wildlife, it is recommended that the safety of the 0.5 μg/g level be reevaluated as soon as possible.

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Section IV—MARINE AQUATIC LIFE AND WILDLIFE

TABLE OF CONTENTS

INTRODUCTION

The Panel on Marine Aquatic Life and Wildlife took as its prime responsibility the development of recommendations that would reasonably assure protection of the marine ecosystem. The recommendations have been discussed at various meetings of the members of the Panel and represent a consensus on the best statement that can be made in the light of present knowledge. The recommendations are not inflexible and may be modified as our understanding of the marine ecosystem improves.

Many parts of the marine ecosystem do not meet the quality requirements recommended here. As a result of man's activities, the marine ecosystem has been greatly modified; many species are excluded from areas where they were once abundant, and many areas have been closed for the harvesting of marine products as human food because of pollution. The decision as to what part, and how much, of the marine ecosystem should be protected for normal aquatic life and wildlife has political, social, and economic aspects, and such decisions cannot be based upon scientific evidence alone. Although some marine pollution problems are local in character, many are global and only the broadest possible approach can solve these problems. Food from the sea is already an important source of animal protein for human nutrition, and this continuing supply must not be diminished by pollution.

At the same time, the Panel recognizes that additions of pollutants to the oceans as by-products of our present mode of living will continue. But if pollution is kept within the boundaries and constraints which are defined in the recommendations, the Panel believes that the marine ecosystem can be protected.

In many ways the marine ecosystem is similar to the freshwater, but there are significant differences which should be briefly described. For more details which summarize the extensive literature on this subject, the reader is referred to *The Oceans* by Sverdrup, et al. (1942)[6],* *The Sea,* particularly volume 2 edited by M. N. Hill (1964),[3] and *Estuaries,* edited by G. H. Lauff (1967).[4]

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* Citations are listed at the end of the Section. They can be located alphabetically within subtopics or by their superior numbers which run consecutively across subtopics for the entire Section.

The marine environment is a significant source of animal protein with an annual production of about 60 million tons fresh weight of fisheries products (Food and Agriculture Organization 1967).[2] Various estimates of the potential expansion of this harvest have been made and are summarized by Ryther (1969)[5] who concludes that the potential harvest might double this figure. Some of the existing stocks are already fished to capacity or overfished, but aquaculture (pp. 222–224) may increase world marine production.

The importance of this supply of animal protein to the world population has been emphasized by Borgstrom (1961).[1] He estimates that more than two billion people of the world's population receive 50 per cent or more of their animal protein from marine products. In the United States fish contributes only about 5 per cent of our animal protein consumption, but even so it has been estimated by Pruter (*unpublished* 1972)[8] that over ten billion pounds of commercial fish and shellfish were harvested from the estuaries and continental shelf of the United States in 1970. Furthermore, in the United States a great deal of fishmeal is used to fortify animal feeds, particularly for chickens. It is obvious that this valuable food resource of the marine environment must be sustained.

The estuaries are regions where the impact of man's activity is greatest, and they are also areas of great value for marine fish production. They serve not only as nursery areas and breeding grounds for many species of fish, but also as the regular home for the entire life cycle of some valuable species, such as oysters and crabs. Sykes (1968)[7] has estimated that 90 per cent or more of the commercial catch of finfish in some geographical regions of the United States consists of estuarine–dependent species. The estuaries are the most variable regions of the marine ecosystem (see pp. 219–221) and organisms which inhabit them are exposed to extreme variations. Since these organisms survive, they are obviously adapted to the stress imposed by these variations. During the tidal cycle, a sessile organism will be exposed to variations in temperature and salinity as the tide ebbs and flows. On a seasonal basis, because of variations in river flow, organisms at a fixed location may be exposed to fresh water during flood periods or to nearly undiluted sea wa during droughts. The oscillatory nature of the tidal cu.

rents can also lead to an accumulation of pollutants within an estuary, as is discussed in the section on waste capacity of receiving waters (pp. 228–232).

Migratory fishes must also pass through estuaries in order to reach their breeding grounds. Anadromous fishes, such as the alewife, salmon, shad, and striped bass, move upstream to breed in the highly diluted seawater or in fresh water. In contrast the catadromous species such as the eel spend their adult stages in fresh water and migrate downstream in order to breed in the open sea. Conditions within the estuaries should be maintained so that these seasonal breeding migrations are not interfered with.

The conditions in the coastal waters are less variable than those in the estuaries, but in temperate regions, the seasonal range of conditions can be considerable. The coastal waters, particularly in areas of upwelling, are the most highly productive parts of the marine environment and have been estimated by Ryther (1969)[5] to produce half of the potential marine fish production, even though they constitute only 0.1 per cent of the total area of the oceans. The coastal zones, including near shore areas of high production such as fishing banks, constitute 9.9 per cent of the area of the ocean and contribute nearly half of the world fish production. In tropical waters, the seasonal variation in conditions is less extreme than in temperate waters. However, as will be discussed in the section on temperature (p. 238) many tropical species are living near their upper extreme temperature during the summer, and this fact presents considerable problems in the disposal of waste heat in tropical areas.

The open ocean constitutes 90 per cent of the area of the world ocean and is the least variable of the marine environments. The deep sea produces only a minor fraction of the world's fish production, and this consists mainly of the large pelagic carnivores such as the tuna (Ryther 1969).[5] During the 19th century, the whale harvest was substantially greater than it is at present, but the whales captured were not as effectively utilized as they are in modern whaling methods. Many species of whales were grossly over-fished, and there is considerable question today whether some of these species can recover their original population sizes even in those cases where a complete moratorium on their capture is in effect.

The waters of the deep sea below the permanent thermocline (the depths below which seasonal temperature changes do not occur) constitute the largest and most constant environment on earth. During the history of modern oceanography, which covers the last century, no significant changes in either salinity or temperature of the deep sea have been observed, the organisms living in this abyssal environment having evolved under conditions which were presumably constant for millenia. To protect the coastal environment many proposals have been made to dump materials, such as solid waste, sewage sludge, and contaminated spoils in the deep sea. Since the organisms inhabiting the depths of the ocean have been exposed to a constant

environment, they are not accustomed to unusual stresses which might be created by such dumping operations (see pp. 278–283). Consequently, dumping of organic wastes in the deep sea is not recommended (pp. 277, 282–283).

Development of Recommendations

In most cases, recommendations are not applicable to every local situation. The marine environment varies widely, and only an understanding of local conditions will make it possible to determine what can or cannot be added in each situation. Many materials are accumulated by marine organisms, and the concentration is often increased at higher levels of the food web. With substances that are toxic and persistent, it is the concentration in the highest predators, fish or birds, that is critical. One example is DDT and its derivatives which have accumulated in birds to levels that interfere with their breeding. Materials that decompose or are otherwise removed from the marine environment present lesser hazards.

The application of any recommendation to a local situation is unique because it requires (a) an understanding of the circulation of the water and the resultant mixing and dilution of the pollutant, (b) a knowledge of the local biological species in the environment and the identification of those that are most sensitive to the pollutant being considered, and (c) an evaluation of the transport of the material through the food web because of the possibility that the pollutant may reach concentrations hazardous either to the normal aquatic species present, or to man through his use of aquatic species as food.

The normal cycle of variation in the environment of many substances or conditions that occur naturally, such as oxygen, temperature, and nutrients, must be determined before decisions can be made as to possible permissible changes. In many estuaries and coastal waters "normal" conditions have been modified by man's activities and may already have changed to the extent that some species that might have been found at earlier times have been eliminated. In some circumstances, a recommendation may not be applicable because it may be necessary to specify no additional change beyond that which has already occurred. There is no generally applicable formula for recommendations to protect marine aquatic life and wildlife; a study of local environmental conditions is essential prior to application of the recommendations.

The Panel recognizes that what can or should be done in a given situation cannot wait for the completion of time-consuming studies. The degree of protection desired for a given location involves social and political decisions. The ecological nature and quality of each water mass proposed for modification must be assessed prior to any decision to modify. This requires appropriate information on the physical and chemical characteristics, on the distribution and abundance of species, and on the normal variations in these

attributes over the annual cycle. In addition, there must be sufficient knowledge to permit useful prediction of the significant effects of the proposed pollutant on the stages in the life cycle of important species, on populations, and on the biological communities present. The possible impact of that pollutant upon the ecosystem can then be assessed. These subjects are covered in greater detail in other parts of this Section, but they are mentioned here to emphasize the primary importance in determining how the recommendations should be used in local situations.

USES OF THE MARINE SYSTEM TO BE PROTECTED

Coastal marine waters serve a wide variety of exceptionally important human uses. Many of these uses produce high local benefits such as the yield of shellfish and recreational activities. Others involve regional benefits or the global unity of the marine system, since local events influence, and are influenced by, water quality at distant points. Many of the human uses of marine waters are directly dependent upon the nature and quality of the biological, chemical, and physical systems present. Efforts to protect and enhance these uses will be limited principally by our ability to understand and protect the environmental conditions which are essential for the biota.

Water quality criteria for marine aquatic life and wildlife define the environmental requirements for specified u: ive of these are discussed in this Section, namely, ma...enance of the ecosystem; fisheries; aquaculture; wildlife protection; and waste disposal. These are not sharply separable, but the water quality requirements for each use are briefly summarized. The effects of transportation, harbor development, dredging and dumping of spoils have also been considered in developing the recommendations.

NATURE OF THE ECOSYSTEM

Many of the principal human uses of marine waters depend upon successful maintenance and enhancement of the existing ecosystems or, in a few circumstances, upon creating and continuing new and artificial ecosystems for specific purposes. The ecosystem includes all of the biological and non-biological (geological, physical, and chemical) components of the environment and their highly complex interactions. Studies of ecosystems must include all that is within the body of water as well as the imports to and exports from it. Research in such situations has shown that the biotic elements include producers of organic material, several levels of consumers, and decomposers. In the least complex situation, these act at rates controlled by the abiotic factors to transfer energy and recycle materials. In those aquatic environments which continuously or intermittently exchange l·   quantities of energy or materials with other parts of t.   .otal global system, understanding and management

become more difficult. In the marine environment imports and exports continually occur from coastal runoff, tidal action, oceanic currents, meterological actions, and exchanges with adjacent water bodies or with the benthos and atmosphere. These exchanges are only partially understood, but it is clear that each marine site is connected intimately to the rest of the oceans and to total global mechanisms.

The estuaries are in many ways the most complicated and variable of aquatic ecosystems. Materials carried from the land by rivers vary in quantity and quality, sometimes with strong seasonal patterns of high biological significance. Tidal oscillations cause vigorous reversals of flow. Inherent hydrographic patterns can lead to accumulation of materials and to upstream transport from the point of addition. Dense urban populations on the shores of estuaries produce large amounts of waste, and engineering projects have changed the boundaries and flows of water courses. The biologically rich estuaries are the most variable and the most endangered part of the marine environment.

In each environment the existing characteristics of the system have been produced by dynamic interaction among the components, forces, and processes present. Some of these are small or transitory, but others are massive and enduring. If any one of these forces or processes is changed, a new balance is produced in the system. Relative stability, therefore, results from the balancing of forces, not the absence. The biota are the product of evolution, and each ecosystem contains those species and communities which have adapted to the specific environment over a long period of time and which are successful in that environment. Drastic and rapid modification of the environment, as by pollution, may eliminate some species and encourage others in ways which can reduce the value of the ecosystem for man's use or enjoyment.

Effects of Water Quality Change on Ecosystems

The introduction of a chemical compound or a change in the physical environment may affect a natural marine ecosystem in many ways. In coastal waters undisturbed for long periods of time, the ecosystem has adjusted to the existing

conditions. The system is productive, species are diverse, the biomass is high, and the flow of energy is comparatively efficient. The addition of pollutants to such a system might:

- reduce the input of solar energy into the ecosystem;
- increase the input of organic matter and nutrients which might stimulate the growth of undesirable species;
- reduce the availability of nutrients by increased sorption and sedimentation;
- create intolerable physical extremes for some organisms, as by the addition of heat;
- kill or reduce the success of individual organisms, as by lethal toxicity or crippling with oil;
- eliminate species by adding a toxic material or making an essential element unavailable;
- interfere with the flow of energy from species to species, as by a chemical that interferes with feeding behavior;
- reduce species diversity in the system;
- interfere with regenerative cycling by decomposers;
- decrease biomass by reduction of abundant species, or disruption of the processes of ecosystems;
- increase biomass by removing important consumers allowing runaway production of other species.

All of these may involve changes in production and lowered human usefulness of the system. These are examples; additional effects can occur. The specific impacts of pollution at a site can be determined only through long-term study of that portion of the ocean and the changes that occur.

It is clear that man, through his numbers and his actions, is having increasingly pronounced effects on organisms, populations, and entire ecosystems. Many people willingly accept the consequences of advanced technology that are markedly deleterious, but most people become alarmed when an entire large ecosystem undergoes transformation. When society recognizes that catastrophe threatens due to its carelessness, it seeks to rearrange its demands on such ecosystems in ways that can be accommodated within the inherent capacities of the system. To provide adequate answers we need understanding of ecosystems, since knowledge at the species and population levels, however defined, will be too limited in scope to answer the questions that arise at the more highly organized level of the ecosystem.

The study of the effects of pollution on ecosystems may be undertaken by considering pollution as an additional stress on the mechanisms that keep ecosystems organized. Unless the living parts of an ecosystem are already under stress, the early effects of the introduction of toxic pollutants may contribute to the extinction of particularly susceptible species leaving the more resistant forms in a less diverse community. In communities already under stress, relatively low levels of pollution may cause the disruption of the communities.

Estuaries and intertidal regions are naturally exposed to stressful conditions. In the estuaries the ebb and flow of the tide and the fluctuating freshwater flow create changes in salinity on various time scales ranging from hourly seasonally. In the intertidal zone the normal inhabitants are exposed to air during part of each tidal cycle. They are also subjected to vigorous wave actions on exposed beaches and headlands. Unique assemblages of organisms have evolved which manage to survive these rigorous conditions if waters remain unpolluted.

Pollutants are commonly released into such aquatic ecosystems of high natural variation in their nonliving components, and the rate of pollutant discharge usually varies from time to time. The immediate effect of these conditions is that at any fixed point in the habitat the concentration of a pollutant varies markedly with time, but not in such a way that a community can adapt itself to these variations. The result is that short-lived opportunistic species are likely to be favored in areas subject to variable aquatic pollution.

Any single toxicant may be equally virulent towards long-lived or short-lived species in the normal aquatic community. Except at outfalls where toxicants reach lethal concentrations, as in continuous discharges in stable environments, toxicants act discontinuously through time. Where water mass instabilities are such that poisonous concentrations occur on the average of once a week, for instance, it is possible for organisms with much shorter life spans to flourish briefly with large population fluctuations. Where they occur once a month, a community may evolve rapidly through successional sequence involving a few longer-lived organisms before the next toxic concentration occurs. Where lethal dosages are as infrequent as once a year, the succession may go to the stage of some fish of medium life span, particularly if access to the area is relatively free. Because of the fluctuations with time, the community nearest an outfall is most primitive from a successional viewpoint, and as distance from the outfall increases, there is a successional gradient toward the usual climax community of an unpolluted environment.

Evaluation of the effects of pollution or of other environmental changes on the ecosystem involves studies of biological production, species diversity, energy flow, and cycling of materials. The process may be complicated by massive imports and exports at any one site. Although pathways of energy flow and efficiencies are not yet completely understood, they offer a unifying approach to these problems such as proposed by Odum (1967,[12] 1971[13]).

Species diversity is a useful attribute of biological systems. Diversity is affected by a number of factors as evidenced by the papers presented at a symposium on Diversity and Stability in Ecological Systems (Brookhaven National Laboratory 1969),[10] as well as other symposia (American Society of Civil Engineering and Stanford University 1967,[9] Olson and Burgess 1967,[14] NAS-NRC Committee on Oceanography 1970,[11] Royal Society of London 1971[15]). Some s.

ess has been achieved in the use of diversity measurements, however, and their potential for future use is high. (See the discussion of Community Structure in Section III on Fresh-water Aquatic Life and Wildlife and in Appendix II-B.)

There are potentials for managing additions to coastal ecosystems in ways that benefit human uses. These are as yet poorly understood, and efforts to utilize waste heat, nutrients and other possible resources are primitive. Such possibilities merit vigorous exploration and, eventually, careful application.

FISHERIES

Major marine and coastal fisheries are based upon the capture of wild crops produced in estuaries, coastal waters, and oceans. The quantity and quality of the available supply of useful species are controlled by the nature and efficiency of the several ecosystems upon which each species depends for its life cycle. Shad, for instance, depend upon freshwater areas at the head of estuaries for spawning and for survival as eggs and larvae, open estuaries for the nutrition of juveniles, and large open coastal regions for growth and maturation. As do many other species, shad migrate over large distances. Serious pollution at any point in the lower river, the estuary, or the inshore ocean might, therefore, break the necessary patterns and reduce the fishery.

Estuaries have exceptional usefulness in support of fisheries. At least three quarters of the species in the commercial and recreational fisheries of the nation are dependent upon the estuarine ecosystem at one or more stages of their life history. Estuaries are used as obligatory spawning grounds, nursery areas, havens from parasites and predators, and as rich sources of food because of high productivity.

American fisheries exploit several levels of the coastal ecosystem. We do not utilize the plants, the producers, directly as food or in commerce except for a comparatively small harvest of kelp and other seaweeds. The primary consumers, however, are extensively utilized. These include oysters, clams, mussels, and vast quantities of filter-feeding fish such as sardines, anchovies, menhaden, and herring. Second and third level consumers, which are less abundant but frequently more desired than plankton feeders, include most of our sports fish and major commercial species such as tuna, striped bass, cod, halibut, and sea trout, as well as squid, sharks, and other species which hold potential for increased future use.

Pollutants can be detrimental to fisheries by reducing desired species through direct mortality from toxicity, smothering, intolerable heat, or other killing changes. Reduction may also occur when a pollutant has a sublethal stressing effect that significantly interferes with feeding, movement, reproduction, or some other essential function. Pollution has an indirect deleterious effect when it increases predators or parasites, reduces food organisms or essential consorts, or damages the efficiency of the ecosystem functions pertinent to the species in question. Consideration of all these occurrences must enter into efforts to protect and enhance fisheries.

Pollutants also damage marine organisms by imparting characteristics that make them unacceptable for commercial or recreational use. Economic loss has resulted from flesh tainting of fish and shellfish by oil, phenolics, and other materials affecting taste, flavor, or appearance. DDT and other persistent organics, applied on land, have accumulated in fish to levels that exceed established standards for acceptable human food. Heavy metals, e.g., mercury, can reach levels in fish several thousand times the concentration in the ambient water, destroying the economic value of the organisms involved.

More than 90 per cent of the American commercial catch and virtually all of the sport fish are taken from the estuaries and continental shelf. The total yield is difficult to estimate, involving as it does migratory species, catches by both foreign and domestic vessels, and recreational fisheries which are only partially measured. Stroud (1971)[26] estimated that the estuarine-dependent fishery of the Atlantic coast yields 535 pounds per acre of estuary for a total annual yield of 6.6×10^9 lbs. He concludes that shrinking of estuaries by filling or other destruction would reduce the yield by a directly proportional quantity. Further, he predicts that reduction of the productivity of estuaries by pollution would also produce a proportional decrease in fish production. The U.S. commercial fisheries of largest volume, in order of decreasing harvest, include menhaden, salmon, shrimp, crabs, herring, and oysters (Riley 1971).[24] The most valuable commercial harvests include shrimp, salmon, lobsters, crabs, menhaden, oysters, clams, flounders, and scallops (Riley 1971).[24]

The estuaries, as recipients of wastes both from rivers entering them and cities and industries along their shores, are obviously more immediately susceptible to pollution damage than any other part of the marine system (Clark 1967,[18] American Society of Civil Engineering and Stanford University 1967,[16] U.S. Dept. of Interior 1969,[27] and U.S. Dept. of Interior, Fish and Wildlife Service 1970[28]). Although the vulnerability of such inshore bodies of water to physical and chemical damage is exceptional, the open waters along the coast are also subject to damage from the use of these waters for waste disposal. Approximately 250 waste disposal sites are in use along the coast of the United States, and 48 million tons of wastes are estimated to have been dumped in 1968. (Council on Environmental Quality 1970).[19] These dumped wastes included dredge spoils, industrial wastes, sewage sludge, construction and demolition debris, solid wastes, and explosives (see pp. 278–283 of this Section for a more extended discussion of dumped wastes). Increased populations and technological concentration along the coasts, with simultaneous resistance to the use of land, rivers, and estuaries for disposal has stimulated pro-

posals to increase the use of oceanic areas as receivers of wastes.

The effects of such coastal disposal on fisheries are not yet clearly established. Bechtel Corp. (1969)[17] has suggested that continued expansion of waste disposal along the Atlantic coast at the present rate of increase may, in about 30 years, significantly reduce the quality of water over the continental shelf by increased suspended solids, phosphate or nitrate enrichment, oxygen demand, heavy metals, or simultaneous effects from all of these. Preliminary studies of the effects of dumping of sewage sludge and dredging spoils from the metropolitan New York area indicate that an area of about 20 square miles has been impoverished by reduction of normal benthic populations; and indirect effects may be far more extensive (Pearce 1970).[23]

More general approaches to disposal of wastes in ocean waters have been presented by Foyn (1965)[20] Olson and Burgess (1967)[22], NAS-NRC Committee on Oceanography (1970)[21] and the Royal Society of London (1971).[25] Some discernible and disturbing changes in coastal waters are documented that prove the urgent need for better understanding of pollution effects at the edge of the oceans. The limitation that must be placed upon any such releases must be learned and put to use quickly, and we should proceed carefully while we are learning.

Fisheries provide useful indications of the biological health and productivity of marine waters. Continuous high yield of a harvestable crop of indigenous fish or shellfish free of toxicants or pathogens is an indication that water quality is satisfactory, that the environmental conditions are favorable for the total biological community, and that no contaminant is present in sufficient quantity to destroy major components of the ecosystem. Fisheries production statistics can thus serve as a sensitive indicator of environmental quanity.

Specific criteria for categories of pollutants will be given in subsequent parts of this Section. The general requirements for water quality in relation to successful fisheries include:

- favorable, not merely tolerable, environmental conditions at every location which is required in the life history of each species: this places special value on water quality of estuaries which are obligate environments for many species during at least some portion of their life cycles;

- freedom from tainting substances or conditions where useful species exist, including elements and compounds which can be accumulated by organisms to unacceptable levels;

- absence of toxic conditions or substances wherever useful species occur at any time in their life history;

- absence of sublethal deleterious conditions which reduce survival and reproductive success;

- water sufficient to maintain the health of the biological systems which support useful species;

- absence of environmental conditions which are exceptionally favorable to parasites, predators, and competitors of useful species.

MARINE AQUACULTURE

Although often considered a new approach to the world food problem, aquaculture is an ancient practice in many parts of the world. In the Orient, aquatic organisms have been successfully cultivated for centuries, usually with rather primitive and empirical techniques, but nevertheless with impressive success.

The annual world production of food through aquaculture has recently been estimated at over four million metric tons, about 6.5 per cent of the total world fish landings. Although this is derived largely from fresh water, and open-ocean mariculture is in its infancy, an unknown but significant fraction of the production is brackish-water organisms taken from estuarine systems. The distinction between freshwater and marine aquaculture is quite artificial. Because the principles, techniques, potentials, and environmental requirements for growing organisms in either fresh or salt water are much the same, the distinction is also unnecessary for the purposes of the present discussion, except as noted below.

It is difficult to assess the potential yield from marine aquaculture, dependent as it is on a primitive art undergoing rapid technological development. The introduction of present methods into new, undeveloped parts of the world could at least double the present harvest within the next decade. Judging from the experience in agriculture and terrestrial animal husbandry, much greater increase in yields should presumably be possible with advances in such fields as genetic selection and control, nutrition, habitat management and elimination or control of disease, predation, and competition. It is not inconceivable that the yield from aquaculture might one day surpass that from the harvest of wild, untended stocks of aquatic organisms. Further, since only the most desirable species are selected for aquaculture, both the economic and nutritional value per pound of cultivated organisms greatly exceeds that of the average fishery product. In the United States, expanded recent interest in coastal aquaculture will hopefully produce new techniques, products, and quantities, although economic feasibility has been difficult to achieve thus far.

Although no firm distinction can be drawn, it is convenient to think of most forms of marine aquaculture in one of two categories that will be referred to here as *extensive* and *intensive* culture. In extensive culture, animals are reared at relatively low densities in large impoundments, embayments, or sections of estuaries, either natural or man-made. The impoundments may be closed off or open to the depending upon the desired degree of control, but

hose that are enclosed must be located near a source of eawater so that the water may be exchanged frequently o r ʳᵉⁿt stagnation and to regulate such factors as tem- ʲe. ᵉ and salinity. Such exchanges are accomplished by dal action or by pumping.

The cultivated animals may be stocked or may consist of ᵗatural populations that enter the system as larvae or ᵘveniles. They are usually not fed but subsist on natural ᵒods that grow in the area or are carried in with the outside eawater.

Extensive aquaculture systems are most common in the ᵗndeveloped parts of the world (e.g., Southeast Asia) where ᵃrge areas of coastal mangrove swamps, marshes, and estu- ᵣies are available and are not presently in use or demand ᵒr other purposes. For example, it has been estimated that ᵗhere are over six million acres of mangrove swamps in ᵗndonesia alone that would be suitable for some form of fish ᵃrming.

In such coastal impoundments, milkfish, mullet, shrimp, ᵗnd other free-swimming species are grown. In the more ᵗpen situations such as embayments and arms of estuaries, ᵗon-fugitive organisms are cultivated. The oldest and most ᵗighly-developed form of marine aquaculture practiced in ᵗhe United States and Europe, that of oyster culture, falls ᵗnto this category. Seaweed culture in Japan and China is ᵗnother interesting example of this general approach to ᵗquaculture.

Yields from extensive aquaculture range from a few hun- ᵗʳ ᵗunds to, at best, about one ton per acre per year. ᵗt.ᵗ, in some cases almost no, capital investment is re- ᵗuired, and it is not a labor-intensive form of enterprise. ᵗne or two unskilled laborers can manage 100 acres or ᵗore of shrimp or milkfish ponds in Malayasia or the ᵗhilippines except during stocking and harvesting opera- ᵗons. This is normally a highly profitable form of business ᵗo the culturist and, despite the modest yields, extensive ᵗquaculture is capable of making a significant contribution ᵗo the protein nutrition of many of the undeveloped parts ᵗf the world.

Intensive aquaculture makes use of flowing-water sys- ᵗems using flumes or raceways and is best typified by trout ᵗnd salmon hatcheries that have been operated successfully ᵗn the United States and Europe for many years and have ᵗow reached a relatively high level of technical sophistica- ᵗion. Although originally designed to produce fish to be ᵗtocked in natural waters to enhance commercial or sports fishing, such systems are now being increasingly used for the production of fish to be marketed directly as food. Such systems were originally developed and used exclusively for rearing freshwater species, but they are now also finding application in saltwater areas for the production of marine ᵗr anadromous species.

A variation of the raceway system of intensive aquacul- tu ᵗhat of floating cage culture in which the animals are heᵗ ᵗn nets suspended by a floating wooden framework.

These may be moored in estuaries or other protected arms of the sea, where they are exposed to strong tidal currents.

A common feature of the various kinds of intensive aqua- culture is that the animals are grown closely packed at ex- tremely high densities and depend upon the flow of large volumes of water over and around them to provide oxygen and carry away wastes. When feasible, the animals are fed artifically on prepared, pelletized food. The entire system must be carefully controlled and monitored.

Intensive aquaculture systems for the commercial pro- duction of food are in an early stage of development and have yet to prove themselves as profitable and reliable for marine species. Rapid progress is being made in this area, however, particularly in highly developed parts of the world where technological skill is available, where coastal marine areas are scarce and in high demand, and where the price of luxury seafoods is escalating. Various species of molluscs, crustaceans, and finfish are now being grown in this way, and many more are likely candidates as soom as funda- mental aspects of their life history and nutrition are mastered.

The yield from intensive aquaculture per unit of area in which the organisms are grown is ecologically meaningless (as is that from a cattle feed-lot, for example) but amounts to as much as hundreds of tons per acre. More realistically, the yield from such systems may be expressed per cubic foot per minute of water flowing through it, which is usually the limiting factor.

In contrast to extensive aquaculture, intensive systems usually require high capital outlay and have a relatively high labor demand. Profits or losses are determined by small differences in the costs of food, labor, marketing, and the demand for the product.

Both extensive and intensive forms of aquaculture are heavily dependent on high quality water to sustain them. Neither is independent of the adjacent coastal marine en- vironment. Extensive pond culture may be semi-autono- mous, but as explained above, the water must be occasion- ally and sometimes frequently exchanged. Intensive aqua- culture systems are vitally dependent on a continuous large supply of new seawater. Because of the large investment and, at best, small margin of profit, and because of the dense populations of animals maintained at any one time, inten- sive aquaculture represents a far greater risk.

Freshwater aquaculture systems, if strategically located near an adequate source of underground water, may be largely independent of man's activities and relatively free from the threat of pollution. This, unfortunately, is never quite true of marine aquaculture. The contiguous oceans of the world circulate freely, as do the substances man adds to them. While water movements may be predicted on large geographical and time scales, they are quite unpredictable on a local and short-term basis. An embayment or estuary whose shores are uninhabited and which may suffer no ill effects from the surrounding land may suddenly become in-

fused with materials added to the water hundreds of miles distant and carried to the scene by winds, tides, and coastal currents. In this sense, marine aquaculture is not only more vulnerable to change than freshwater culture, but the dangers are also far less predictable.

Application of Water Quality to Aquaculture

The various toxic or otherwise harmful wastes that man adds to the coastal marine environment affect cultivated organisms much the same as they do the natural populations of the same species. These are discussed in detail elsewhere and need not be repeated here. In general the deleterious effects of wastes on organisms that are used as food by man are: (1) to kill, injure, or interfere with the growth or other vital functions of the organisms, or (2) to become concentrated in the organisms to such an extent as to render them unfit for human consumption by exceeding public health standards or by making them unpalatable. In the latter case, this may occur with no apparent accompanying impairment of the organism.

Certain aspects of aquaculture, particularly the intensive forms of culture described above, are particularly sensitive and vulnerable to various kinds of pollution—more so than their freeliving counterparts in nature. These are enumerated and discussed briefly below.

- The carrying capacity of intensive aquaculture systems is based on the flow of water and its supply of oxygen. If the concentration of oxygen in the water suddenly decreases due to an organic overload, a temperature increase, or other external causes, it may be inadequate to support the cultivated animals.
- Captive organisms cannot avoid localized unfavorable conditions (e.g., oxygen, temperature, turbidity) as can free-swimming natural populations.
- Many organisms can tolerate alterations in their environment if they are allowed to adapt and become acclimated to such changes slowly. Cultivated organisms may be, and often are subjected to sudden changes in water quality and cannot endure the initial shock, while the free-swimming natural populations can enter an affected area slowly and cautiously and allow themselves to adapt to the altered conditions.
- Cultivated organisms, particularly in the densely-crowded conditions of intensive aquaculture, may be and perhaps always are under rather severe physiological stress. Artificial diets are often incomplete or otherwise unbalanced. Unnaturally crowded living conditions may cause hormonal or other biochemical imbalance. The animals may already suffer the effects of poor water quality from their own pollutants. They are therefore particularly susceptible and vulnerable to any additional deterioration in water quality that may increase their stress condition.
- Disease is a spectre that perpetually haunts the aquaculturist. Virtually impossible to avoid or eliminate in any open system, it is usually, at best, held in check. Again, the additional stress caused by a deterioration in water quality, while not fatal in itself, may lower the resistance of the cultivated animals to epidemic disease.
- Artificially-fed cultivated organisms may be no less susceptible to accumulation of wastes, although intensively cultivated organisms that are fed entirely on an artificial diet would appear to have one advantage over natural populations of the same animals living in polluted waters. Many toxic substances such as chlorinated hydrocarbons may reach toxic or unacceptable levels in larger organisms because of concentration and amplification at each successive step in the food chain that ultimately supports the animal in question. However, there is increasing evidence that these substances also enter fishes and other organisms directly from solution in the water, across respiratory or digestive membranes. Such direct absorption of toxic material may in some cases exceed the quantities ingested and assimilated with food.

Therefore, the general recommendations for the quality of water for use in culture include: (1) continuously adequate control of those materials and conditions which required for good health and efficient production of the cultured species; (2) absence of deleterious chemical and physical conditions, even for short or intermittent periods; (3) environmental stability; and (4) prevention of introduction of diseases that attack the organisms under culture. The specific requirements for each culture effort must be with reference to the species involved, the densities desired, and the operational design of the culture system.

MARINE WILDLIFE

Marine wildlife for the purposes of this Section is defined as those species of mammals, birds, and reptiles which inhabit estuaries or coastal and marine waters for at least a portion of their life span. The fish, invertebrates, and plankton that constitute the food webs upon which these species depend are not, therefore, considered to be wildlife in this context. The recommendations for marine wildlife, however, necessarily include all recommendations formulated to protect the fish, invertebrate, and plant communities, because wildlife can be adequately protected only if the diversity and integrity of food webs are maintained. Moreover, the recommendations must protect wildlife from pollutants that are relatively persistent in the environment, transported by wind or water currents, and concentrate recycled in the food webs. Because of trophic accumulat.

birds and mammals that occupy the higher trophic levels in the food web may acquire body burdens of toxicants that are lethal or that have significant sublethal effects on reproductive capacity, even though the concentrations of these substances in the water remain extremely low. Pollutants of concern or of potential concern are the radionuclides, heavy metals, chlorinated hydrocarbons, and other synthetic chemicals that are relatively resistant to biological and chemical degradation.

Recommendations to protect wildlife dependent upon freshwater ecosystems may in general also apply to estuaries. This is particularly true for protection of food and shelter for wildlife, pH, alkalinity, light penetration, settleable substances, and temperature. These are discussed in Section III on Freshwater Aquatic Life and Wildlife.

Marine and coastal waters constitute major sinks for persistent pollutants. Accumulation rates and steady-state levels are complex functions of input, rates of degradation, and rates of deposition in the sediments. As yet no research programs have measured accumulation rates of pollutants in coastal waters or determined whether steady-state concentrations have already been attained.

Current knowledge of the partition coefficients among concentrations in water, in sediments, and in tissues of representative species in food webs is at best fragmentary. It is assumed, however, in the evaluation of water quality that the distribution and concentration of gradients of a pollutant in an aqueous ecosystem satisfy thermodynamic equilibria requirements. The pollutants considered here are not essential to physiological functions, and do not require energy to maintain the concentration gradients. Thus the chlorinated hydrocarbons are concentrated in the lipid pools of organisms from ambient water but will not accumulate indefinitely. Rather, under equilibrium conditions, these pollutants will also be lost to ambient water, particulate matter, and sediments in satisfying thermodynamic requirements. Because the internal environments of birds and mammals are more isolated from the ambient environment than those of invertebrates and most fish, equilibrium concentrations of pollutants, particularly the chlorinated hydrocarbons, may be substantially higher.

Theoretically, therefore, measurements of pollutant concentrations in one component of an ecosystem are sufficient to indicate the level in the system as a whole when the partition coefficients among water, suspended particulate and organic material, sediments, lipid pools, surface films, and the atmosphere are known. The methodologies for measuring pollutant concentrations in sea water are as yet imperfect, and very few good measurements have so far been made. Consequently it is not practical at present to make recommendations for the relatively persistent organic pollutants based upon water concentrations, especially when partition coefficients are not known. Residue concentrations in fish are more easily determined and can more readily be associated with harm to bird and mammal populations that consume them. Recommendations for the toxic organic compounds that are trophically accumulated by marine wildlife are therefore based upon concentrations in fish.

It cannot be assumed that there is a level or concentration in the ecosystem as a whole of pollutants which are mutagens or teratogens that causes no effect on any of the wildlife species. The chlorinated dibenzo-p-dioxins are highly toxic to developing embryos (Verret 1970)[71] and are contaminants in compounds prepared from chlorinated phenols, including the herbicide 2,4, 5-T (Verrett 1970)[71] and the widely used fungicide pentachlorophenol (Jensen and and Renberg 1972).[53] The closely related chlorinated dibenzofurans are contaminants in some PCB preparations (Vos and Koeman 1970,[74] Vos et al., 1970,[75] Vos *in press* 1972).[72] Embryonic mortality in birds is induced by these or other derivatives of PCB (Peakall et al., *in press* 1972,[59] Vos *in press* 1972).[72] For the present time the chlorinated dibenzofurans are included with PCB in the recommendations. When environmental mutagens and teratogens affect only relatively few individuals of a population, it is assumed that these will be eliminated by natural selection without harm to the species as a whole.

For other pollutants which affect specific enzyme systems or other physiological processes but not the genetic material or embryological development, it is assumed that there are levels in the environment of each below which all organisms are able to function without disrupting their life cycles. Manifestations of physiological effects, such as a certain amount of eggshell thinning or higher level of hormone metabolism, might be detectable in the most sensitive species. If environmental levels increase, the reproductive capacity of the most sensitive species would be affected first. The object of the recommendations presented is to maintain the steady-state concentrations of each pollutant below those levels which interfere with the life cycles of the most sensitive wildlife species. Input should not therefore be measured only in terms of concentrations of each pollutant in individual effluents, but in relation to the net contribution to the ecosystem. At the steady-state level, the net contribution would be zero, with the total input equal to the sum of degradation and permanent deposition in the sediments.

Bases For Recommendations

Recommendations based upon pollutant concentrations in fish must take into account the individual variation in residue concentration. The distribution is usually not Gaussian (Holden 1970;[51] Anderson and Fenderson 1970;[30] Risebrough et al. *in press* 1972),[65] with several individual fish in a sample frequently containing much higher residue concentrations than the majority. Fish samples should therefore consist of pooled collections. Samples as large as 100 fish may not be sufficient to determine mean concentrations of a pollutant with a precision of 10 per cent (Risebrough et al. *in press* 1972).[65] Practicality, however, frequently

dictates against sample sizes of this magnitude, and samples consisting of 25 or more fish are suggested as a reasonable compromise.

Radionuclides

Recommendation

In the absence of data that would indicate that any of the radionuclides released by human activities are accumulated by wildlife species, it is recommended that the recommendations established for marine fish and invertebrates apply also to wildlife.

Heavy Metals

The results obtained during the baseline study of the International Decade of Ocean Exploration (IDOE) in 1971–72 have failed to indicate any evidence of pollution by heavy metals, including mercury and cadmium, above background levels in marine species (Goldberg 1972).[45] The results, suggested, however, local patterns of coastal contamination. The heavy metal analyses carried out to date of tissues of several species of petrels, strictly pelagic in their distribution (Anderlini et al. 1972);[32] and of coastal fish-eating species such as the Brown Pelican, *Pelecanus occidentalis*, (Connors et al. *in press* 1972a);[40] and the Common Tern, *Sterna hirundo* (Connors et al. *in press* 1972b)[41] have confirmed this conclusion.

Recommendation

In the absence of data indicating that heavy metals are present in marine wildlife in concentrations above natural levels, it is recommended that recommendations formulated to protect other marine organisms also apply to wildlife in order to provide protection in local areas.

Polychlorinated Biphenyls (PCB)

Evidence is accumulating that PCB does not contribute to the shell thinning that has been a major symptom of the reproductive failures and population declines of raptorial and fish-eating birds. Dietary PCB produced no shell thinning of eggs of Mallard Ducks (*Anas platyrhynchos*) (Heath et al. *in press* 1972),[49] nor did PCB have any effects on eggs of Ring Doves (*Streptopelia risoria*) (Peakall 1971).[58] A PCB effect could not be associated with the thinning of Brown Pelican (*Pelecanus occidentalis*) eggshells (Risebrough *in press* 1972).[62] PCB may increase susceptibility to infectious agents such as virus diseases (Friend and Trainer 1970).[44] Like other chlorinated hydrocarbons, PCB increases the activity of liver enzymes that degrade steroids, including the sex hormones (Risebrough et al. 1968;[64] Street et al. 1968).[67] The ecological significance of this phenomenon is not clear.

Because laboratory studies have indicated that PCB, with its derivatives or metabolites, causes embryonic death of birds (Vos et al. 1970;[75] Vos and Koeman 1970;[74] Vos *in press* 1972;[72] Peakall et al. *in press* 1972[59]) and because exceptionally high concentrations are occasionally found fish-eating and raptorial species (Risebrough et al. 1968, Jensen et al. 1969[52]), it is highly probable that PCB has had an adverse effect on the reproductive capacity of some species of birds that have shown population declines.

Median PCB concentrations in whole fish of eight species from Long Island Sound, obtained in 1970, were in the order of one milligram per kilogram (mg/kg) (Hays and Risebrough 1972),[47] and comparable concentrations have been reported from southern California (Risebrough 1969).[61] On the basis of the high probability that PCB in the environment has contributed to the reproductive failures of fish-eating birds, it is desirable to decrease these levels by at least a factor of two (see Section III on Freshwater Aquatic Life and Wildlife pp. 175–177).

Recommendation

It is recommended that PCB concentrations in any sample consisting of a homogenate of 25 or more whole fish of any species that is consumed by fish-eating birds and mammals, within the same size range as the fish consumed by any bird or mammal, be no greater than 0.5 mg/kg of the wet weight.

In the absence of a standardized methodology for the determination of PCB in environmer samples, it is recommended that estimates of P concentrations be based on the commercial Aroclor® preparation which it most closely resembles in chlorine composition. If the PCB composition should resemble a mixture of more than one Aroclor®, it should be considered a mixture for the basis of quantitation, and the PCB concentration reported should be the sum of the component Aroclor® equivalents.

DDT Compounds

DDT compounds have become widespread and locally abundant pollutants in coastal and marine environments of North America. The most abundant of these is DDE [2,2-bis(p-chlorophenyl) dicholoroethylene], a derivative of the insecticidal DDT compound, p,p'-DDT. DDE is more stable than other DDT derivatives, and very little information exists on its degradation in ecosystems. All available data suggest that it is degraded slowly. No degradation pathway has so far been shown to exist in the sea, except deposition in sediments.

Experimental studies have shown that DDE induces shell thinning of eggs of birds of several families, including Mallard Ducks (*Anas platyrhynchos*) (Heath et al. 1969),[48] American Kestrels (*Falco sparverius*) (Wiemeyer and P 1970),[77] Japanese Quail (*Coturnix*) (Stickel and Rl 1970)[66] and Ring Doves (*Streptopelia risorial*) (Peakall 1970).[57]

Studies of eggshell thinning in wild populations have reported an inverse relationship between shell thickness and concentrations of DDE in the eggs of Herring Gulls (*Larus argentatus*) (Hickey and Anderson 1968).[50] Double-crested Cormorants (*Phalacrocorax auritus*) (Anderson et al. 1969),[31] Great Blue Herons (*Ardea herodias*) (Vermeer and Reynolds 1970),[70] White Pelicans (*Pelecanus erythrorhynchos*) (Anderson et al. 1969),[31] Brown Pelicans (*Pelecanus occidentalis*) (Blus et al. 1972;[36] Risebrough *in press* 1972),[62] and Peregrines *Falco peregrinus*) (Cade et al. 1970).[37]

Because of its position in the food webs, the Peregrine accumulates higher residues than fish-eating birds in the same ecosystem (Risebrough et al. 1968).[64] It was the first North American species to show shell thinning (Hickey and Anderson 1968).[50] It is therefore considered to be the species most sensitive to environmental residues of DDE.

The most severe cases of shell thinning documented to date have occurred in the marine ecosystem of southern California (Risebrough et al. 1970)[63] where DDT residues in fish have been in the order of 1–10 mg/kg of the whole fish (Risebrough *in press* 1972).[62] In Connecticut and Long Island, shell thinning of eggs of the Osprey (*Pandion haliaetus*) is sufficiently severe to adversely affect reproductive success; over North America, shell thinning of Osprey eggs also shows a significant negative relationship with DDE Spitzer and Risebrough, *unpublished results*).[78] DDT residues in collections of eight species of fish from this area in 1970 ranged from 0.1 to 0.5 mg/kg of the wet weight (Hays and Risebrough 1972).[47] Evidently this level of contamination is higher than one which would permit the successful reproduction of several of the fish-eating and raptorial birds.

Recommendation

It is recommended that DDT concentrations in any sample consisting of a homogenate of 25 or more fish of any species that is consumed by fish-eating birds and mammals, within the same size range as the fish consumed by any bird or mammal, be no greater than 50 µg/kg of the wet weight. DDT residues are defined as the sum of the concentrations of p,p'-DDT, p,p'-DDD, p,p'-DDE and their ortho-para isomers.

Aldrin, Dieldrin, Endrin, and Heptachlor

Aldrin, dieldrin, endrin, and heptachlor constitute a class of closely related, highly toxic, organochlorine insecticides. Aldrin is readily converted to dieldrin in the environment, and heptachlor to a highly toxic derivative, heptachlor epoxide. Like the DDT compounds, dieldrin may be dispersed through the atmosphere (Tarrant and Tatton 1968,[68] Risebrough et al. 1968).[64] The greatest hazard of dieldrin is to fish-eating birds such as the Bald Eagle (*Haliaeetus leucocephalus*) (Mulhern et al. 1970);[56] the Common Egret (*Casmerodius albus*) (Faber et al. 1972)[43] and the Peregrine (*Falco peregrinus*) (Ratcliffe 1970),[60] which may

accumulate lethal amounts from fish or birds that have not themselves been harmed.

These compounds are somewhat more soluble in water than are other chlorinated hydrocarbons such as the DDT group (Gunther et al. 1968);[46] partition coefficients between water and fish tissues can be assumed to be lower than those of the DDT compounds. Equivalent concentrations in fish would therefore indicate higher environmental levels of dieldrin, endrin, or heptachlor epoxide than of DDE or any of the other DDT compounds. Moreover, these compounds are substantially more toxic to wildlife than are other chlorinated hydrocarbon pesticides (Tucker and Crabtree 1970).[69] More conservative recommendations are therefore necessary.

Recommendation

It is recommended that the sum of the concentrations of aldrin, dieldrin, endrin, and heptachlor epoxide in any sample consisting of a homogenate of 25 or more whole fish of any species that is consumed by fish-eating birds and mammals, within the size range consumed by any bird or mammal, be no greater than 5 µg/kg of the wet weight.

Other Chlorinated Hydrocarbon Pesticides

Other chlorinated hydrocarbon insecticides include lindane, chlordane, endosulfan, methoxychlor, mirex, and toxaphene. Hexachlorobenzene is likely to have increased use as a fungicide as mercury compounds are phased out. This compound is toxic to birds and is persistent (Vos et al. 1968).[73] With the possible exception of hexachlorobenzene, recommendations that protect the invertebrate and fish life of estuaries from injudicious use of these pesticides will also protect the wildlife species. In light of the experience with DDT and dieldrin, the large scale use of a compound such as mirex can be expected to have adverse effects on wildlife populations.

Recommendation

It is recommended that the concentration of any of these chlorinated hydrocarbon insecticides, including lindane, chlordane, endosulfan, methoxychlor, mirex, and toxaphene, and of hexachlorobenzene, in any sample consisting of a homogenate of 25 or more whole fish of any species that is consumed by fish-eating birds and mammals, with the size range that is consumed by any bird or mammal, be no greater than 50 µg/kg of the wet weight.

Lead

No data was found to indicate that lead released into the atmosphere through the combustion of leaded gasolines has posed a hazard to wildlife populations or has resulted in an

increase in body burdens of lead over background levels. Critical studies, however, have not yet been carried out. Ingestion of lead shot by waterfowl, which often mistake spent lead shot for seed or grit, kills many birds, and the pollution of marshes by lead shot is a serious problem.

Jordan (1952)[54] found that female waterfowl are about twice as sensitive to poisoning as males, and that toxicity varied greatly, depending on species, sex, and quantity and quality of food intake. A corn diet greatly increased the toxicity of lead. A study carried out by Bellrose (1951)[34] indicated that the incidence of lead shot in gizzards of waterfowl averaged 6.6 per cent in 18,454 ducks. Among infected ducks, 68 per cent contained only one shot in their gizzards, and only 17.7 per cent contained more than two (Jordan and Bellrose 1951).[55] The incidence of ingested shot appears to increase throughout the hunting season with a subsequent decline afterwards. Most losses of waterfowl due to ingested lead shot are in fall, winter, and early spring (Jordan 1952).[54] Different species show different propensities to ingest shot. Redhead (*Aythya americana*), Canvasback (*Aythya valisneria*) and Ringnecked Ducks (*Aythya collaris*) are prone to ingest shot, while Gadwall (*Anas strepera*), Teal (*Anus* sp.) and Shoveler (*Spatula clypeata*) show a low incidence. Ingestion of one shot does not appear to produce measurable changes in longevity, but six No. 6 shot are a lethal dose to Mallards, Pintail (*Anus acuta*) and Redheads (Wetmore 1919).[76] Cook and Trainer (1966)[42] found that four to five pellets of No. 4 lead shot were a lethal dose for Canada Geese (*Branta canadensis*). On a body weight basis, 6 to 8 mg/kg/day is detrimental to Mallards (Coburn et al. 1951).[39]

Lead concentrations in livers of poisoned birds are of a comparable order of magnitude, ranging from 9 to 27 mg/kg in Canada Geese (Adler 1944),[29] 18 to 37 mg/kg in Whistling Swans (*Olor columbianus*) (Chupp and Dalke 1964)[38] and an average of 43 mg/kg in Mallards (*Anas platyrhynchos*) (Coburn et al. 1951).[39] These levels are 10 to 40 times higher than background, which is in the order of one mg/kg of the wet weight liver (Bagley and Locke 1967).[33]

Lead poisoning in waterfowl tends to occur especially in areas where a few inches of soft mud overlay a hard substrate. In marshes where waterfowl are hunted, the number of lead pellets per acre of marsh bottom is on the order of 25,000 to 30,000 per acre and is frequently higher (Bellrose 1959).[35] 30,000 pellets per acre are equivalent to 0.7 pellets per square foot.

The data examined indicate that the annual loss is between 0.7 per cent and 8.1 per cent of a population estimated to be 100 million birds. Although there is apparently no evidence that a loss of this magnitude has long-term detrimental effects on any species, it is considered unacceptable. Levels of lead shot in the more polluted marshes should therefore be reduced. The ultimate solution to this problem is the production of non-toxic shot.

Recommendation

In order to reduce the incidence of lead poisoning in freshwater and marine waterfowl, it is recommended that: non-toxic shot be used, or that no further lead shot be introduced into zones of shot deposition if lead shot concentrations exceed 1.0 shot per 4 square feet in the top two inches of sediment.

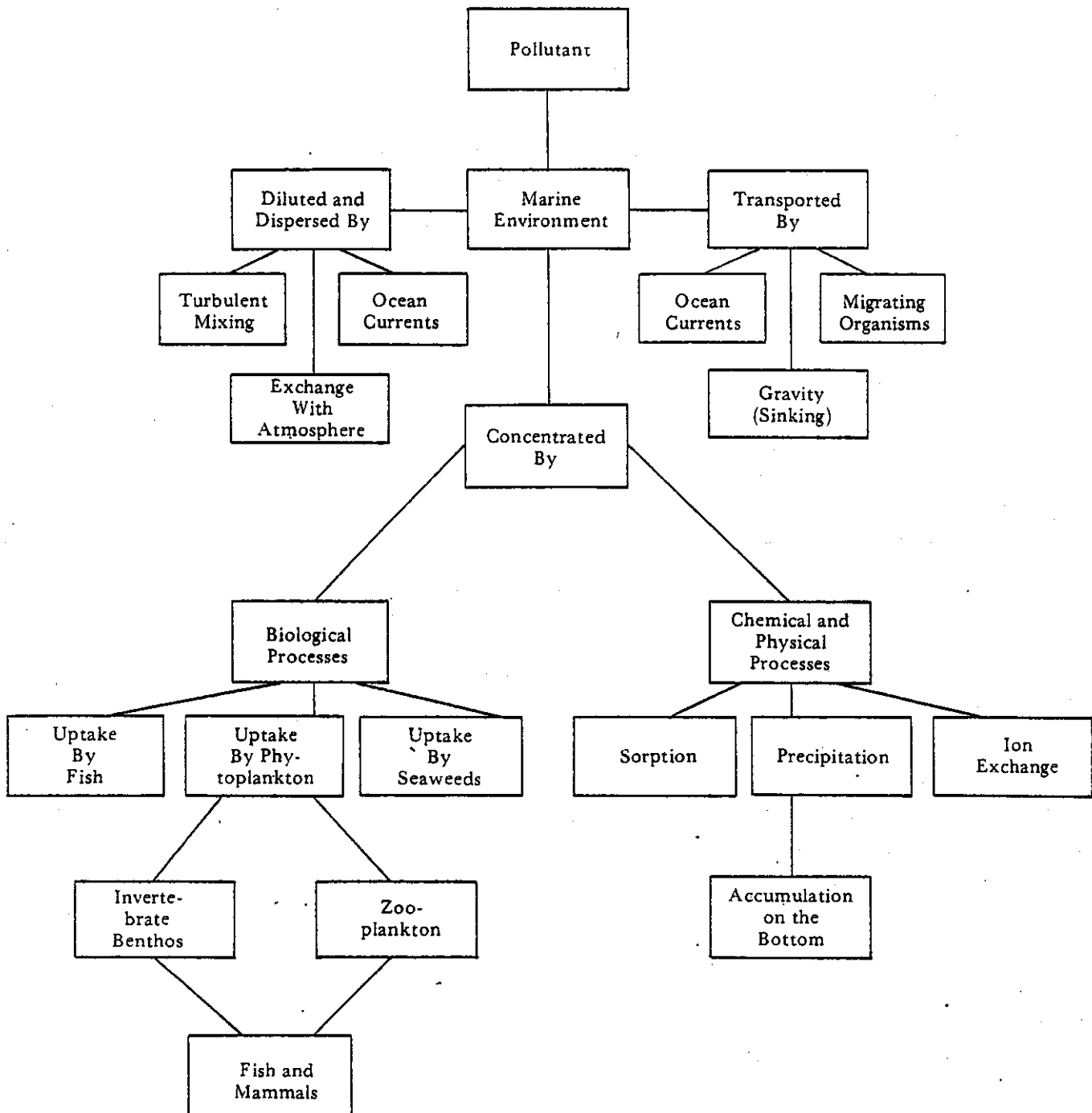## WASTE CAPACITY OF RECEIVING WATERS

When waste disposal to any natural body of water is considered, the receiving capacity of the environment must be taken into account. Waste disposal has been one of the many uses man has required of estuaries and coastal waters. These waters are capable of assimilation of definable quantities and kinds of wastes that are not toxic and that do not accumulate to unacceptable levels. In many locations wastes are being added to these waters at rates that exceed their capacity to recover; and when the rate of addition exceeds the recovery capacity, the water quality deteriorates rapidly. It is essential to understand the local conditions and the processes that determine the fate, concentration, and distribution of the pollutant in order to determine the amount of the pollutant and the rate of disposal that will not exceed the recommended levels.

A simplified diagram of the various processes that may determine the fate and distribution of a pollutant added to the marine environment is presented in Figure 1 (Ketchum 1967).[82] The waste material may be diluted, dispersed, and transported by various physical processes, such as turbulent mixing, ocean currents, or exchanges with the atmosphere. It may be concentrated by various biological processes, such as the direct uptake by organisms of a dissolved material in the water, and it may be transferred from organism to organism in various trophic levels of the food web. Additional concentration of the material may occur at the higher trophic levels, particularly if some organ or tissue of the body accumulates the substance, such as DDT or petroleum products that accumulate in the fatty tissues, various metals that may accumulate in the bone or liver, and iodine which accumulated in the thyroid.

Substances can also be concentrated from the environment by chemical, physical, and geological processes such as sorption. Natural waters contain a certain amount of suspended material, and some material added to the water may be sorbed on these particles. In sea water, which already contains in solution most of the known elements, added materials may be precipitated from the water by various chemical reactions. As fresh waters carry pollutants to the sea, the change in salinity causes flocculation of some of the materials suspended in the fresh water and results in their precipitation from the medium. Ion exchange reactions with the various organic compounds dissolved in sea can also occur.

The average concentration of a given pollutant continuously added to a body of water, will tend to approach a ~~te~~ ~~·tate~~ in the system. This concentration is determined by the rate of addition of the pollutant, the rate of its removal or dilution by the circulation, and the rate of its decomposition or removal by biological, chemical, or geo-

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                          ┌──────────────┐
                          │  Pollutant   │
                          └──────┬───────┘
                                 │
        ┌────────────────────────┼────────────────────────┐
┌───────────────┐        ┌──────────────┐          ┌───────────────┐
│ Diluted and   │────────│   Marine     │──────────│  Transported  │
│ Dispersed By  │        │ Environment  │          │      By       │
└───────┬───────┘        └──────┬───────┘          └───────┬───────┘
    ┌───┴────┐                  │                  ┌────────┴─────┐
┌─────────┐ ┌─────────┐    ┌──────────┐      ┌──────────┐  ┌───────────┐
│Turbulent│ │ Ocean   │    │Concentra-│      │ Ocean    │  │ Migrating │
│ Mixing  │ │Currents │    │ted By    │      │Currents  │  │ Organisms │
└─────────┘ └─────────┘    └──────────┘      └──────────┘  └───────────┘
     ┌──────────┐                                  ┌──────────┐
     │Exchange  │                                  │ Gravity  │
     │With      │                                  │(Sinking) │
     │Atmosphere│                                  └──────────┘
     └──────────┘
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tchum 1967[82]

FIGURE IV-1—Processes That Determine the Fate and Distribution of a Pollutant Added to the Marine Environment.

logical processes. The average concentration is not always the critical concentration to be evaluated. For example, if bioaccumulation occurs, the amount accumulated in the critical organism should be evaluated, rather than the average concentration in the system as a whole. The processes of circulation and mixing may leave relatively high concentrations in one part of the system and low concentrations in another. The average conditions thus set an upper limit on what can be added to the system but do not determine the safe limit. It is clear, however, that a pollutant might be added to a body of water with vigorous circulation at a rate that could result in acceptable water quality conditions, while the same rate of addition of the pollutant to a sluggish stream might produce unacceptable levels of contamination. Thus, the characteristics of the receiving body of water must be taken into account when evaluating the effects of the pollutant upon the environment.

In a stream, the diluting capacity of a system is relatively easy to determine from the rate of addition of the pollutant and the rate of stream flow. The pollutant is carried downstream by the river flow, and "new" water is always available for the dilution of the pollutant. This is not necessarily true of lakes where the pollution added over a long period of time may accumulate, because only a small fraction of the added pollutant may be removed as a result of flushing by the outflow. In estuaries, the situation is further complicated by the mixture of salt and fresh water, because a pollutant added at a mid-point in the estuary can be carried upstream by tidal mixing just as the salt is carried upstream. The upstream distribution of a conservative pollutant is porportional to the upstream distribution of salt, whereas the downstream distribution of the pollutant is proportional to the downstream distribution of fresh water.

In either lakes or estuaries, the average retention time or the half-life of the material in the system can be used to estimate the average concentration that the pollutant will achieve in the system. In lakes, an estimate of the average retention time can be derived from the ratio of the volume of the lake divided by the rate of inflow (or outflow). When the lake is stratified, only part of the volume of the lake enters into the active circulation, and an appropriate correction must be made. In estuaries and coastal waters, a similar calculation can be made by comparing the volume of fresh water in the estuary with the rate of river inflow. The amount of fresh water in any given sample can be computed from the determination of salinity. In stratified estuaries such as a fjord, only the part of the system that is actively circulated should be taken into account. This may be adequately done by the choice of the appropriate base salinity in computing the fresh water content. Examples of the mean retention time of a few bodies of water calculated as described above are presented in Table IV-1.

Lakes with large volumes superficially appear to have a great capacity to accept waste materials. If the retention time is long, however, this merely means that it takes a long

TABLE IV-1—Average Retention Times and Half Lives for River Water in the Great Lakes and in Various Estuaries and Coastal Regions

	Surface area mi²	Mean retention time	Half life	Reference
Lake Superior......	31,820	183 yrs.	128 yrs.	Beeton (1969)[79]
Lake Michigan......	22,420	100 yrs.	69 yrs.	Beeton (1969)[79]
Lake Huron......	23,010	30 yrs.	21 yrs.	Beeton (1969)[79]
Lake Erie......	9,930	2.8 yrs.	1.9 yrs.	Beeton (1969)[79]
Lake Ontario......	7,520	8 yrs.	5.6 yrs.	Beeton (1969)[79]
Continental Shelf				
Capes Cod to Hatteras to 1,000 ft. contour	29,000	1.6-2.0 yrs.	1.1-1.4 yrs.	Ketchum and Keen (1955)[64]
New York Bight......	483 to 662	6.0-7.4 days	4.1-5.05 days	Ketchum et al. (1951)[65]
Bay of Fundy......	3,300	76 days	52 days	Ketchum and Keen (1953)[63]
Delaware Bay				
high river flow......		48-128 days	33-87 days	
low river flow......				Ketchum (unpublished) (1952)[67]
Raritan Bay				
high river flow......	45	15-30 days	10-21 days	Ketchum (1951a,[60] b[61])
low river flow				
Long Island Sound......	930	36 days	25 days	Riley (1952)[86]

time to build up to steady-state concentration, and it will take a comparably long time to recover from a steady-state concentration once it is achieved. For Lake Superior, for example, it would take 128 years to remove half of the steady-state concentration of a pollutant that had been achieved over 185 years at the average rate of input. Aquatic environments in which the circulation is more rapid will achieve a steady-state concentration of a pollutant more quickly and will also recover more quickly.

Nonconservative pollutants are those that change with time by processes which are additional to circulation and dilution. The half-life of these substances in the environment is the product of these processes and the processes of circulation and dilution. For radioactivity, for example, the half-life is the time needed for the normal radioactive decay to dissipate half of the radiation of the material. This is different for each radioisotope and may vary from fractions of a second to centuries. The half-life for the decomposition of the organic matter in sewage in marine systems is probably on the order of days and will be dependent on temperature. The decomposition of sewage, however, releases the fertilizing elements in the organic molecule, and these will persist in the environment. In contrast to these rapid changes, the half-life of the chlorinated hydrocarbon pesticides is probably of the order of 10 years in the marine environment, though this is an estimate and not a direct determination. Heavy toxic metals, which may also pollute the environment, do not decay but persist indefinitely, though their location and forms in the system may change with time.

The greatest pollution danger arises from the addition of persistent materials to those ecosystems with slow circulations. Under these conditions, the waste concentration will increase slowly until a steady-state level is reached. If c.

ation is more rapid, the system will reach steady-state more quickly, but the concentration for a given rate of addition will be less. If the material is not persistent, the rate of deposition may be more important than circulation in determining the steady-state concentration. If the products of decomposition are persistent, however, these will accumulate to levels greater than those in the original discharge. Local concentrations, such as can be found in the deeper waters of stratified systems or in trapping embayments, may be more significant than the average concentration for the whole system. In short, the recommendations cannot be used to determine the permissible amount of a pollutant to be added or a rate of addition without detailed knowledge of the specific system which is to receive the waste.

Mixing Zones

When a liquid discharge is made to a receiving system, a zone of mixing is created. In the past, these zones have frequently been approved as sites of accepted loss, exempted from the water quality standard for the receiving water. Physical description, biological assessment, and management of such zones have posed many difficult problems. The following discussion deals with criteria for assuring that no significant damage to marine aquatic life occurs in such mixing zones. Although recent public, administrative, and scientific emphasis has focused on mixing zones for the dispersion of waste heat, other uses of the mixing zone concept are also included in these considerations.

Definition of a Mixing Zone A mixing zone is a region in which an effluent is in transit from the outfall source of the receiving waters. The effluent is progressively diluted, but its concentration is higher than in the receiving waters.

Approach to the Recommendation Mixing zones must be considered on a case-by-case basis because each proposed site involves a unique set of pertinent considerations. These include the nature, quantity, and concentration of the effluent material; the physical, chemical and biological characteristics of the mixing area and receiving waters; and the desired uses of the waters. However, the following general recommendation can be established for the purpose of protecting aquatic life in areas where effluents are mixing with receiving waters:

The total time-toxicity exposure history must not cause deleterious effects in affected populations of important species, including the post-exposure effects.

Meeting the Recommendation Special circumstances distinguish the mixing zone from the receiving waters. In the zone, the duration of exposure to an effluent may be quite brief, and it is usually substantially shorter than in the receiving waters, so that assays involving long periods of exposure are not as helpful in predicting damage. In addition, the concentration of effluent is higher than in receiving waters. Therefore, the development of specific

requirements for a specific mixing zone must be based upon the probable duration of the exposure of organisms to the effluent as well as on the toxicity of the pollutant.

The recommendation can be met in two ways: use of a probably-safe concentration requirement for all parts of the mixing zone; or accurate determination of the real concentrations and duration of exposures for important species and good evidence that this time-toxicity exposure is not deleterious. The latter, more precise approach to meeting the recommendation will require:

- determination of the pattern of exposure of important species to the effluent in terms of time and concentration in the mixing zone;
- establishment of the summed effects on important species;
- determination that deleterious effects do not occur.

Complexities in the Marine Environment Some of the problems involved in protecting marine aquatic life are similar to those in lacustrine and fluvial fresh waters and, in general, the recommendations in Section III, pp. 112–115 are applicable to marine situations. There are, however, special complexities in evaluating mixing zones in coastal and oceanic waters. These include:

- the exceptional importance of sessile species, especially in estuaries and near shore, where effluents originate;
- the presence of almost all species in the plankton at some stage in the life history of each, so that they may be entrained in the diluting waters;
- obligate seasonal migrations by many fish and some invertebrates;
- oscillation in tidal currents, mixing mechanisms and in resulting concentrations, dilution rates, and dispersion patterns.

None of these affect the general recommendation, but they do contribute to the difficulty of applying it.

Theoretical Approach to Meeting the Recommendation Any measure of detrimental effects of a given concentration of a waste component on aquatic or marine organisms is dependent upon the time of exposure to that waste concentration, at least over some restricted but definable period of time. For a given species and substance, under a given set of environmental conditions, there will be some critical concentration below which a particular measure of detrimental effects will not be observed, regardless of the duration of exposure. Above the critical concentration, the detrimental effects will be observed if the exposure time is sufficiently long. The greater the concentration of the substance, the shorter the time of exposure to cause a specified degree of damage. The water quality characteristics for mixing zones are defined so that the organisms to be protected will be carried or move through the

zone without being subjected to a time-exposure history that would produce unacceptable effects on the population of these species in the water body.

In order to quantify this statement, the following quantities are defined:

T50,C,E = time of exposure of a critical aquatic or marine species to a concentration, C, of a given pollutant, under a constant set of environmental conditions, E, which produces 50 per cent mortality of the critical species.

T0,C′,E = time of exposure of a critical aquatic or marine species to a concentration, C′, of a given pollutant, under a constant set of environmental conditions, E, which produces *no unacceptable* effects on the critical species.

For some pollutants, C and C′ for a given time of exposure may be related by:

$$C' = C - \Delta C_0$$

where ΔC_0 is the amount by which the concentration which produces a 50 per cent mortality must be decreased in order that *no unacceptable* effects of the pollutant on a given critical species will occur. For example, in the case of temperature, it has been shown that at temperatures 2 C below those which produce a 50 per cent mortality, no observable detrimental effects occur. For temperature, then, 2 C is a conservative value of ΔC_0.

For other pollutants, notably chemical toxicants, C′ is related to C by the relationship:

$$C' = k \cdot C$$

where k is the ratio of the concentration at which *no unacceptable* effects occur to the concentration which produces a 50 per cent mortality with both concentrations determined over the same exposure time.

It is difficult to establish with statistical confidence a relationship.between T0, C′, E and C′, for a large number of species, by direct laboratory experiments. However, laboratory experiments can be used to determine, for the critical species of the receiving waterbody, the relationship between pollutant concentration and the time period of exposure necessary to produce a 50 per cent mortality. Thus, it is necessary to obtain, by experiment, the form and constants of a function of the pollutant concentration, $f_1(C)$, such

that

$$T50, C, E = f_1(C).$$

Conservative estimates of ΔC_0 or of k can be obtained dependent upon decisions as to acceptable effects from additional laboratory studies. Once ΔC_0 or k have been established, the relationship $C' = C - \Delta C_0$, or the relationships $C' = k \cdot C$, depending on the properties of the particular waste materials, can be combined with the above equation relating T50, C, E and C, to produce an equation relating T0, C′, E and C′. That is:

$$T0, C', E = f_2(C').$$

This equation gives the maximum time that a particular species could be exposed to a concentration C′ without resulting in unacceptable effects on the population of this species. The water quality recommendations for the mixing zone are satisfied if, for any organisms carried through the mixing zone with the flow or purposefully moving through the zone, the time of exposure satisfies the relationship

$$1 \geqslant \frac{\text{time of exposure}}{f_2(C')}$$

where C′ is the concentration of a specified pollutant in the mixing zone.

Because, in fact, the concentration in the mixing zone decreases with distance from the point of discharge, and hence organisms carried through the plume will be subjected to concentrations which are continually decreasing with time, a more suitable quantitative statement of water quality characteristics necessary for the mixing zone is:

$$1 \geqslant \frac{\Delta T1}{f_2(C'_1)} + \frac{\Delta T2}{f_2(C'_2)} + \frac{\Delta T3}{f_2(C'_3)} \cdots \frac{\Delta Tn}{f_2(C'_n)}$$

where the time of exposure of an organism passing through the mixing zone has been broken into n increments, $\Delta T1$, $\Delta T2$, $\Delta T3$, etc. long. The organism is considered to be exposed to concentration C'_1 during the time interval $\Delta T1$, to concentration C'_2 during the time interval $\Delta T2$, etc. The sum of the individual ratios must then not exceed unity.

The above theory is applied in the recommendations and examples in Section III on Freshwater Aquatic Life and Wildlife, pp. 112–115, and in the Freshwater Appendix II-A, pp. 403–407.

METHODS OF ASSESSMENT

It is the purpose of this discussion to explain the approaches considered in deriving the recommendations given this Section. Because the biological effects of a pollutant e manifest in a variety of ways, the specific technique to : used in estimating biological impact must be tailored to ich specific problem. For example, acute or lethal toxicity a given pollutant to a marine species can be evaluated by ort-term bioassay in the laboratory designed to deter- ine the concentration of the material which is lethal to alf of the selected population in a fixed period of time, mmonly four days (LC50-96 hours). The "safe" limit ill be much lower than the concentration derived in such bioassay, and appropriate safety factors must be applied. h limit should permit reproduction, growth, and all or. life processes in the natural habitat.

When a pollutant is discharged to the environment at a ife concentration determined in this way, the living or- anisms are exposed to a chronic, sublethal concentration. ome stages of the life cycle of the species to be protected, ich as the eggs or larvae, may be more sensitive than the dult stages. It is sometimes possible to identify the critical fe stage which can then be used in a bioassay. Long-term ioassays covering a substantial part of the life cycle of the rganism can be conducted in the laboratory to determine hronic sublethal effects of pollutants. Various processes i the organism, such as respiration, photosynthesis, or ctivity may be used to evaluate sublethal effects. Some ongterm chronic effects may be more subtle and more diffi- ult to evaluate under laboratory conditions. Examples of his type include changes in breeding or migratory behavior r the development of a general debility making the orga- isms more suceptible to disease, predation, or to environ- nental stresses.

A pollutant in the marine environment may also have an ffect on the ecosystem not directly associated with its effect in an individual species. Ecosystem interactions are diffi- ult to assess in the laboratory, and techniques for evaluat- ng them in the field are not completely satisfactory. Such nt tions must be considered, however, in applying e endations to any specific situation.

ACUTE TOXICITIES—BIOASSAYS

Detailed methods for laboratory bioassays are described in Section III, Freshwater Aquatic Life and Wildlife, and can serve as guidlines for application to the marine system. The ability to extrapolate from results of bioassay tests is limited, and the need for safety factors in their application to the environment must be emphasized. The methodologies discussed are illustrative and should be considered as guide- lines for meaningful bioassays.

The most important uses of bioassays for evaluating water quality are:

- analysis of the concentration of a specific material in natural waters by means of a biological response;
- detection of toxic substances in organisms used as food for man;
- analysis of the suitability of natural waters for the support of a given species or ecosystem;
- determination of critical toxic levels of substances to selected species;
- evaluation of bio-stimulation effects by materials such as nutrients.

These purposes fall into two general categories: bio- analysis and bioresponse.

BIOANALYSIS

Bioanalysis has been used for many years to measure effects of substances on organisms. These assays may give quantitative measurements, such as weight per volume, or be expressed in arbitrary units defined by the degree of response. They are most valuable when the organism re- sponds to a lower concentration than can be detected by available chemical or physical techniques. Such bioassays require carefully controlled procedures, and organisms and experimental conditions must be standardized. Responses are used that have been shown to have a correlation with the amount of test substance present. Preparation of test materials is rigidly controlled to avoid problems arising from synergists or antagonists administered with the test

material. This is difficult and often impossible in the bioassay of materials obtained from the environment.

Bioanalysis has potential in measuring pollutants in materials to be discharged to the environment. For toxic materials, the amount of material relative to the biomass of the test organism must usually be controlled, because most toxicants exhibit a threshold effect. *It is usual to determine the concentration of material at which some fraction of the maximal effect* (commonly 50 per cent) occurs in a population of known and constant biomass. The fact that far lower concentrations present for a longer time might ultimately produce the same effect does not invalidate this type of assay, because quantitation is obtained by comparison with standard curves. It should, however, be realized that in the presence of detoxification mechanisms, the assay should be conducted for a period of time at which the desired effect (such as 50 per cent inhibition) occurs at the lowest possible concentration.

In assays of materials for which an organism has a natural or induced requirement, it must first be established that of all substances which could be present in the sample, only one can produce the response measured. Second, no substances present should reduce the availability of the material. *If the first of these conditions is satisfied, the second can often be approached using a "system of adds"* in which a graded series of concentrations of standard material are added to the unknown amount of material in the sample. The intercept of the response curve with the concentration axis is a measure of the amount present in the sample.

If zero response is at a finite concentration, a biologically effective threshold concentration (zero) must be used which has been derived from a separate experimental series in the same medium devoid of unknown amounts of test material.

BIORESPONSE

Bioassays which measure the biological *effect* of a substance or mixture on a single organism or artificial ecosystem can be used to establish water quality criteria, to monitor compliance with standards stated in terms of biological effect, *or to measure the relative effects of various materials*. Natural processes of equilibration, chemical degradation, and physical adsorption are specifically desired, because it is the biological *effect* rather than the *amount* of test material that is of concern. The observed effect will be determined by the availability of the material, the rate of formation or degradation, and the effect of chemical by-products; and by alterations of the environment caused by addition of the material. Whether conducted in the laboratory or in the field, this type of bioassay is performed on time scales varying from determinations of acute toxicity (commonly 96 hours or less) through determinations of incipient LC50 levels (Sprague 1969,[94] 1971[96]), and on time scales which include multiple generation chronic exposures. Each of these has its own utility and limitations.

Short-term determinations of TLm or TL50 values are primarily of value in comparing toxicities of a number of formulations which have similar modes of action. They are also useful in determining the dilution to be employed long-term, flow-through exposure and in comparing sensitivities of various life stages of the same organism. In practical terms, each life stage must be considered a physiologically distinct organism with its own particular environmental requirements: immature stages commonly have quite a different habitat and may have different sensitivity.

It has been common practice to use information from acute toxicity studies to establish concentrations tolerable for natural waters. This is done by multiplying the level found in the bioassay by *some more or less arbitrary "application factor"* (Henderson 1957,[91] Tarzwell 1962[97]). Recently, there have been attempts to establish the application factor experimentally (Mount 1968,[92] Brungs 1969[90]). Application factors are discussed in Section III, Freshwater Aquatic Life and Wildlife, and that discussion is applicable to the marine system. If, in the process of conducting these assays, organisms are periodically removed to an uncontaminated medium, the time of exposure which the organism can withstand and still survive, should it escape the pollutant or should the pollutant degrade rapidly after a single addition, can also be estimated.

Determination of incipient LC50 is a valid measurement of acute toxicity, because the assay is continued until maximum effect is observed at any given concentration (Sprague 1969,[94] 1970,[95] 1971[96]). These bioassays must be condu under conditions of continuous flow, because the degree response cannot be limited by the absolute amount of toxicant available in the system or by the relationship between biomass and absolute amount. In practice, the technique is most applicable to compounds which reach equilibrium rapidly. Otherwise, it takes a long time to achieve maximum effect at low toxicant levels. Here, too, application factors are needed to use data from bioassayed concentrations in estimating levels for environmental protection. Theoretically, application factors account for variations in sensitivity between the life stage tested and that life stage or developmental period during which the organism is most sensitive to the compound or conditions. Application factors should also safely permit a range of naturally-occurring environmental variations that would increase sensitivity.

Long-term bioassay, in which the organism is kept through at least one complete life cycle under conditions of continuous-flow exposure, is perhaps the closest but most conservative laboratory approach to estimating environmental hazards. Where a chemical or physical attraction occurs or where the population is sessile or restricted by hydrographic features, continuous exposure to freshly added material will be a realistic model. However, where the organism might escape in nature, such a captive exposure will be unrealistic. The experimental cond' s chosen may either be held constant or varied to ap

late local natural changes or intermittent discharges to be expected. Adequate modelling of a particular environmental circumstance often requires varying degrees of delay between the time of test material addition and exposure of the organisms.

Duration of chronic toxicity studies is determined by the life span and reproductive cycle of the organism chosen. Micro-organisms have relatively short life cycles but may require several generations to deplete metabolite reserves and show maximum response. A greater variety of measurements can be used in long-term than in short-term testing. This variety, together with the longer period available for response and the certainty of testing the most sensitive life stage, serves to increase both the sensitivity and relevance of such tests. Differences in sensitivity between species, that may be evident in short-term tests, tend to narrow as the tests approach a full life cycle.

The maintenance of a resident population of sensitive organisms in an effluent stream or portion of a natural stream receiving effluent, can create a long-term flow-through bioassay. This technique is primarily useful as a verification of safety based on other estimates, but because the response time may be long, the results are of little use where rapid feedback of information is essential.

DESIGN OF BIOASSAYS

The bioassay system may be compartmentalized for purposes of design into (1) the substance to be tested, (2) the environment into which it will be introduced, (3) the organism(s) which will be exposed to the resultant system, and (4) the observations to be made. Each affects and is affected by the others.

The chemical and physical nature of the material to be tested has a bearing on the way it will distribute in nature and in the test system—and thus on which organisms will encounter it and in what form it will be. For example, a pure substance, highly soluble in water, may be tested for its effect directly on organisms inhabiting the water column. A material which precipitates rapidly may be readily available to organisms which ingest the precipitate and resolubilize it under conditions prevailing in the digestive tract. Materials which are only slightly soluble are often readily available to micro-organisms which have a high surface–area–to–volume ratio and are capable of taking up some substances at exceedingly low (10^{-8} to 10^{-10} M) concentrations. A highly hydrophobic material which is readily adsorbed to sediments or detritus may appear in free solution to only a limited extent or for a short time and exert a prolonged direct effect mainly on those organisms which inhabit sediments or which process sediments or detritus for food. Valid interpretation of bioassay results requires sensitive and highly specific analytical chemistry as part of the procedure. Results obtained for any bioassay organism are subject to question if anomalous behavior of

the substance tested or the organisms used are subsequently established.

The organism for bioassay should be chosen on the basis of the relationship of its life stages to the various toxicant compartments and information desired. Organisms will be useful if they are readily available and can be reared and propagated in the laboratory. The size of the organisms in relation to available facilities will in part dictate a choice. All too often, these have been the primary if not the only considerations. There is a temptation to give priority to organisms that are available from standard sources with a known genetic line or from a single clone. This approach is essential when using bioassay as an analytical tool. However, it is a distinct liability when performing measurements of biological effect in natural environmental situations. Such organisms have necessarily undergone selection for traits that favor survival in artificial environments with no selective advantage given to the capacity to adapt to alterations in those environments. Furthermore, physiologically distinct races often develop in nature in response to characteristics of different localities. Maintenance of laboratory stocks may be necessary, but these stocks should be frequently renewed from fresh isolates representing the gene pool and enzymatic adaptations of the inhabitants of the particular water mass to which recommendations are to be applied.

The organisms used should be drawn from those that are most sensitive or respond most quickly to the substance or condition being tested. Bioassays of various life stages of these sensitive organisms are desirable. It is especially important that life stages to be tested include those that will most probably encounter the test material as it is expected to be found in the environment, and that the test organisms be acclimated to the test system until the characteristics to be measured become constant.

Some of the foregoing recommendations for selection assume that the developmental biology of the test organism is known. This is not often so in marine biology. Organisms should not be excluded from consideration if their absence would leave no representatives of local species which tolerate the extremes in ranges of natural environmental stress or which fill an important ecological niche.

Once an understanding of both the test material and the bioassay organism is established, a test system usually can be designed that will permit the organism to encounter the test material under circumstances approximating those in nature. In some cases it will be necessary to go to the natural water system or to impoundments, live cars, or plastic bags in order to obtain a workable approximation of environmental exposure. Care should be taken that the physical system does not interfere with the distribution of the test material or the behavior of the organism. The system selected should reflect in all important aspects the habitat to which the test organism has become adapted. Factors of importance include feeding behavior, opportunity for diurnal

behavior alterations, emergence, salinity variations, turbidity, water movement, and other factors, depending on the organisms being studied.

The response or responses to be observed during long-term testing must be carefully chosen. A prime requirement is that the response being measured bear a demonstrable and preferably quantitative relationship to the survival and productivity of the test organism or of an organism which is directly or indirectly dependent on its activities. For example, a correlation may exist between the level of a test material and the amount of an enzyme present in some tissue. This is clear evidence that the organism's pattern of energy utilization has changed, but it should be demonstrated that the change in enzyme level is correlated with or predictive of changes in growth, behavior, reproduction, quality of flesh, or some other manifestation to provide an immediately meaningful interpretation.

The degree to which a response can be reported in quantitative terms affects its usefulness. Behavior, because of a high degree of variability, is much more difficult to express numerically than growth; and growth measurements are usually disruptive of the system or destructive of the organism. A balance must be sought for each system so that enough organisms and replicate treatments can be used to assure an acceptable level of statistical confidence in the results. Considerations of equipment required, rapidity, and simplicity of measurements, the inherent (control) variability of the characteristic being measured, and possible interference with the measurement by the substance being tested must enter into the choice of measurements and their frequency.

Biological characteristics that can be measured are innumerable, but some may be singled out as being more basic than others. When a given characteristic reflects many diverse processes, it is most useful in interpreting results in terms of environmental protection. Thus, measurements of reproductive success, growth, life span, adaptation to environmental stress, feeding behavior, morphology, respiration, histology, genetic alterations, and biochemical anomalies occupy a descending scale in order of the confidence that can be placed in their interpretation. This is not to say that profound changes in the structure and function of an ecosystem cannot result from subtle, prolonged, low intensity effects on some cellular process. The elimination of important species by low intensity selective factors is no less serious than instantaneous death of those species. In a sense, it is more serious, because it is less likely to be noticed and traced to its source in time to permit recovery of the ecosystem.

SUBLETHAL EFFECTS

Many biological effects of pollution may not show up in the bioassay test for acute toxicity. This would be true if the effect were slow to develop, or if the effect were to produce a general debility that might interfere with some of the normal life functions of the organism rather than killing it directly. Long-term exposure to sublethal concentrations may be necessary to produce the effect, and evaluation this type of action is difficult in a laboratory analysis. There are a number of ways in which pollutants might affect a given population without being lethal to the adult organism used in the test such as:

Migrations

Sublethal concentrations may interfere with the normal migration patterns of organisms. The mechanisms used for orientation and navigation by migrating organisms are not well known, but in some cases chemotaxis clearly plays an important role. For example, salmon and many other anadromous fishes have been excluded from their home streams by pollution, though it is not known whether the reason is that a chemical cue has been masked or because the general chemical environment of pollution is offensive to the fish.

Behavior

Much of the day-to-day behavior of species may also be mediated by means of chemotaxic responses. The finding and capture of food or the finding of a mate during the breeding season would be included in this category of activity. Again, any pollutant that interfered with the chemoreceptors of the organism would interfere with behavioral patterns essential to the survival of the population.

Incidence of Disease

Long-term exposure to sublethal concentrations of pollutants may make an organism more susceptible to a disease. It is also possible that some pollutants which are organic in nature may provide an environment suitable for the development of disease-producing bacteria or viruses. In such cases, even though the pollutant is not directly toxic to the adult organism, it could have a profound effect on the population of the species over a longer period of time.

Life Cycle

The larval forms of many species of organisms are much more sensitive to pollution than are the adults, which are commonly used in the bioassay. In many aquatic species millions of eggs are produced and fertilized, but only two of the larvae produced need to grow to maturity and breed in order to maintain the standing stock of the species. For these species the pre-adult mortality is enormous even under the best of natural conditions. Because of an additional stress on the developing organisms, enough individuals might fail to survive to maintain the population of the species. Interrupting any stage of the life cycle can be as disastrous for the population as would death of the a' because of acute toxicity.

Physiological Processes

Interference with various physiological processes, without necessarily causing death in a bioassay test, may also interfere with the survival of the species. If photosynthesis of the phytoplankton is inhibited, algal growth will be decreased, and the population may be grazed to extinction without being directly killed by the toxin.

Respiration or various other enzymatic processes might also be adversely affected by sublethal concentrations of pollutants. The effect of DDT and its decomposition products on the shells of bird eggs is probably the result of interference with enzyme systems (Ackefors et al. 1970).[88] Mercury is a general protoplasmic poison, but it has its most damaging effect on the nervous system of mammals.

Genetic Effects

Many pollutants produce genetic effects that can have long range significance for the survival of a species. Oil and other organic pollutants may include both mutagenic and carcinogenic compounds. Radioactive contamination can cause mutations directly by the action of the radiation on the genetic material. From genetic studies in general, it is known that a large majority of mutations are detrimental to the survival of the young, and many are lethal. Little is known about the intensity or frequency of genetic effects of pollutants, except for radioactive materials where the mutation rates have been measured in some cases. Induction of mutation by contaminants should be reviewed in the context of the increase of total mutation from all causes.

Nutrition and Food Chains

Pollutants may interfere with the nutrition of organisms by affecting the ability of an organism to find its prey, by interfering with digestion or assimilation of food, or by contaminating the prey species so that it is not accepted by the predator. On the other hand, if predator species are eliminated by pollution, the prey species may have an improved chance of survival. An example of the latter effect was shown for the kelp resurgence after the oil spill in Tampico Bay, California (North 1967).[93] The oil killed the sea urchins which used young, newly developing kelp as food. When the urchins were killed, the kelp beds developed luxurious growth within a few months (see p. 258).

Effects on the Ecosystem

The effects of pollution on the aquatic ecosystem are the most difficult to evaluate and establish. Each environment is somewhat different, but the species inhabiting any given environment have evolved over long periods of time, and each individual species in a community plays its own role. Any additional stress, whether natural or man-made, applied to any environment will tend to eliminate some species leaving only the more tolerant forms to survive. The effect may be either direct on the species involved or indirect through the elimination of some species valuable as a food supply. For some of the species in the system the result may be beneficial by the removal of their predators or by stimulated and accelerated growth of their prey.

Food Value for Human Use

Sublethal concentrations of pollutants can so taint seafood that it becomes useless as a source of food. Oil can be ingested by marine organisms, pass through the wall of the gut, and accumulate in the lipid pool. Blumer (1971)[89] stated that oil in the tissues of shellfish has been shown to persist for months after an oil spill; the oil–polluted area was closed for shellfishing for a period of 18 months. Seafood may be rendered unfit for human consumption because of the accumulation of pollutants. California mackeral and coho salmon from Lake Michigan were condemned because they contained more DDT than the permissible amount in human food (5 mg/kg). Likewise tuna fish and swordfish were removed from the market, because the mercury content of the flesh exceeded the allowable concentration (0.5 mg/kg). There was no evidence that these concentrations had any adverse effect on the fish, or in the case of mercury that the concentrations in tuna and swordfish resulted from pollution; nevertheless their removal from the market has adversely affected the economics of the fisheries.

CATEGORIES OF POLLUTANTS

TEMPERATURE AND HEAT

An extensive discussion of heat and temperature is presented in Section III on Freshwater Aquatic Life and Wildlife (pp. 151–171). Although we accept those recommendations concerning temperature, there are certain characteristics of the marine environment that are unique and require enumeration. Some of the characteristics of the marine environment have been discussed in the introduction to this Section showing that the range of variability is greatest in the estuary, considerably less in the coastal waters, and even less in the surface waters of the open ocean; and that conditions in the deep ocean are virtually constant. Among the most important variables shown in the changes is temperature, although salinity variations are *equally important under certain conditions.*

The seasonal range of temperature variations is greatest in the temperate regions and becomes less as one approaches either the tropics or the poles. In the United States, the maximum seasonal temperature variation is found in the coastal waters on the southern side of Cape Cod, Massachusetts, where in winter the water may be freezing at −2.8 C and in summer the inshore coastal waters reach temperatures of 23 C, or even 25 C over wide shoal areas. At the same latitude on the Pacific coast, the water is neither so cold in the winter nor so warm in the summer. North of Cape Cod, the water is as cold in the winter time, but it does not reach as high a summer temperature; and south of Cape Cod the waters rarely reach a freezing point in winter.

Hutchins (1947)[100] discusses these ranges of variations and illustrates how they affect geographical distribution of marine species on the Atlantic European coasts and on the east and west coasts of the United States. As is obvious from the above comments, Cape Cod is a geographical boundary in the summertime but not in winter. Because temperature can control both the breeding cycle and survival of organisms, a variety of different geographical distributions can be dominated by the temperature variations at various locations along the coast (Hutchins 1947).[100]

There is increasing pressure to site power plants in the coastal zone because of the large available supply of water for cooling purposes. In 1969 there were over 86 fossil fuel power plants in the eastern coastal zones (Sorge 1969)[101] and 32 on the west coast (Adams 1969).[98] In addition, nuclear power plants are in operation, and many more are planned for siting on the coast in the future. Provided that the temperatures are kept within the limit prescribed in the recommendations and that the recommendations for mixing zones (pp. 228–232) are complied with, these heated effluents may have no serious impact on the marine environment. However, organisms passing through the cooling system of the power plants may be killed either by the direct effect of temperature, by pressure changes in the system, or by chlorination if it is used to keep the cooling system free of attached growth.

In the tropics, disposal of waste heat in the marine vironment may be impossible in the summertime. B and Roessler (1972)[99] discussed the temperature problems created by the power plants at Turkey Point, near Miami, Florida. Thorhaug et al. (1972)[102] showed that tropical marine organisms live precariously close to their upper thermal limit and are thus susceptible to the stress of additional thermal effluents. To abide by the temperature recommendations in tropical waters, it is generally necessary to prohibit discharge of heated effluents during the summertime.

It is clear from this and from the discussion in Section III that additional studies will be needed on the temperature tolerances of the species directly involved. Organisms from estuaries and marine waters have not been studied as extensively as have freshwater fishes, but some data are included in the tabular material in the freshwater report. On the basis of information available at this time, the marine panel finds that the recommendations in Section III, Freshwater Aquatic Life and Wildlife, appear to be valid for the estuarine and marine waters as well (see pp. 160, 161, 164, 165, and 166–171 of Section III).

INORGANIC CHEMICALS, INCLUDING HEAVY METALS AND pH

The hazardous and biologically active inorganic chcals are a source of both local and world-wide threa

.he marine environment. Certain of these chemicals may ꞁose no immediate danger but may lead to undesirable ꞁong-term changes. Others, such as boron, may pose serious ꞁt hazards and yet have poorly understood biological ffe..s in the marine environment. Nevertheless, they can ꞁe a significant constituent in certain waste waters and .hould be discussed here.

The inorganic chemicals that have been considered in :his study are listed alphabetically in Table IV–2; those most significant to the protection of the marine environment .re discussed below.

TABLE IV-2—Inorganic Chemicals to be Considered in Water Quality Criteria for Aquatic Life in the Marine Environment

Elements	Equilibrium species (reaction)	Natural concentration in sea water[a] μg/l	Pollution categories[b]
Aluminum	Al(OH)₃, solubility of Al₂O₃ approx. 300 μg/l	10	IV c
Ammonia	NH₃, NH₄⁺	....	IV c
Antimony	Sb(OH)₆⁻	0.45	IV c ?
Arsenic	As₂O₃ is oxidized to HAsO₄²⁻	2.6	II c
Barium	Ba²⁺	20	IV c
Beryllium	Be(OH)₂, solubility of BeO approx. 10 μg/l	0.0006	IV c ?
Bismuth	Bi(OH)₃, solubility of Bi₂O₃ is unknown (low)	0.02	IV c ?
Boron	B(OH)₃, B(OH)₄⁻	4.5×10³	IV c
Bromine	Br⁰, HBrO, Br⁻	6.7×10⁴	IV c
Cadmium	CdCl⁺, CdCl₂, CdCl₃⁻ (the last two are probably the main forms)	0.02	II c
Calcium	Ca²⁺	4.1×10⁵	IV c
Chlorine	Cl⁰, HClO	....	IV c
Chr	Cr(OH)₃, solubility of Cr₂O₃ unknown (low)	0.04	IV c ?
Cob.	Co²⁺	0.4	IV c
Copper	Cu²⁺, CuOH⁺, CuHCO₃⁺, CuCO₃ (probably main form) CuCl⁺, complexed also by dissolved amino acids	1	IV c
Cyanide	HCN (90%), CN⁻ (10%)	....	III c
Fluoride	F⁻ (50%), MgF⁺ (50%)	1340	IV c
Gold	AuCl₂⁻	.01–2	IV c
Hydrogen Ion (Acids)	HCl+HCO₃⁻—H₂O+Cl⁻+CO₂ H₂SO₄+2HCO₃⁻—2H₂O+SO₄²⁻+2CO₂	pH=8 (alk=0.0024 M)	III c
Iron	Fe(OH)₃, solubility of FeOOH approx. 5 μg/l	10	IV c
Lead	Pb²⁺, PbOH⁺, PbHCO₃⁺, PbCO₃, PbSO₄, PbCl⁺ (probably main form)	0.02	I a
Magnesium	Mg²⁺	1.3×10⁶	IV c
Manganese	Mn²⁺	2	IV c
Mercury	HgCl₂, HgCl₃⁻, HgCl₄²⁻ (main form)	0.1	I b
Molybdenum	MoO₄²⁻	10	IV c
Nickel	Ni²⁺	7	III c
Nitrate	NO₃⁻	6.7×10²	III c
Phosphorus	Red phosphorus reacts slowly to phosphate H₂PO₄⁻ and HPO₄²⁻		
Selenium	SeO₄²⁻	0.45	III c ?
Silicon	Si(OH)₄, SiO(OH)₃⁻	3×10³	IV c
Silver	AgCl₂⁻	0.3	III c
Sulfide	S²⁻	....	II c
Thallium	Tl⁺	0.1	III c
Titanium	Ti(OH)₄, solubility of TiO₂ unknown (low)	2	IV b ?
Uranium	UO₂(CO₃)₃⁴⁻	3	III c
Vanadium	VO₂OH⁻	2	IV a ?
Zinc	Zn²⁺, ZnOH⁺, ZnCO₃, ZnCl⁺ (probably main form)	2	III c

[a] These values are approximate but they are representative for low levels in unpolluted sea water.
[b] I–IV order of decreasing menace; a—worldwide, b—regional, c—local (coastal, bays estuaries, single dumpings). : indicates some question of the ranking as a menace and/or whether the pollutional effect is local, regional, or worldwide.

ꞁ d modified from the Report of the Seminar on Methods of Detection, Measurement and Monitoring of Poll. ꞁ the Marine Environment. Food and Agriculture Organization 1971[144].

Forms of Chemical and Environmental Interactions

The form in which a chemical appears in the environment depends on the chemical and physical characteristics of the element, its stability, and the characteristics of the environment in which it is found. An element that is easily reduced or oxidized will undergo rapid changes, especially in sediments that alternate between oxidized and reduced states; while an element that is highly stable, such as gold, will retain its elemental identity in virtually all environmental conditions. Most elements are found in combined states, such as ore which can be a sulfide or a complex mineral containing oxygen, silica, and sulfur.

Certain elements are released into the environment by the processing of ores. Cadmium, for example, is not found uncombined in nature to any large extent but is a commercial by-product of zinc smelting. Other metallic elements can be brought into solution by the action of bacteria. Contamination from base metals may arise in abandoned mines, where tailings or slag heaps are attacked by physical and chemical weathering processes and bacteria to allow leaching of metallic ions into receiving waters. In strip mining, sulfides are oxidized to produce sulfuric acid, which may be a pollutant in itself or help to bring certain elements into solution.

The action of bacteria also transforms metals in another way. In anaerobic sediments, bacteria can convert inorganic metallic mercury into methyl mercury compounds. Such organo-metallic complexes are highly toxic to mammals, including man.

Biological Effects

Acute toxicity data for inorganic chemical compounds under controlled laboratory conditions, as represented for example by 96-hour LC50, are presented in Appendix III, Table 1, (pp. 449–460). Because of the lack of marine data, most of the information is based on freshwater bioassay data, which provide some measure of acute toxicity for the marine environment as well.

The concentrations of elements at which sublethal, chronic effects become manifest are also important. Sublethal concentrations of pollutants can have serious consequences in estuaries where migrating anadromous fishes linger to become acclimatized to changing salinities. Although the fish may not be killed outright, the stress of the sublethal concentrations may cause biochemical and physiological deficiencies that could impair life processes of the fish, preventing migrating adults from reaching their spawning grounds or reproducing. Pippy and Hare (1969)[247] suggested that heavy metals put fish under stress and may lead to infestation by diseases. Appendix III, Table 2 (pp. 461–468), summarizes data on the sublethal chronic effects of inorganic chemicals on fish and other aquatic organisms. As in Appendix III, Table 1, information on freshwater organisms has been included because of the

paucity of tests in sea water. There is a clear need for toxicological work on the sublethal effects of pollutants on marine organisms.

At low concentrations, many elements are necessary to life processes, while at higher concentrations the same elements may be toxic. The effects of long-term exposure to low levels of most chemicals, singly or in combination, are generally unknown.

Laboratory bioassays are conducted under controlled conditions usually with single chemicals. Such tests provide toxicological information that must precede *studies with* mixtures closer to actual conditions. These mixtures must reflect the conditions and the composition of water in specific areas of discharge, because substances are rarely isolated when found in the environment. The probabilities of synergism and antagonism are enhanced by increased complexity of effluents. Synergism and antagonism in the environment are poorly understood. Copper is more toxic in soft water than in hard water where the calcium and the magnesium salts contributing to water hardness tend to limit or antagonize copper toxicity. Arsenic renders selenium less toxic and has been added to feeds for cattle and poultry in areas high in selenium. As examples of synergism, copper is considerably more toxic in the presence of mercury, zinc, or cadmium salts (LaRoche 1972),[211] and cadmium makes zinc and cyanide more toxic. Synergism or antagonism is expected to occur more frequently in water containing numerous chemical compounds than in one with few such compounds. Therefore, a complex chemical medium such as sea water can increase the probability of synergism or antagonism when a pollutant is introduced.

The effects of pollutants can be considered in terms of their biological end points. Such irreversible effects as carcinogenesis, mutagenesis, and teratogenesis provide identifiable end points in terms of biological consequences of pollutants. The effects of substances may vary with species or with stages of the life cycle (See Methods of Assessment, p. 233).

A *distinction must be made between the effects* of pollutants harmful to the quality of an organism as a product for human consumption and those harmful to the organism itself. While the levels of mercury that render fish unacceptable for marketing do not, on the basis of the limited information available at this time, appear to have any adverse effect on the fish themselves, they cause condemnation of the product for human consumption. This may also be true for other elements that lend themselves to bioaccumulation. Elemental phosphorus leads to illness and eventual mortality of fish themselves (Jangaard 1970).[191] At the concentrations of phosphorus found in the liver and other vital organs, the fish may have been toxic to human beings as well. The recommendations for the elements subject to biological accumulation in the marine environment must be set at a low level to protect the organisms. There is also need to establish recommendations based on human

health, and a need to protect the economic value of fisheries affected by accumulations of some of these elements.

Data on the accumulation of inorganic chemicals by aquatic organisms are given in Appendix III, Table (pp. 469–480). The maximum permissible concentrations of inorganic chemicals in food and water, as prescribed by the U.S. Food and Drug Administration and by drinking water standards of various agencies, are given in Appendix III, Table 4 (pp. 481–482).

The elements essential to plant and animal nutrition in the marine environments have been included in Table IV-2. They constitute some of the ordinary nutrients, e.g., silicon and nitrate, as well as the micro-constituents, such as iron, molybdenum, and cobalt. Although it is recognized that these elements are required for algal nutrition, one must not be caught in the misconception that "if a little is good, a lot is better."

Metals

Metals reach the marine environment through a variety of routes, including natural weathering as well as municipal and industrial discharges. Metals are particularly susceptible to concentration by invertebrates. Vinogradov's (1953)[294] classic work on the accumulation of metals by organisms in the marine environment has been expanded in more recent treatises (Fukai and Meinke 1962,[166] Polikarpov 1966,[249] Bowen et al. 1971,[129] Lowman et al. 1971).[221]

Metals present in the marine environment in an similable form usually undergo bioaccumulation throu__ the food chain. Thus, elements present in low concentrations in the water may be accumulated many thousandfold in certain organisms. Established maximum permissible levels of some of these metallic ions render fish unacceptable for the commercial market (U.S. Department of Health, Education, and Welfare, Food and Drug Administration 1971,[236] Kolbye 1970[206]). Food and drug control agencies must impose stringent requirements on the content of certain hazardous elements, such as mercury, which, during 1970, led to condemnation of much of the fish caught in waters of the Canadian Prairies and the southern Great Lakes. Much of the swordfish and about 25 per cent of the tuna caught by the Japanese have exceeded the maximum permissible limit (Wallace et al. 1971).[295]

Studies conducted on Atlantic salmon (*Salmo salar*) in St. Andrew's, New Brunswick, show that low concentrations of zinc and copper mixtures will set up avoidance reactions (Sprague 1965,[268] Sprague and Saunders 1963[271]). Adult salmon migrating to spawn can be diverted by low concentrations of these base metals such as those leached from mine tailings. There are indications that as much as 25 per cent of spawning salmon (*Salmo salar*) may return to sea without going through the spawning act if concentrations of zinc and copper are high enough to induce avoid reactions (Sprague 1965).[268] There may be other si

important behavioral reactions stimulated by low concentrations of some of the metals.

In the following review of different inorganic constituents, the total amount of each element is considered in the discussion and recommendation, unless otherwise stated. Whereas some of the methods of analysis for constituents recommended for fresh water and waste water can also be used in marine environments, the interference from salt demands other specialized techniques for many elements (Strickland and Parsons 1968,[273] Food and Agriculture Organization 1971[164]).

Not only has the recent literature been reviewed in this examination of the properties and effects of inorganic constituents, but various bibliographic and other standard references have been liberally consulted (The Merck Index 1960,[228] McKee and Wolf 1963,[226] Wilber 1969,[299] NRC Committee on Oceanography 1971,[237] U.S. Department of the Interior Federal Water Pollution Control Administration 1968,[287] Canada Interdepartmental Committee on Water 1971[136]).

Alkalinity or Buffer Capacity, Carbon Dioxide, and pH

The chemistry of sea water differs from that of fresh water largely because of the presence of salts, the major constituents of which are present in sea water in constant proportion. The weak-acid salts, such as the carbonates, bicarbonates, and borates, contribute to the high buffering capacity or alkalinity of sea water. This buffering power renders many wastes of a highly acidic or alkaline nature, which are often highly toxic in fresh water, comparatively innocuous after mixing with sea water.

The complex carbon dioxide-bicarbonate-carbonate system in the sea is described in standard textbooks (Sverdrup et al. 1946,[276] Skirrow 1965[264]). Alkalinity and the hydrogen-ion concentration, as expressed by pH (Strickland and Parsons 1968),[273] are the best measure of the effects of highly acidic or highly alkaline wastes.

European Inland Fisheries Advisory Commission (1969)[158] and Kemp (1971)[202] reviewed the pH requirements of freshwater fishes. Because of the large difference in buffer capacities, techniques for measurement and definitions of alkalinity are quite different for marine and fresh waters. The normal range of pH encountered in fresh water is considerably wider than that found in sea water, and for this reason, freshwater communities are adapted to greater pH extremes than are marine communities.

Sea water normally varies in pH from surface to bottom because of the carbon dioxide-bicarbonate-carbonate equilibria. Photosynthetic and respiratory processes also contribute to variations in pH. At the sea surface, the pH normally varies from 8.0 to 8.3, depending on the partial pressure of carbon dioxide in the atmosphere and the salinity and temperature of the water. A large uptake of carbon dioxide during photosynthesis in the euphotic zone leads to high pH values exceeding 8.5 in exceptional cases.

Release of carbon dioxide during decomposition in intermediate and bottom waters results in a lowering of pH. In shallow, biologically-active waters, particularly in warm tropical and subtropical areas, there is a large diurnal variation in pH with values ranging from a high of 9.5 in the daytime to a low of 7.3 at night or in the early morning.

The toxicity of most pollutants increases as the pH increases or decreases from neutral (pH 7). This is true for complex mixtures, such as pulp mill effluents (Howard and Walden 1965),[183] for constituents which dissociate at different pH (e.g., H_2S and HCN), and for heavy metals. The toxicity of certain complexes can change drastically with pH. Nickel cyanide exhibits a thousandfold increase in toxicity with a 1.5 unit decrease in pH from 8.0 to 6.5 (Robert A. Taft Sanitary Engineering Center 1953,[255] Doudoroff et al. 1966[152]). pH may also determine the degree of dissociation of salts, some of which are more toxic in the molecular form than in the ionic form. Sodium sulfide is increasingly toxic with decreasing pH as S^- and HS^- ions are converted to H_2S (Jones 1948).[200] The tolerance of fish to low concentrations of dissolved oxygen, high temperatures, cations, and anions varies with pH. Therefore, non-injurious pH deviations and ranges depend on local conditions.

There are large fluctuations in natural pH in the marine environment. Changes in pH indicate that the buffering capacity of the sea water has been altered and the carbon dioxide equilibria have shifted. The time required for mixing of an effluent with a large volume of sea water is exceedingly important. When the pH of the receiving sea water undergoes an increase or decrease, its duration can be important to the survival of organisms. At present, there are not sufficient data with which to assign time limits to large departures of pH.

Fish tolerate moderately large pH changes in the middle of their normal pH ranges. Small pH changes at the limits of their ranges and also in the presence of some pollutants can have significant deleterious effects.

Plankton and benthic invertebrates are probably more sensitive than fish to changes in pH. Oysters appear to perform best in brackish waters when the pH is about 7.0. At a pH of 6.5 and lower, the rate of pumping decreases notably, and the time the shells remain open is reduced by 90 per cent (Loosanoff and Tommers 1948,[219] Korringa 1952[207]). Oyster larvae are impaired at a pH of 9.0 and killed at 9.1 in a few hours (Gaarder 1932).[167] The upper pH limit for crabs is 10.2 (Meinck et al. 1956).[227]

Recommendation

Changes in sea water pH should be avoided. The effects of pH alteration depend on the specific conditions. In any case, the normal range of pH in either direction should not be extended by more than 0.2 units. Within the normal range, the pH should not vary by more than 0.5 pH units. Ad-

dition of foreign material should not drop the pH below 6.5 or raise it above 8.5.

Aluminum

Aluminum, one of the most abundant elements in the earth's crust, does not occur in its elemental form in nature. It is found as a constituent in all soils, plants, and animal tissues. Aluminum is an amphoteric metal; it may be in solution as a weak acid, or it may assume the form of a flocculent hydroxide, depending on the pH. In the aluminum sulfate form (alum), it is used in water treatment as a coagulant for suspended solids, including colloidal materials and microorganisms.

Aluminum may be adsorbed on plant organisms, but very little ingested by animals is absorbed through the alimentary canal. Goldberg et al. (1971)[172] reported an aluminum concentration factor for phytoplankton (*Sargassum*) ash of 65 and for zooplankton ash of 300. However, Lowman et al. (1971),[221] in their compilation of concentration factors for various elements, noted that aluminum was reported to be concentrated 15,000 times in benthic algae, 10,000 times in plankton (phyto- and zoo-), 9,000 times in the soft parts of molluscs, 12,000 times in crustacean muscle, and 10,000 times in fish muscle.

In fresh water, the toxicity of aluminum salts varies with hardness, turbidity, and pH. Jones (1939)[198] found the lethal threshold of aluminum nitrate for stickleback (*Gasterosteus aculeatus*) in very soft water to be 0.07 mg/l. Using tap water with the same compound tested on the same species, Anderson (1948)[112] reported a toxic threshold of less than 5×10^{-5} molar aluminum chloride (1.35 mg/l Al). Average survival times of stickleback in different concentrations of aluminum in the nitrate form have been reported as one day at 0.3 mg/l and one week at 0.1 mg/l (Doudoroff and Katz 1953).[160] It was noted by the same authors that 0.27 mg/l aluminum in the nitrate form did not apparently harm young eels in 50 hours' exposure.

Because of the slightly basic nature of sea water, aluminum salts tend to precipitate in the marine environment. These salts have exhibited comparatively low toxicities with 96-hour LC50's of 17.8 mg/l for redfish tested in sea water with aluminum chloride (Pulley 1950).[252] Concentrations of 8.9 mg/l of aluminum (from $AlCl_3$) did not have a lethal effect on marine fish and oysters tested (*Cynoscion nebulosus, Sciaenops oscellatus, Fundulus grandis, Fundulus similis, Cyprindon variegatus, Ostrea virginica*) (Pulley 1950).[252] The flocs of precipitated aluminum hydroxide may affect rooted aquatics and invertebrate benthos. Wilder (1952)[300] noted no significant effect on lobsters (*Homarus americanus*) of a tank lined with an aluminum alloy (Mn, 1 to 1.5 per cent; Fe, 0.7 per cent; Si, 0.6 per cent; Cu, 0.2 per cent, and Zn, 0.1 per cent).

Aluminum hydroxide can have an adverse effect on bottom communities. Special precautions should be taken to avoid disposal of aluminum-containing wastes in water supporting commercial populations of clams, scallops, oysters, shrimps, lobsters, crabs, or bottom fishes.

Recommendation

Because aluminum tends to be concentrated by marine organisms, it is recommended that an application factor of 0.01 be applied to marine 96-hour LC50 data for the appropriate organisms most sensitive to aluminum. On the basis of data available at this time, it is suggested that concentrations of aluminum exceeding 1.5 mg/l constitute a hazard in the marine environment, and levels less than 0.2 mg/l present minimal risk of deleterious effects.

Ammonia

Most of the available information on toxicity of ammonia is for freshwater organisms. For this reason, the reader is referred to the discussion of ammonia in Section III on Freshwater Aquatic Life and Wildlife (p. 186). Because of the slightly higher alkalinity of sea water and the larger proportion of un-ionized ammonium hydroxide, ammonia may be more toxic in sea water than in fresh water (Doudoroff and Katz 1961).[151] Holland et al. (1960)[182] noted a reduction in growth and a loss of equilibrium in chinook salmon (*Oncorhynchus tshawytscha*) at concentrations 3.5 to 10 mg/l of ammonia. Dissolved oxygen and carbon dioxide decrease the toxicity of ammonia (U.K. Department of Science and Research 1961).[284] Lloyd and ſ (1969),[217] in their studies on the effect of un-ionized ammonia at a pH of 8 to 10, found 100 per cent mortality with 0.44 mg/l NH_3 in 3 hours for rainbow trout (*Salmo gairdneri*). This confirmed earlier results of 100 per cent mortality in 24 hours at 0.4 mg/l. The toxicity increased with pH between 7.0 and 8.2.

Recommendation

It is recommended that an application factor of 0.1 be applied to marine 96-hour LC50 data for the appropriate organisms most sensitive to ammonia. On the basis of freshwater data available at this time, it is suggested that concentrations of un-ionized ammonia equal to or exceeding 0.4 mg/l constitute a hazard to the marine biota, and levels less than 0.01 mg/l present minimal risk of deleterious effects.

Antimony

Antimony occurs chiefly as sulfide (stibnite) or as the oxides cervantite (Sb_2O_4) and valentinite (Sb_2O_3) and is used for alloys and other metallurgical purposes. It has also been used in a variety of medicinal preparations and in numerous industrial applications. Antimony salts are used in the fireworks, rubber, textile, ceramic, glass ſ paint industries.

Few of the salts of antimony have been tested on fish in bioassays, particularly in sea water. However, antimony potassium tartrate ("tartar emetic") gave a 96-hour LC50 as antimony of 20 mg/l in soft water and 12 mg/l in hard water (Tarzwell and Henderson 1956,[277] 1960[278]). Cellular division of green algae was hindered at 3.5 mg/l, and movement of *Daphnia* was retarded at 9 mg/l (Bringmann and Kuhn 1959a).[131] Antimony trichloride, used in acid solution as a mordant for patent leather and in dyeing, was examined in exploratory tests on fathead minnows *(Pimephales promelas)* and gave a 96-hour LC50 as antimony of 9 mg/l in soft water and 17 mg/l in hard water (Tarzwell and Henderson 1960).[278] Applegate et al. (1957)[114] reported that rainbow trout *(Salmo gairdneri)*, bluegill sunfish *(Lepomis macrochirus)*, and sea lamprey *(Pertomyzon marinus)* were unaffected by 5 mg/l of SbCl₃ or SbCl₅ in Lake Huron water at 13 C, saturated with dissolved oxygen, and pH 7.5 to 8.2. Jernejcic (1969)[183] noted that as little as 1.0 mg/l of antimony in the form of tartar emetic caused projectile vomiting in large mouth bass *(Micropterus salmoides)*.

Antimony can be concentrated by various marine forms to over 300 times the amount present in sea water (Goldberg 1957,[171] Noddack and Noddack 1939[240]).

Recommendation

Because of the hazard of antimony poisoning to humans and the possible concentration of antimony by edible marine organisms, it is recommended that an application factor of 0.02 be applied to marine 96-hour LC50 data for the appropriate organisms most sensitive to antimony. On the basis of data available at this time, it is suggested that concentrations of antimony equal to or exceeding 0.2 mg/l constitute a hazard in the marine environment. There are insufficient data available at this time to recommend a level that would present minimal risk of deleterious effects.

Arsenic

Arsenic occurs in nature mostly as arsenides or pyrites. It is also found occasionally in the elemental form. Its consumption in the U.S. in 1968 amounted to 25,000 tons as As₂O₃ (U.S. Department of the Interior, Bureau of Mines 1969).[289] Arsenic is used in the manufacture of glass, pigments, textiles, paper, metal adhesives, ceramics, linoleum, and mirrors (Sullivan 1969),[274] and its compounds are used in pesticides, wood preservatives, paints, and electrical semiconductors. Because of its poisonous action on microorganisms and lower forms of destructive aquatic organisms, it has been used in wood preservatives, paints, insecticides, and herbicides. Sodium arsentite has been used for weed control in lakes and in electrical semiconductors.

In small concentrations, arsenic is found naturally in some bodies of water. In its different forms, including its valence states, arsenic varies in toxicity. Trivalent arsenic

is considerably more toxic than the pentavalent species in the inorganic form. It is acutely toxic to invertebrates and for this reason has found application in the control of *Teredo* and other woodborers in the As⁺³ form. Arsenious trioxide (As₂O₃) has been used for control of the shipworm *Bankia setacia*. In the arsenate form (As⁺⁵), it is of relatively low toxicity, *Daphnia* being just immobilized at 18 to 31 mg/l sodium arsenate, or 4.3 to 7.5 mg/l as arsenic, in Lake Erie water (Anderson 1944,[110] 1946[111]). The lethal threshold of sodium arsenate for minnows has been reported as 234 mg/l as arsenic at 16 to 20 C (Wilber 1969).[299]

Arsenic is normally present in sea water at concentrations of 2 to 3 µg/l and tends to be accumulated by oysters and other molluscan shellfish (Sautet et al. 1964,[258] Lowman et al. 1971[221]). Wilber (1969)[299] reported concentrations of 100 mg/kg in shellfish. Arsenic is a cumulative poison and has long-term chronic effects on both aquatic organisms and on mammalian species. A succession of small doses may add up to a final lethal dose (Buchanan 1962).[135] The acute effects of arsenic and its compounds on aquatic organisms have been investigated, but little has been done on the sublethal chronic effects.

Surber and Meehan (1931)[275] found that fish-food organisms generally can withstand concentrations of approximately 1.73 mg/l of arsenious trioxide in sodium arsenite solution. Meinck et al. (1956)[227] reported that arsenic concentrations were toxic at 1.1 to 2.2 mg/l to pike perch *(Stizostedion vitreum)* in 2 days, 2.2 mg/l to bleak in 3 days, 3.1 mg/l to carp *(Cyrinus carpio)* in 4 to 6 days and to eels in 3 days, and 4.3 mg/l to crabs in 11 days.

Recommendation

Because of the tendency of arsenic to be concentrated by aquatic organisms, it is recommended that an application factor of 0.01 be applied to marine 96-hour LC50 data for the appropriate organisms most sensitive to arsenic. On the basis of freshwater and marine toxicity data available, it is suggested that concentrations of arsenic equal to or exceeding 0.05 mg/l constitute a hazard in the marine environment, and levels less than 0.01 mg/l present minimal risk of deleterious effects.

Barium

Barium comes largely from ores (BaSO₄, BaCO₃). It is being used increasingly in industry. The U.S. consumption in 1968 was 1.6 million tons, a growth of 78 per cent in 20 years (U.S. Department of the Interior, Bureau of Mines 1969).[289] Barium is used in a variety of industrial applications, including paper manufacturing, fabric printing and dyeing, and synthetic rubber production.

All water- or acid-soluble barium compounds are poisonous. However, in sea water the sulfate and carbonate present tend to precipitate barium. The concentration of barium in sea water is generally accepted at about 20 µg/l

(Goldberg et al. 1971),[172] although it has been reported as low as 6.2 µg/l (Bowen 1956).[128] Wolgemuth and Broecker (1970)[303] reported a range of 8 to 14 µg/l in the Atlantic and 8 to 31 µg/l in the Pacific, with the lower values in surface waters. Barium ions are thought to be rapidly precipitated or removed from solution by adsorption and sedimentation.

Bijan and Deschiens (1956)[123] reported that 10 to 15 mg/l of barium chloride were lethal to an aquatic plant and two species of snails. Bioassays with barium chloride showed that a 72-hour exposure to 50 mg/l harmed the nervous system of coho salmon (*Oncorhynchus kisutch*) and 158 mg/l killed 90 per cent of the test species (ORSANCO 1960).[245] Barium can be concentrated in goldfish (*Carassius auratus*) by a factor of 150 (Templeton 1958).[279] Soviet marine radioactivity studies showed accumulation of radioactive barium in organs, bones, scales, and gills of fish from the Northeast Pacific (Moiseev and Kardashev 1964[230]). Lowman et al. (1971)[221] listed a concentration factor for barium of 17,000 in phytoplankton, 900 in zooplankton, and 8 in fish muscle.

In view of the widespread use of barium, the effects of low doses of this element and its compounds on marine organisms under different environmental conditions should be determined. Disposal of barium-containing wastes into waters when precipitates could affect rooted aquatics and benthic invertebrates should be avoided.

Recommendation

Because of the apparent concentration of barium by aquatic organisms and the resultant human health hazard, it is recommended that an application factor of 0.05 be applied to marine 96-hour LC50 data for the appropriate organisms most sensitive to barium. On the basis of data available at this time, it is suggested that concentrations of barium equal to or exceeding 1.0 mg/l constitute a hazard in the marine environment, and levels less than 0.5 mg/l present minimal risk of deleterious effects.

Beryllium

Beryllium is found mainly in the mineral beryl and is almost nonexistent in natural waters. Its concentration in sea water is 6×10^{-4} µg/l. Beryllium is used in a number of manufacturing processes, in electroplating, and as a catalyst in organic chemical manufacture. It has also been used experimentally in rocket·fuels and in nuclear reactors (Council on Environmental Quality 1971).[144] In 1968, the U.S. consumption of beryllium was 8,719 tons, a 500 per cent increase over 1948 (U.S. Department of the Interior, Bureau of Mines 1969).[289]

Beryllium has been shown to inhibit photosynthesis in terrestrial plants (Bollard and Butler 1966).[127] It would be of interest to know if there is any inhibition of photo-synthesis by beryllium compounds in the marine environment.

Beryllium chloride and nitrate are highly soluble in water, and the sulfate is moderately so. The carbonate and hydroxide are almost insoluble in cold water. Toxicity tests gave a 96-hour LC50 for beryllium chloride of 0.15 mg/l as beryllium for fathead minnows (*Pimephales promelas*) in soft water; 15 mg/l for the same species in hard water (Tarzwell and Henderson 1960);[273] and 31.0 mg/l for *Fundulus heteroclitus* (Jackim et al. 1970).[190]

Beryllium has been reported to be concentrated 1000 times in marine plants and animals (Goldberg et al. 1971).[172]

Recommendation

In the absence of data specifically related to effects of beryllium on marine organisms, and because of its accumulation by marine organisms and its apparent toxicity to humans, it is recommended that an application factor of 0.01 be applied to marine 96-hour LC50 data for the appropriate organisms most sensitive to beryllium. On the basis of data available for hard fresh water, it is suggested that concentrations of beryllium equal to or exceeding 1.5 mg/l constitute a hazard to marine organisms, and levels less than 0.1 mg/l present minimal risk of deleterious effects.

Bismuth

Bismuth is used in the manufacture of bismuth sa⁻ fusible alloys, electrical fuses, low-melting solders, a. fusible boiler plugs, and in tempering baths for steel, in "silvering" mirrors, and in dental work. Bismuth salts are used in analytical chemical laboratories and commonly formulated in pharmaceuticals.

The concentration of bismuth in sea water is low, about 0.02 µg/l, probably because of the insolubility of its salts. It is unknown how much bismuth actually gets into the sea from man-made sources, but the quantity is probably small. The total U.S. production in 1969 as subcarbonate $(Bi_2O_2CO_3)_2 \cdot H_2O$ was 57 short tons (U.S. Department of Commerce 1971).[285]

There are no bioassay data on which to base recommendations for bismuth in the marine environment.

Boron

Boron is not found in its elemental form in nature; it normally occurs in mineral deposits as sodium borate (borax) or calcium borate (colemanite). The concentration of boron in sea water is 4.5 mg/l as one of the 8 major constituents in the form of borate. Boron has long been used in metallurgy to harden other metals. It is now being used in the elemental form as a neutron absorber in nuclear installations.

Available data on toxicity of boron to aquatic organi⁻ are from fresh water (Wurtz 1945,[306] Turnbull et al. 195

LeClerc and Devlaminck 1955,[214] Wallen et al. 1957,[296] LeClerc 1960[213]). Boric acid at a concentration of 2000 n⋯ ⋯howed no effect on one trout and one rudd (*Scardinius ⋯y. ⋯hthalmus*); at 5000 mg/l it caused a discoloration of ⋯he skin of the trout, and at 80,000 mg/l the trout became ⋯mmobile and lost its balance in a few minutes (Wurtz 1945).[306] The minimum lethal dose for minnows exposed to ⋯oric acid at 20 C for 6 hours was reported to be 18,000 ⋯o 19,000 mg/l in distilled water and 19,000 to 19,500 mg/l in hard water (LeClerc and Devlaminck 1955,[214] LeClerc 1960[213]). Testing mosquito fish (*Gambusia affinis*) at 20 ⋯o 26 C and a pH range of 5.4 to 9.1, Wallen et al. (1957)[296] established 96-hour LC50's of 5,600 mg/l for boric acid and 3,600 mg/l for sodium borate.

Since the toxicity is slightly lower in hard water than in distilled water, it is anticipated that boric acid and borates would be less toxic to marine aquatic life than to freshwater organisms. In the absence of sea water bioassay data, an estimate of 500 mg/l of boron as boric acid and 250 mg/l as sodium borate is considered hazardous to marine animals, based on freshwater data (Wallen et al. 1957).[296] Concentrations of 50 mg/l and 25 mg/l, respectively, are expected to have minimal effects on marine fauna.

An uncertainty exists concerning the effect of boron on marine vegetation. In view of harm that can be caused to terrestrial plants by boron in excess of 1 mg/l. (Wilber 1969),[299] special precautions should be taken to maintain bo⋯ ⋯ at normal levels near eel grass (*Zostera*), kelp (*Macro-c⋯* ⋯ and other seaweed beds to minimize damage to these plants.

Recommendation

On the basis of data available at this time, it is suggested that concentrations of boron equal to or exceeding 5.0 mg/l constitute a hazard in the marine environment, and levels less than 5.0 mg/l present minimal risk of deleterious effects. An application factor of 0.1 is recommended for boron compounds applied to marine 96-hour LC50 data for the appropriate organisms most sensitive to boron.

Bromine

In concentrated form, bromine is a strong oxidizing agent and will attack all metals and organic materials. It is one of the major constituents in sea water, present at about 67 mg/l in bromate, and is commercially extracted from the sea.

Bromine is used medicinally and for sterilization of swimming pools. It is also used in the preparation of dye-stuffs and anti-knock compounds for gasolines. Molecular bromine may be discharged in effluents from salt works and c⋯ ⋯ chemical industries. Bromination of certain organic su⋯⋯ances, such as phenols and amines, may impart offensive taste and make waters more toxic to aquatic organisms.

Kott et al. (1966)[208] found that *Chlorella pyrenoidosa*, when exposed to 0.42 mg/l bromine for 4 days, were reduced in concentration from 2,383 cells/mm² to 270 cells, but remained virtually unchanged at 0.18 mg/l bromine (2,383 cells/mm² in controls compared to 2,100 cells/mm² in the exposed sample).

At concentrations of 10 mg/l in soft water, bromine killed *Daphnia magna* (Ellis 1937),[156] and at 20 mg/l in water of 18 to 23 C, goldfish (*Carassius auratus*) were killed (Jones 1937).[201] A violent irritant response in marine fish was observed at 10 mg/l bromine, but no such activity was perceived at 1 mg/l (Hiatt et al. 1953).[181]

The salts of bromine are relatively innocuous. The threshold of immobilization for *Daphnia magna* was 210 mg/l of sodium bromate ($NaBrO_3$) and 8200 mg/l of sodium bromide ($NaBr$) (Anderson 1946).[111]

Recommendation

It is recommended that free (molecular) bromine in the marine environment not exceed 0.1 mg/l and that ionic bromine in the form of bromate be maintained below 100 mg/l.

Cadmium

U.S. consumption of cadmium was 6,662 short tons in 1968 (U.S. Department of the Interior, Bureau of Mines 1969).[289] These quantities indicate that cadmium might be a significant pollutant.

Pure cadmium is not found in commercial quantities in nature. It is obtained as a by-product of smelting zinc. Cadmium salts in high concentrations have been found in a Missouri spring originating from a mine (up to 1,000 mg/ml cadmium) (ORSANCO 1955),[244] and up to 50 to 170 mg/kg of cadmium are found in superphosphate fertilizers (Athanassiadis 1969).[116] Cadmium is also present in some pesticides. It is being used in increasing amounts by industry (Council on Environmental Quality 1971).[144] Water-carrying pipes are also a source of cadmium (Schroeder 1970)[239] as is food (Nilsson 1969).[239] Cadmium is present in most drainage waters (Kroner and Kopp 1965)[209] and may be contributing substantially to the cadmium present in inshore coastal waters. It is not known, however, whether man's input has resulted in higher levels of cadmium in estuarine or coastal waters. In sea water, cadmium is generally present at about 0.1 μg/l (Goldberg et al. 1971).[172]

Cadmium pollution resulting in the "Itai-itai" disease in the human population has been documented (Yamagata and Shigematsu 1970).[307] Schroeder et al. (1967)[260] have found that oysters may concentrate cadmium from very low levels in ambient water. Cadmium concentrations in some marine plants and animals have been given by Mullin and Riley (1956).[233]

Concern exists that cadmium may enter the diet, like

mercury, through seafood. Cadmium, like mercury, could conceivably form organic compounds which might be highly toxic or lead to mutagenic or teratogenic effects.

Cadmium has marked acute and chronic effects on aquatic organisms. It also acts synergistically with other metals. A 15-week LC50 of 0.1 mg/l and inhibition of shell growth for *Crassostrea virginica* (Pringle et al. 1968),[250] and a 96-hour LC50 of 0.03 mg/l cadmium in combination with 0.15 mg/l zinc for fry of chinook salmon (*Oncorhynchus tshawytscha*) (Hublou et al. 1954)[184] have been reported.

Fundulus heteroclitus exposed to 50 mg/l cadmium showed pathological changes in the intestinal tract after 1-hour exposure, in the kidney after 12 hours, and in the gill filaments and respiratory lamellae after 20 hours (Gardner and Yevich 1970).[170] Copper and zinc, when present at 1 mg/l or more, substantially increase the toxicity of cadmium (LaRoche 1972).[211]

Cadmium is concentrated by marine organisms, particularly the molluscs (e.g., *Pecten novazetlandicae*), which accumulated cadmium in the calcareous tissues and in the viscera (Brooks and Rumbsby 1965).[133] Lowman et al. (1971)[221] reported a concentration factor of 1000 for cadmium in fish muscle.

Cadmium levels in tissues of Ashy Petrel (*Oceanodroama homochroa*) from coastal waters of California were approximately twice as high as in tissues of Wilson's Petrel (*Oceanites oceanicus*) obtained in Antarctica, which had summered in the North Atlantic and Australian regions, respectively. Cadmium levels in tissues of the Snow Petrel (*Pelagodroma nivea*), a species which does not leave the Antarctic ice pack region, obtained at Hallett Station, Antarctica, were of the same order of magnitude as those in the Wilson's Petrel. Cadmium levels in eggs of the Common Tern (*Sterna hirundo*) from Long Island Sound were in the order of 0.2 mg/kg dry weight, not appreciably higher than those in the Antarctic Tern (*Sterna vittata*) from the Antarctic with levels in the order of 0.1 mg/kg (Anderlini et al. *in press*).[109] Cadmium pollution may therefore be significant locally in estuaries, but on the basis of these limited data, it does not appear to be a problem in more remote marine ecosystems. However, in view of the comparatively unknown effects of cadmium on the marine ecosystem, its apparent concentration by marine organisms, and the human health risk involved in consumption of cadmium-contaminated seafood, it is suggested that there be no artificial additions of cadmium to the marine environment.

Recommendation

The panel recommends that an application factor of 0.01 be applied to marine 96-hour LC50 data for appropriate organisms most sensitive to cadmium. On the basis of data available at this time, it is suggested that concentrations of cadmium equal to or exceeding 0.01 mg/l constitute a hazard in the marine environment as well as to human populations, and levels less than 0.2 µg/l present minimal risk of deleterious effects. In the presence of copper and/or zinc at 1 mg/l or more, there is evidence that the application factor for cadmium should be lower by at least one order of magnitude.

In the absence of sufficient data on the effects of cadmium upon wildlife, it is recommended that cadmium criteria for aquatic life apply also to wildlife.

Chlorine

Chlorine is generally present in the stable chloride form which constitutes about 1.9 per cent of sea water. Elemental chlorine, which is a poisonous gas at normal temperature and pressure, is produced by electrolysis of a brine solution. Among its many uses are the bleaching of pulp, paper and textiles, and the manufacture of chemicals.

Chlorine is used to kill so-called nuisance organisms that might interfere with the proper functioning of hydraulic systems. Chlorine disinfection is also used in public water supplies and in sewage effluents to insure that an acceptable degree of coliform reduction is achieved before the effluents enter various bodies of water. In all instances the intent is to eliminate undesirable levels of organisms that would degrade water uses. This goal is only partially reached, because the effect of chlorine on desirable species is a serious hazard.

When dissolved in water, chlorine completely hydrolizes to form hypochlorous acid (HOCl) or its dissociated ions, at concentrations below 1000 mg/l, no chlorine exists in solution as Cl_2. The dissociation of HOCl to H^+ and OCl^- depends on the pH: 4 per cent is dissociated at pH 6, 25 per cent at pH 7, and 97 per cent at pH 9. The undissociated form is the most toxic (Moore 1951).[231] Although free chlorine is toxic in itself to aquatic organisms, combinations of chlorine with ammonia, cyanide, and organic compounds, such as phenols and amines, may be even more toxic and can impart undesirable flavors to seafood.

Chlorine at 0.05 mg/l was the critical level for young Pacific salmon exposed for 23 days (Holland et al. 1960).[182] The lethal threshold for chinook salmon (*Oncorhynchus tshawytscha*) and coho salmon (*O. kisutch*) for 72-hour exposure was noted by these investigators to be less than 0.1 mg/l chlorine. In aerated freshwater, monochloramines were more toxic than chlorine and dichloramine more toxic than monochloramine. Studies of irritant responses of marine fishes to different chemicals (Hiatt et al. 1953)[181] showed a slight irritant activity at 1 mg/l and violent irritant activity at 10 mg/l. Oysters are sensitive to chlorine concentrations of 0.01 to 0.05 mg/l and react by reducing pumping activity. At Cl_2 concentrations of 1.0 mg/l effective pumping could not be maintained (Galtsoff 1946).[169]

Preliminary results show that at 15 C, salinity 30 parts per thousand (%o), mature copepods (*Acartia tonsa* a...

TABLE IV-3—Copepod Mortality from Chlorine Exposure
Acartia Tonsa

chlorine mg/l	Exposure time in minutes to give 50 percent mortality	Exposure time in minutes to give 100 percent mortality
1.0	220	>500
2.5	8.5	120
5.0	1.2	10.0
10.0	0.6	1.0

Eurytemona Affinis

Chlorine mg/l	Exposure time in minutes to give 50 percent mortality	Exposure time in minutes to give 100 percent mortality
2.5	33	125
5.0	3.6	30.0
10.0	2.0	5.0

Gentile (unpublished data) 1972.[312]

Eurytemona affinis) have great difficulty in surviving exposures to chlorine (Table IV-3).

Clendenning and North (1960)[141] noted that at 5 to 10 mg/l chlorine, the photosynthetic capacity of bottom fronds of the giant kelp (*Macrocystis pyrifera*) was reduced by 10 to 15 per cent after 2 days and 50 to 70 per cent after 5 to 7 days.

Chlorination in seawater conduits to a residual of 2.5 mg/l killed all fouling organisms tested (anemones, mussels, b cles, Mogula, Bugula) in 5 to 8 days; but with 1.0 m a few barnacles and all anemones survived 15 days' exposure (Turner et al. 1948).[282]

It should be further stressed that chlorine applications may often be accompanied by entrainments where the organisms are exposed to strong biocidal chlorine doses, intense turbulence, and heat (Gonzales et al. *unpublished* 1971).[313] Consideration should also be given to the formation of chlorinated products, such as chloramines or other pollutants, which may have far greater and more persistent toxicity than the original chlorine applications.

Recommendation

It is recommended that an application factor of 0.1 be used with 96-hour LC50 data from seawater bioassays for the most sensitive species to be protected.

However, it is suggested that free residual chlorine in sea water in excess of 0.01 mg/l can be hazardous to marine life. In the absence of data on the *in situ* production of toxic chlorinated products, it appears to be premature to advance recommendations.

Chromium

Most of the available information on toxicity of chromium i ... freshwater organisms, and it is discussed in Section II.., p. 180.

Chromium concentrations in seawater average about 0.04 μg/l (Food and Agriculture Organization 1971),[184] and concentration factors of 1,600 in benthic algae, 2,300 in phytoplankton, 1,900 in zooplankton, 440 in soft parts of molluscs, 100 in crustacean muscle, and 70 in fish muscle have been reported (Lowman et al. 1971).[221]

The toxicity of chromium to aquatic life will vary with valence state, form, pH, synergistic or antagonistic effects from other constituents, and the species of organism involved.

In long-term studies on the effects of heavy metals on oysters, Haydu (*unpublished data*)[314] showed that mortalities occur at concentrations of 10 to 12 μg/l chromium, with highest mortality during May, June, and July. Raymont and Shields (1964)[253] reported threshold toxicity levels of 5 mg/l chromium for small prawns (*Leander squilla*), 20 mg/l chromium in the form Na_2CrO_4 for the shore crab (*Carcinas maenus*), and 1 mg/l for the polychaete *Nereis virens*. Pringle et al. (1968)[250] showed that chromium concentrations of 0.1 and 0.2 mg/l, in the form $K_2Cr_2O_7$, produced the same mortality with molluscs as the controls. Doudoroff and Katz (1953)[150] investigated the effect of $K_2Cr_2O_7$ on mummichogs (*Fundulus heteroclitus*) and found that they tolerated a concentration of 200 mg/l in sea water for over a week.

Holland et al. (1960)[182] reported that 31.8 mg/l of chromium as potassium chromate in sea water gave 100 per cent mortality to coho salmon (*Oncorhynchus kisutch*). Gooding (1954)[173] found that 17.8 mg/l of hexavalent chromium was toxic to the same species in sea water.

Clendenning and North (1960)[141] showed that hexavalent chromium at 5.0 mg/l chromium reduced photosynthesis in the giant kelp (*Macrocystis pyrifera*) by 50 per cent during 4 days exposure.

Recommendation

Because of the sensitivity of lower forms of aquatic life to chromium and its accumulation at all trophic levels, it is recommended that an application factor of 0.01 be applied to marine 96-hour LC50 data for the appropriate organisms most sensitive to chromium. On the basis of data available at this time, it is suggested that concentrations of chromium equal to or exceeding 0.1 mg/l constitute a hazard to the marine environment, and levels less than 0.05 mg/l present minimal risk of deleterious effects. In oyster areas, concentrations should be maintained at less than 0.01 mg/l.

Copper

Copper has been used as a pesticide for eliminating algae in water, and its salts have bactericidal properties. Copper is toxic to invertebrates and is used extensively in marine antifouling paints which release it to the water. It is also toxic to juvenile stages of salmon and other sensitive species

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(Sprague 1964,[267] 1965,[268] Sigler et al. 1966,[263] Cope 1966[142]).

Copper was the fifth metal in U.S. consumption during 1968, following iron, manganese, zinc, and barium (U.S. Department of the Interior Bureau of Mines 1969).[289] Copper is used for such products as high transmission wires, containers, utensils, and currency because of its noncorroding properties.

Copper is widely distributed in nature and is present in sea water in concentrations ranging from 1 to 25 μg/l. In small amounts, copper is nonlethal to aquatic organisms; in fact, it is essential to some of the respiratory pigments in animals (Wilber 1969).[299] Copper chelated by lignin or citrate has been reported to be as effective as copper ion in controlling algae, but apparently it is not as toxic to fish (Ingols 1955).[186] Copper affected the polychaete *Nereis virens* at levels of approximately 0.1 mg/l (Raymont and Shields 1964)[263] and the shore crab (*Carcinus maenus*) at 1 to 2 mg/l (Wilber 1969).[299] Copper at concentrations of 0.06 mg/l inhibited photosynthesis of the giant kelp (*Macrocystis pyrifera*) by 30 per cent in 2 days and 70 per cent in 4 days (Clendenning and North 1960).[141]

Copper is toxic to some oysters at concentrations above 0.1 mg/l (Galtsoff 1932)[168] and lethal to oysters at 3 mg/l (Wilber 1969).[299] The American oyster (*Crassostrea virginica*) is apparently more sensitive to copper than the Japanese species (*Crassostrea gigas*) (Reish 1964).[254] The 96-hour LC50 for Japanese oysters exposed to copper has been reported as 1.9 mg/l (Fujiya 1960).[165] However, oysters exposed to concentrations as low as 0.13 mg/l turn green in about 21 days (Galtsoff 1932).[168] Although such concentrations of copper are neither lethal to the oysters nor, apparently, harmful to man, green oysters are unmarketable because of appearance. Therefore, in the vicinity of oyster grounds, the recommendation for maximum permissible concentrations of copper in the water is based on marketability, and it is recommended that copper not be introduced into areas where shellfish may be contaminated or where seaweed is harvested.

Copper acts synergistically when present with zinc (Wilber 1969),[299] zinc and cadmium (LaRoche 1972),[211] mercury (Corner and Sparrow 1956),[143] and with pentachlorophenate (Cervenka 1959).[137] Studies on sublethal effects of copper show that Atlantic salmon (*Salmo salar*) will avoid concentrations of 0.0024 mg/l in laboratory experiments (Sprague et al. 1965,[270] Saunders and Sprague 1967,[257] Sprague 1971[269]).

Copper is accumulated by marine organisms, with concentration factors of 30,000 in phytoplankton, 5,000 in the soft tissues of molluscs, and 1000 in fish muscle (Lowman et al. 1971).[221]

Bryan and Hummerstone (1971)[134] reported that the polychaete *Nereis diversicolor* shows a high takeup of copper from copper-rich sediments and develops a tolerance. Mobile predators feeding on this species could receive doses toxic to themselves or accumulate concentrations that would be toxic to higher trophic levels.

Recommendation

It is recommended that an application factor of 0.01 be applied to marine 96-hour LC50 data for the appropriate organisms most sensitive to copper. On the basis of data available at this time, it is suggested that concentrations of copper equal to or exceeding 0.05 mg/l constitute a hazard in the marine environment, and levels less than 0.01 mg/l present minimal risk of deleterious effects.

Cyanides

Most of the available information on toxicity of cyanides is for freshwater organisms, and is discussed in the Freshwater Aquatic Life and Wildlife section, p. 189.

Recommendation

As a guideline in the absence of data for marine organisms the panel recommends that an application factor of 0.1 be applied to marine 96-hour LC50 data for the appropriate organisms most sensitive to cyanide. On the basis of data available at this time it is suggested that concentrations of cyanide equal to or exceeding 0.01 mg/l constitute a hazard in the marine environment, and levels less than 0.005 mg/l present minimal risk of deleterious effects.

Fluorides

Fluorides have been brought to public attention in recent years because of their effects at low concentrations in human dental development and in prevention of decay. However, it must be remembered that fluorides at higher concentrations are poisons afflicting human and other mammalian skeletal structures with fluorosis (see Section II, p. 66).

Fluorine is the most reactive non-metal and does not occur free in nature. It is found in sedimentary rocks as fluorspar, calcium fluoride, and in igneous rocks as cryolite, sodium aluminum fluoride. Seldom found in high concentrations in natural surface waters because of their origin only in certain rocks in certain regions, fluorides may be found in detrimental concentrations in ground waters.

Fluorides are emitted to the atmosphere and into effluents from electrolytic reduction plants producing phosphorus and aluminum. They are also used for disinfection, as insecticides, as a flux for steel manufacture, for manufacture of glass and enamels, for preserving wood, and for assorted chemical purposes.

A review of fluoride in the environment (Marier and Rose 1971)[225] indicates that the concentration of unbound ionic fluoride (F$^-$) in sea water ranges between 0.4 ? 0.7 mg/l. Approximately 50 per cent of the total seawa

fluoride (0.77 to 1.40 mg/l) is bound as the double ion MgF+.

Concentrations as low as 1.5 mg/l of fluoride have af l hatching of fish eggs (Ellis et al. 1946),[157] and 2.3 ng/l, introduced as sodium fluoride, was lethal to rainbow trout (*Salmo gairdneri*) at 18 C (Angelovic et al. 1961).[113] Virtually no information exists on long-term chronic effects of low concentrations of fluorides in sea water.

Recommendation

In the absence of data on the sublethal effects of fluorides in the marine environment, it is recommended that an application factor of 0.1 be applied to marine 96-hour LC50 data for the appropriate organisms most sensitive to fluoride. On the basis of data available at this time it is suggested that concentrations of fluoride equal to or exceeding 1.5 mg/l constitute a hazard in the marine environment, and levels less than 0.5 mg/l present minimal risk of deleterious effects.

Iron

Because of the widespread use of iron by man for his many industrial activities, iron is a common contaminant in the aquatic environment. Iron may enter water naturally from iron ore deposits; but iron is more often introduced from acid mine drainage, mineral processing, steel pickling, and corrosion. Iron usually occurs in the ferrous form, w' t is released from processing plants or in mine drainage, out becomes rapidly oxidized to the ferric form in natural surface waters. The ferric salts form gelatinous hydroxides, agglomerate and flocculate, settling out on the bottom or becoming adsorbed on various surfaces. Depending on the pH and Eh, groundwater may contain a considerable amount of iron in solution, but well aerated waters seldom contain high, dissolved iron. In the marine environment, iron is frequently present in organic complexes and in adsorbed form on particulate matter.

Most of the investigations on biological effects of iron have been done in fresh water (Knight 1901,[204] Bandt 1948,[117] Minkina 1946,[229] Southgate 1948,[265] Lewis 1960,[215] ORSANCO 1960[245]). Deposition of iron hydroxides on spawning grounds may smother fish eggs, and the hydroxides may irritate the gills and block the respiratory channels of fishes (Southgate 1948,[265] Lewis 1960[215]). Direct toxicity of iron depends on its valence state and whether it is in solution or suspension.

Warnick and Bell (1969)[297] examined the effects of iron on mayflies, stoneflies, and caddisflies and obtained a 96-hour LC50 of 0.32 mg/l for the three insects. Dowden and Bennett (1965)[153] examined the effect of ferric chloride to *Daphnia magna* in static acute bioassays. They noted LC50's of 36, 21, and 15 mg/l for 1, 2, and 4 days, respectively.

ic hydroxide flocs removed the diatoms in the process of flocculation and settling, coating the bottom; and the iron precipitate coated the gills of white perch (*Morone americana*), minnows, and silversides in upper Chesapeake Bay (Olson et al. 1941).[242]

Tests on three types of fish gave a lethality threshold for iron at 0.2 mg/l (Minkina 1946)[229] and on carp at 0.9 mg/l if the pH was 5.5 or lower. Ebeling (1928)[155] found that 10 mg/l of iron caused serious injury or death to rainbow trout (*Salmo gairdneri*) in 5 minutes. La Roze (1955)[212] reported that dogfish were killed in 3 hours at 5 mg/l iron, whereas other research (National Council for Stream Improvement 1953)[236] indicated no deaths during one week at 1 to 2 mg/l.

Because of the slightly alkaline condition of sea water, much of the iron introduced to the sea precipitates. This adds a further problem of iron hydroxide flocs contaminating bottom sediments where rooted aquatics and invertebrates could be affected.

Special consideration should be given to avoiding discharge of iron-containing effluents into waters where commercially important bottom species or important food organisms dwell (e.g., oysters, clams, scallops, lobsters, crabs, shrimp, halibut, flounder, and demersal fish eggs and larvae).

Recommendation

On the basis of data available at this time, it is suggested that concentrations of iron equal to or exceeding 0.3 mg/l constitute a hazard to the marine environment, and levels less than 0.05 mg/l present minimal risk of deleterious effects.

Lead

The present rate of input of lead into the oceans is approximately ten times the rate of introduction by natural weathering, and concentrations of lead in surface sea water are greater than in deeper waters (Chow and Patterson 1966).[139] The isotope composition of the lead in surface waters and in recent precipitation is more similar to that of mined ore than to that in marine sediments (Chow 1968).[138] There are almost no data, however, that would suggest that the higher concentrations of lead in surface sea water derived from lead transported through the atmosphere have resulted in higher lead concentrations in marine wildlife. Lead concentrations in Greenland snow have been shown to be 16 times higher in 1964 than in 1904 (Murozumi et al. 1969).[235] In 1968 an estimated 1.8×10^5 tons of lead were introduced to the atmosphere as a result of the combustion of leaded gasoline (Council on Environmental Quality 1971).[144] This represents 14 per cent of the total lead consumption of the United States for that year. Lead poisoning of zoo animals in New York City was attributed to their breathing lead-contaminated air (Bazell 1971).[119]

Blood serum aldolase activity in higher animals exposed to small amounts of lead increased, although there were no

overt signs or symptoms of poisoning (Yaverbaum 1963,[308] Wilber 1969[299]). Chronic lead poisoning in man is symptomatically similar to multiple sclerosis (Falkowska et al. 1964).[169] Muscular dystrophy has been reported as occurring in fishes and amphibians (Stolk 1962,[272] Wilber 1969[299]) and in view of these findings could, in fact, be unnatural.

Data are needed on the sublethal, long-term effects of lead on aquatic organisms, particularly those in sea water. Evidence of deleterious effect to freshwater fish has been reported for concentrations of lead as low as 0.1 mg/l (Jones 1938).[197]

Wilder (1952)[300] reported lobster dying in 6 to 20 days when held in lead-lined tanks. Pringle (*unpublished data*)[315] observed a 12-week LC50 of 0.5 mg/l lead and an 18-week LC50 of 0.3 mg/l lead with the oyster (*Crassostrea virginica*). There was noticeable change in gonadal and mantle tissue following 12 weeks exposure at concentrations of 0.1 to 0.2 mg/l of lead. Calabrese et al. (*unpublished data*)[310] found a 48-hour LC25 of 1.73 mg/l and an LC50 of 2.45 mg/l for oyster eggs of the same species.

North and Clendenning (1958)[241] reported that lead nitrate at 4.1 mg/l of lead showed no deleterious effect on the photosynthesis rate in kelp (*Macrocystis pyrifera*) exposed for four days. They concluded that lead is less toxic to kelp than mercury, copper, hexavalent chromium, zinc, and nickel.

Recommendation

In the absence of more definitive information on the long-term chronic effect of lead on marine organisms, it is recommended that concentrations of lead in sea water should not exceed 0.02 of the 96-hr LC50 for the most sensitive species, and that the 24-hour average concentration should not exceed 0.01 of the 96-hour LC50. On the basis of data available at this time it is suggested that concentrations of lead equal to or exceeding 0.05 mg/l constitute a hazard in the marine environment, and levels less than 0.01 mg/l present minimal risk of deleterious effects. Special effort should be made to reduce lead levels even further in oyster-growing areas.

Lead recommendations for the protection of wildlife are included in the discussion of Marine Wildlife p. 227.

Manganese

Manganese is one of the most commonly used metals in industry. It occurs widely in ores on land and in nodules in the deep sea. U.S. consumption in 1958 exceeded 2.2 million tons, a 45 per cent increase in 20 years (U.S. Department of Interior, Bureau of Mines 1969).[289] The metal is alloyed with iron to produce steel and in smaller quantities with copper for manganese bronze. Its salts are used in inks and dyes, in glass and ceramics, in matches and fireworks, for dry-cell batteries, and in the manufacture of paints and varnishes.

Manganese is often found with iron in ground waters and it can be leached from soil and occur in drainage in high concentrations. The carbonates, oxides, and hydroxides are slightly soluble, so that manganous and manganic ions are rarely present in surface water in excess of 1 mg/l. Manganese is present in sea water at about 2 μg/l in the Mn^{+2} form, and is concentrated through biochemical processes to form manganese nodules, found mainly in the deep sea.

Manganese may have different effects on the lower trophic levels in fresh water and sea water. Concentrations of manganese above 0.005 mg/l had a toxic effect on certain algae in reservoirs (Guseva 1937,[174] 1939[175]), while 0.0005 mg/l in sea water stimulated growth and multiplication of certain phytoplankton (Harvey 1947).[178] Anderson (1944)[110] reported the threshold of immobilization of *Daphnia magna* as 0.63 mg/l of $KMnO_4$ and the threshold concentration for immobilization of *Daphnia magna* in Lake Erie water as 50 mg/l of $MnCl_2$ (Anderson 1948).[112] Bringmann and Kuhn (1959a)[131] reported the threshold effect for the same species as 50 mg/l of $MnCl_3$ as manganese in River Havel water at 23 C.

For the flatworm *Polycelis nigra*, the threshold concentration of manganese was reported as 700 mg/l as manganese chloride and 660 mg/l as manganese nitrate (Jones 1940).[199] Tests on organisms on which fish feed, i.e crustacea, worms, and insect larvae, showed no apparent harm at 15 mg/l of manganese during a 7-day exposure (Schweiger 1957).[261] River crayfish were found to tolerate 1 mg/l (Meinck et al. 1956).[227]

The toxicity of manganese to fish depends on a number of factors which may vary from one situation to another. There is an apparent antagonistic action of manganese toward nickel toxicity for fish (Blabaum and Nichols 1956).[125] This may be true also for cobalt and manganese in combination, as noted for terrestrial plant life (Ahmed and Twyman 1953).[108]

Stickleback survived 50 mg/l manganese as manganese sulphate for 3 days, whereas eels withstood 2700 mg/l for 50 hours (Doudoroff and Katz 1953).[150] The lethal concentration of manganese for stickleback was given as 40 mg/l by Jones (1939),[198] and he noted that the toxic action was slow. The minimum lethal concentration of manganese nitrate for sticklebacks in tap water has been reported to be 40 mg/l as manganese (Anderson 1948,[112] Murdock 1953).[234]

The average survival times of stickleback in manganous nitrate solution were one week at 50 mg/l, four days at 100 mg/l, two days at 150 mg/l, and one day at 300 mg/l, all measured as manganese (Murdock 1953).[234] Young eels tolerated 1500 mg/l manganous sulphate for more than 25 hours (Doudoroff and Katz 1953).[150] Oshima (1931)[246] and Iwao (1936)[189] reported the lethal thresholds of manganese.

CHAPTER 3
WATER QUALITY CRITERIA

The term "water quality criteria" has two different definitions under the Clean Water Act (CWA). Under section 304(a), EPA publishes water quality criteria that consist of scientific information regarding concentrations of specific chemicals or levels of parameters in water that protect aquatic life and human health (see section 3.1 of this Handbook). The States may use these contents as the basis for developing enforceable water quality standards. Water quality criteria are also elements of State water quality standards adopted under section 303(c) of the CWA (see sections 3.2 through 3.6 of this Handbook). States are required to adopt water quality criteria that will protect the designated use(s) of a water body. These criteria must be based on sound scientific rationale and must contain sufficient parameters or constituents to protect the designated use.

3.1 EPA Section 304(a) Guidance

EPA and a predecessor agency have produced a series of scientific water quality criteria guidance documents. Early Federal efforts were the "Green Book" (FWPCA, 1968) and the "Red Book" (USEPA, 1976). EPA also sponsored a contract effort that resulted in the "Blue Book" (NAS/NAE, 1973). These early efforts were premised on the use of literature reviews and the collective scientific judgment of Agency and advisory panels. However, when faced with the need to develop criteria for human health as well as aquatic life, the Agency determined that new procedures were necessary. Continued reliance solely on existing scientific literature was deemed inadequate because essential information was not available for many pollutants. EPA scientists developed formal methodologies for establishing scientifically defensible criteria. These were subjected to review by the Agency's Science

Advisory Board of outside experts and the public. This effort culminated on November 28, 1980, when the Agency published criteria development guidelines for aquatic life and for human health, along with criteria for 64 toxic pollutants (USEPA, 1980a,b). Since that initial publication, the aquatic life methodology was amended (Appendix H), and additional criteria were proposed for public comment and finalized as Agency criteria guidance. EPA summarized the available criteria information in the "*Gold Book*" (USEPA, 1986a), which is updated from time to time. However, the individual criteria documents (see Appendix I), as updated, are the official guidance documents.

EPA's criteria documents provide a comprehensive toxicological evaluation of each chemical. For toxic pollutants, the documents tabulate the relevant acute and chronic toxicity information for aquatic life and derive the criteria maximum concentrations (acute criteria) and criteria continuous concentrations (chronic criteria) that the Agency recommends to protect aquatic life resources. The methodologies for these processes are described in Appendices H and J and outlined in sections 3.1.2 and 3.1.3 of this Handbook.

3.1.1 State Use of EPA Criteria Documents

EPA's water quality criteria documents are available to assist States in:

*   adopting water quality standards that include appropriate numeric water quality criteria;

*   interpreting existing water quality standards that include narrative "no toxics in toxic amounts" criteria;

- making listing decisions under section 304(1) of the CWA;

- writing water quality-based NPDES permits and individual control strategies; and

- providing certification under section 401 of the CWA for any Federal permit or license (e.g., EPA-issued NPDES permits, CWA section 404 permits, or Federal Energy Regulatory Commission licenses).

In these situations, States have primary authority to determine the appropriate level to protect human health or welfare (in accordance with section 303(c)(2) of the CWA) for each water body. However, under the Clean Water Act, EPA must also review and approve State water quality standards; section 304(1) listing decisions and draft and final State-issued individual control strategies; and in States where EPA writes NPDES permits, EPA must develop appropriate water quality-based permit limitations. The States and EPA therefore have a strong interest in assuring that the decisions are legally defensible, are based on the best information available, and are subject to full and meaningful public comment and participation. It is very important that each decision be supported by an adequate record. Such a record is critical to meaningful comment, EPA's review of the State's decision, and any subsequent administrative or judicial review.

Any human health criterion for a toxicant is based on at least three interrelated considerations:

- cancer potency or systemic toxicity,

- exposure, and

- risk characterization.

States may make their own judgments on each of these factors within reasonable scientific bounds, but documentation to support their judgments, when different from EPA's recommendation, must be clear and in the public record. If a State relies on EPA's section 304(a) criteria document (or

other EPA documents), the State may reference and rely on the data in these documents and need not create duplicative or new material for inclusion in their records. However, where site-specific issues arise or the State decides to adopt an approach to any one of these three factors that differs from the approach in EPA's criteria document, the State must explain its reasons in a manner sufficient for a reviewer to determine that the approach chosen is based on sound scientific rationale (40 CFR 131.11(b)).

3.1.2   Criteria for Aquatic Life Protection

The development of national numerical water quality criteria for the protection of aquatic organisms is a complex process that uses information from many areas of aquatic toxicology. (See Appendix H for a detailed discussion of this process.) After a decision is made that a national criterion is needed for a particular material, all available information concerning toxicity to, and bioaccumulation by, aquatic organisms is collected and reviewed for acceptability. If enough acceptable data for 48- to 96-hour toxicity tests on aquatic plants and animals are available, they are used to derive the acute criterion. If sufficient data on the ratio of acute to chronic toxicity concentrations are available, they are used to derive the chronic or long-term exposure criteria. If justified, one or both of the criteria may be related to other water quality characteristics, such as pH, temperature, or hardness. Separate criteria are developed for fresh and salt waters.

The Water Quality Standards Regulation allows States to develop numerical criteria or modify

EPA's recommended criteria to account for site-specific or other scientifically defensible factors. Guidance on modifying national criteria is found in sections 3.6 and 3.7. When a criterion must be developed for a chemical for which a national criterion has not been established, the regulatory authority should refer to the EPA guidelines (Appendix H).

Magnitude for Aquatic Life Criteria

Water quality criteria for aquatic life contain two expressions of allowable magnitude: a criterion maximum concentration (CMC) to protect against acute (short-term) effects; and a criterion continuous concentration (CCC) to protect against chronic (long-term) effects. EPA derives acute criteria from 48- to 96-hour tests of lethality or immobilization. EPA derives chronic criteria from longer term (often greater than 28-day) tests that measure survival, growth, or reproduction. Where appropriate, the calculated criteria may be lowered to be protective ofcomercially or recreationally important species.

Duration for Aquatic Life Criteria

The quality of an ambient water typically varies in response to variations of effluent quality, stream flow, and other factors. Organisms in the receiving water are not experiencing constant, steady exposure but rather are experiencing fluctuating exposures, including periods of high concentrations, which may have adverse effects. Thus, EPA's criteria indicate a time period over which exposure is to be averaged, as well as an upper limit on the average concentration, thereby limiting the duration of exposure to elevated concentrations. For acute criteria, EPA recommends an averaging period of 1 hour. That is, to protect against acute effects, the 1-hour average exposure should not exceed the CMC. For chronic criteria, EPA recommends an averaging period of 4 days. That is, the 4-day average exposure should not exceed the CCC.

Frequency for Aquatic Life Criteria

To predict or ascertain the attainment of criteria, it is necessary to specify the allowable frequency for exceeding the criteria. This is because it is statistically impossible to project that criteria will never be exceeded. As ecological communities are naturally subjected to a series of stresses, the allowable frequency of pollutant stress may be set at a value that does not significantly increase the frequency or severity of all stresses combined.

EPA recommends an average frequency for excursions of both acute and chronic criteria not to exceed once in 3 years. In all cases, the recommended frequency applies to actual ambient concentrations, and excludes the influence of measurement imprecision. EPA established its recommended frequency as part of its guidelines for deriving criteria (Appendix H). EPA selected the 3-year average frequency of criteria exceedence with the intent of providing for ecological recovery from a variety of severe stresses. This return interval is roughly equivalent to a 7Q10 design flow condition. Because of the nature of the ecological recovery studies available, the severity of criteria excursions could not be rigorously related to the resulting ecological impacts. Nevertheless, EPA derives its criteria intending that a single marginal criteria excursion (i.e., a slight excursion over a 1-hour period for acute or over a 4-day period for chronic) would require little or no time for recovery. If the frequency of marginal criteria excursions is not high, it can be shown that the frequency of severe stresses, requiring measurable recovery periods, would be extremely small. EPA thus expects the 3-year return interval to provide a very high degree of protection.

3.1.3 Criteria for Human Health Protection

This section reviews EPA's procedures used to develop assessments of human health effects in developing water quality criteria and reference ambient concentrations. A more complete human health effects discussion is included in the *Guidelines and Methodology Used in the*

Preparation of Health Effects Assessment Chapters of the Consent Decree Water Documents (Appendix J). The procedures contained in this document are used in the development and updating of EPA water quality criteria and may be used in updating State criteria and in developing State criteria for those pollutants lacking EPA human health criteria. The procedures may also be applied as site-specific interpretations of narrative standards and as a basis for permit limits under 40 CFR 122.44 (d)(1)(vi).

Magnitude and Duration

Water quality criteria for human health contain only a single expression of allowable magnitude; a criterion concentration generally to protect against long-term (chronic) human health effects. Currently, national policy and prevailing opinion in the expert community establish that the duration for human health criteria for carcinogens should be derived assuming lifetime exposure, taken to be a 70-year time period. The duration of exposure assumed in deriving criteria for noncarcinogens is more complicated owing to a wide variety of endpoints: some developmental (and thus age-specific and perhaps gender-specific), some lifetime, and some, such as organoleptic effects, not duration-related at all. Thus, appropriate durations depend on the individual noncarcinogenic pollutants and the endpoints or adverse effects being considered.

Human Exposure Considerations

A complete human exposure evaluation for toxic pollutants of concern for bioaccumulation would encompass not only estimates of exposures due to fish consumption but also exposure from background concentrations and other exposure routes. The more important of these include recreational and occupational contact, dietary intake from other than fish, intake from air inhalation, and drinking water consumption. For section 304(a) criteria development, EPA typically considers only exposures to a pollutant that occur through the ingestion of water and contaminated fish and shellfish. This is the exposure default

assumption, although the human health guidelines provide for considering other sources where data are available (see 45 F.R. 79354). Thus the criteria are based on an assessment of risks related to the surface water exposure route only (57 F.R. 60862-3).

The consumption of contaminated fish tissue is of serious concern because the presence of even extremely low ambient concentrations of bioaccumulative pollutants (sublethal to aquatic life) in surface waters can result in residue concentrations in fish tissue that can pose a human health risk. Other exposure route information should be considered and incorporated in human exposure evaluations to the extent available.

Levels of actual human exposures from consuming contaminated fish vary depending upon a number of case-specific consumption factors. These factors include type of fish species consumed, type of fish tissue consumed, tissue lipid content, consumption rate and pattern, and food preparation practices. In addition, depending on the spatial variability in the fishery area, the behavior of the fish species, and the point of application of the criterion, the average exposure of fish may be only a small fraction of the expected exposure at the point of application of the criterion. If an effluent attracts fish, the average exposure might be greater than the expected exposure.

With shellfish, such as oysters, snails, and mussels, whole-body tissue consumption commonly occurs, whereas with fish, muscle tissue and roe are most commonly eaten. This difference in the types of tissues consumed has implications for the amount of available bioaccumulative contaminants likely to be ingested. Whole-body shellfish consumption presumably means ingestion of the entire burden of bioaccumulative contaminants. However, with most fish, selective cleaning and removal of internal organs, and sometimes body fat as well, from edible tissues, may result in removal of much of the lipid material in which bioaccumulative contaminants tend to concentrate.

Fish Consumption Values

EPA's human health criteria have assumed a human body weight of 70 kg and the consumption of 6.5 g of fish and shellfish per day. Based on data collected in 1973-74, the national per capita consumption of freshwater and estuarine fish was estimated to average 6.5 g/day. Per capita consumption of all seafood (including marine species) was estimated to average 14.3 g/day. The 95th percentile for consumption of all seafood by individuals over a period of 1 month was estimated to be 42 g/day. The mean lipid content of fish and shellfish tissue consumed in this study was estimated to be 3.0 percent (USEPA, 1980c).

Currently, four levels of fish and shellfish consumption are provided in EPA guidance (USEPA, 1991a):

- 6.5 g/day to represent an estimate of average consumption of fish and shellfish from estuarine and freshwaters by the entire U.S. population. This consumption level is based on the average of both consumers and nonconsumers of.

- 20 g/day to represent an estimate of the average consumption of fish and shellfish from marine, estuarine, and freshwaters by the U.S. population. This average consumption level also includes both consumers and nonconsumers of.

- 165 g/day to represent consumption of fish and shellfish from marine, estuarine, and freshwaters by the 99.9th percentile of the U.S. population consuming the most fish or seafood.

- 180 g/day to represent a "reasonable worst case" based on the assumption that some individuals would consume fishand shellfish at a rate equal to the combined consumption of red meat, poultry, fish, and shellfish in the United States.

EPA is currently updating the national estuarine and freshwater fish and shellfish consumption default values and will provide a range of recommended national consumption values. This range will include:

- mean values appropriate to the population at large; and

- values appropriate for those individuals who consume a relatively large proportion of fish and shellfish in their diets (maximally exposed individuals).

Many States use EPA's 6.5 g/day consumption value. However, some States use the above-mentioned 20 g/day value and, for saltwaters, 37 g/day. In general, EPA recommends that the consumption values used in deriving criteria from the formulas in this chapter reflect the most current, relevant, and/or site-specific information available.

Bioaccumulation Considerations

The ratio of the contaminant concentrations in fish tissue versus that in water is termed either the bioconcentration factor (BCF) or the bioaccumulation factor (BAF). Bioconcentration is defined as involving contaminant uptake from water only (not from food). The bioaccumulation factor (BAF) is defined similarly to the BCF except that it includes contaminant uptake from both water and food. Under laboratory conditions, measurements of tissue/water partitioning are generally considered to involve uptake from water only. On the other hand, both processes are likely to apply in the field since the entire food chain is exposed.

The BAF/BCF ratio ranges from 1 to 100, with the highest ratios applying to organisms in higher trophic levels, and to chemicals with logarithm of the octanol-water partitioning coefficient (log P) close to 6.5.

Bioaccumulation considerations are integrated into the criteria equations by using food chain

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multipliers (FMs) in conjunction with the BCF. The bioaccumulation and bioconcentration factors for a chemical are related as follows:

$$BAF = FM \times BCF$$

By incorporating the FM and BCF terms into the criteria equations, bioaccumulation can be addressed.

In Table 3-1, FM values derived from the work of Thomann (1987, 1989) are listed according to log P value and trophic level of the organism. For chemicals with log P values greater than about 7, there is additional uncertainty regarding the degree of bioaccumulation, but generally, trophic level effects appear to decrease due to slow transport kinetics of these chemicals in fish, the growth rate of the fish, and the chemical's relatively low bioavailability. Trophic level 4 organisms are typically the most desirable species for sport fishing and, therefore, FMs for trophic level 4 should generally be used in the equations for calculating criteria. In those very rare situations where only lower trophic level organisms are found, e.g., possibly oyster beds, an FM for a lower trophic level might be considered.

Measured BAFs (especially for those chemicals with log P values above 6.5) reported in the literature should be used when available. To use experimentally measured BAFs in calculating the criterion, the (FM x BCF) term is replaced by the BAF in the equations in the following section. Relatively few BAFs have been measured accurately and reported, and their application to sites other than the specific ecosystem where they were developed is problematic and subject to uncertainty. The option is also available to develop BAFs experimentally, but this will be extremely resource intensive if done on a site-specific basis with all the necessary experimental and quality controls.

	Trophic Levels		
Log P	2	3	4
3.5	1.0	1.0	1.0
3.6	1.0	1.0	1.0
3.7	1.0	1.0	1.0
3.8	1.0	1.0	1.0
3.9	1.0	1.0	1.0
4.0	1.1	1.0	1.0
4.1	1.1	1.1	1.1
4.2	1.1	1.1	1.1
4.3	1.1	1.1	1.1
4.4	1.2	1.1	1.1
4.5	1.2	1.2	1.2
4.6	1.2	1.3	1.3
4.7	1.3	1.4	1.4
4.8	1.4	1.5	1.6
4.9	1.5	1.8	2.0
5.0	1.6	2.1	2.6
5.1	1.7	2.5	3.2
5.2	1.9	3.0	4.3
5.3	2.2	3.7	5.8
5.4	2.4	4.6	8.0
5.5	2.8	5.9	11
5.6	3.3	7.5	16
5.7	3.9	9.8	23
5.8	4.6	13	33
5.9	5.6	17	47
6.0	6.8	21	67
6.1	8.2	25	75
6.2	10	29	84
6.3	13	34	92
6.4	15	39	98
6.5	19	45	100
≥6.5	19.2*	45*	100*

* These recommended FMs are conservative estimates; FMs for log P values greater than 6.5 may range from the values given to as low as 0.1 for contaminants with very low bioavailability.

Table 3-1. **Estimated Food Chain Multipliers (FMs)**

Updating Human Health Criteria Using IRIS

EPA recommends that States use the most current risk information in the process of updating human

health criteria. The Integrated Risk Information System (IRIS) (Barns and Dourson, 1988; Appendix N) is an electronic data base of the USEPA that provides chemical-specific risk information on the relationship between chemical exposure and estimated human health effects. Risk assessment information contained in IRIS, except as specifically noted, has been reviewed and agreed upon by an interdisciplinary group of scientists representing various Program Offices within the Agency and represent an Agency-wide consensus. Risk assessment information and values are updated on a monthly basis and are approved for Agency-wide use. IRIS is intended to make risk assessment information readily available to those individuals who must perform risk assessments and also to increase consistency among risk assessment/risk management decisions.

IRIS contains two types of quantitative risks values: the oral Reference Dose (RfD) and the carcinogenic potency estimate or slope factor. The RfD (formerly known as the acceptable daily intake or ADI) is the human health hazard assessment for noncarcinogenic (target organ) effects. The carcinogenic potency estimate (formerly known as q_i^*) represents the upper bound cancer-causing potential resulting from lifetime exposure to a substance. The RfD or the oral carcinogenic potency estimate is used in the derivation of EPA human health criteria.

EPA periodically updates risk assessment information, including RfDs, cancer potency estimates, and related information on contaminant effects, and reports the current information on IRIS. Since IRIS contains the Agency's most recent quantitative risk assessment values, current IRIS values should be used by States in updating or developing new human health criteria. This means that the 1980 human health criteria should be updated with the latest IRIS values. The procedure for deriving an updated human health water quality criterion would require inserting the current Rfd or carcinogenic potency estimate on IRIS into the equations in Exhibit 3.1 or 3.2, as appropriate.
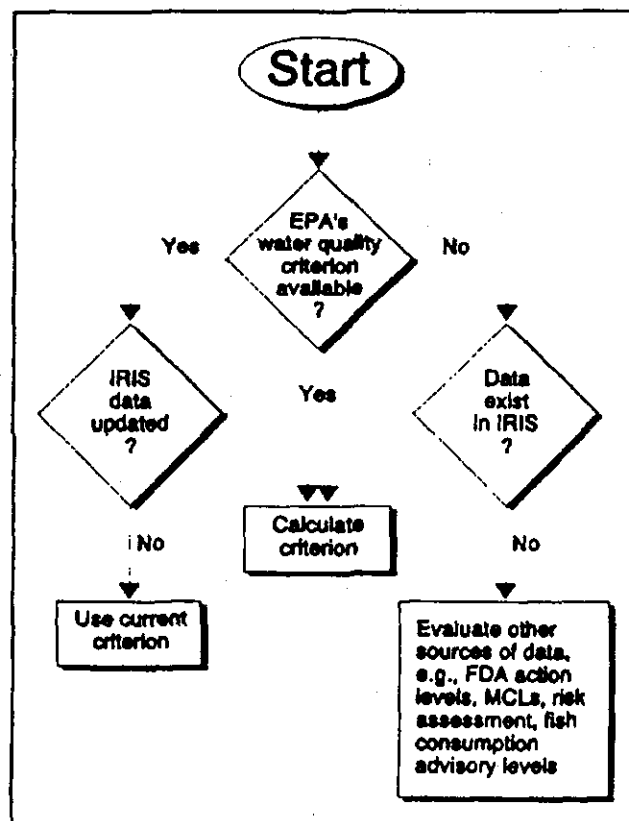

Figure 3-1. Procedure for determining an updated criterion using IRIS data.

Figure 3-1 shows the procedure for determining an updated criterion using IRIS data. If a chemical has both carcinogenic and non-carcinogenic effects, i.e., both a cancer potency estimate and a RfD, both criteria should be calculated. The most stringent criterion applies.

Calculating Criteria for Non-carcinogens

The RfD is an estimate of the daily exposure to the human population that is likely to be without appreciable risk of causing deleterious effects during a lifetime. The RfD is expressed in units of mg toxicant per kg human body weight per day.

RfDs are derived from the "no-observed-adverse-effect level" (NOAEL) or the "lowest-observed-adverse-effect level" (LOAEL) identified from chronic or subchronic human epidemiology studies or animal exposure studies. (Note: "LOAEL"

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and "NOAEL" refer to animal and human toxicology and are therefore distinct from the aquatic toxicity terms "no-observed-effect concentration" (NOEC) and "lowest-observed-effect concentration" (LOEC).) Uncertainty factors are then applied to the NOAEL or LOAEL to account for uncertainties in the data associated with variability among individuals, extrapolation from nonhuman test species to humans, data on other than long-term exposures, and the use of a LOAEL (USEPA, 1988a). An additional uncertainty factor may be applied to account for significant weakness or gaps in the database.

The RfD is a threshold below which systemic toxic effects are unlikely to occur. While exposures above the RfD increase the probability of adverse effects, they do not produce a certainty of adverse effects. Similarly, while exposure at or below the RfD reduces the probability, it does not guarantee the absence of effects in all persons. The RfDs contained in IRIS are values that represent EPA's consensus (and have uncertainty spanning perhaps an order of magnitude). This means an RfD of 1.0 mg/kg/day could range from 0.3 to 3.0 mg/kg/day.

For noncarcinogenic effects, an updated criterion can be derived using the equation in Exhibit 3-1.

If the receiving water body is not used as a drinking water source, the factor WI can be deleted. Where dietary and/or inhalation exposure values are unknown, these factors may be deleted from the above calculation.

Calculating Criteria for Carcinogens

Any human health criterion for a carcinogen is based on at least three interrelated considerations: cancer potency, exposure, and risk characterization. When developing State criteria, States may make their own judgments on each of these factors within reasonable scientific bounds, but documentation to support their judgments must be clear and in the public record.

Maximum protection of human health from the potential effects of exposure to carcinogens through the consumption of contaminated fish and/or other aquatic life would require a criterion of zero. The zero level is based upon the assumption of non-threshold effects (i.e., no safe level exists below which any increase in exposure does not result in an increased risk of cancer) for carcinogens. However, because a publicly acceptable policy for safety does not require the absence of all risk, a numerical estimate of pollutant concentration (in $\mu g/l$) which corresponds to a given level of risk for a population of a specified size is selected instead. A cancer risk level is defined as the number of new cancers that may result in a population of specified size due to an increase in exposure (e.g., 10^{-6} risk level = 1 additional cancer in a population of 1 million). Cancer risk is calculated by multiplying the experimentally derived cancer potency estimate by the concentration of the chemical in the fish and the average daily human consumption of contaminated fish. The risk for a specified population (e.g., 1 million people or 10^{-6}) is then calculated by dividing the risk level by the specific cancer risk. EPA's ambient water quality criteria documents provide risk levels ranging from 10^{-5} to 10^{-7} as examples.

The cancer potency estimate, or slope factor (formerly known as the q_1^*), is derived using animal studies. High-dose exposures are extrapolated to low-dose concentrations and adjusted to a lifetime exposure period through the use of a linearized multistage model. The model calculates the upper 95 percent confidence limit of the slope of a straight line which the model postulates to occur at low doses. When based on human (epidemiological) data, the slope factor is based on the observed increase in cancer risk and is not extrapolated. For deriving criteria for carcinogens, the oral cancer potency estimates or slope factors from IRIS are used.

It is important to note that cancer potency factors may overestimate or underestimate the actual risk. Such potency estimates are subject to great uncertainty because of two primary factors:

$$C \text{ (mg/l)} = \frac{(RfD \times WT) - (DT + IN) \times WT}{WI + [FC \times L \times FM \times BCF]}$$

where:

C = updated water quality criterion (mg/l)

RfD = oral reference dose (mg toxicant/kg human body weight/day)

WT = weight of an average human adult (70 kg)

DT = dietary exposure (other than fish) (mg toxicant/kg body human weight/day)

IN = inhalation exposure (mg toxicant/kg body human weight/day)

WI = average human adult water intake (2 l/day)

FC = daily fish consumption (kg fish/day)

L = ratio of lipid fraction of fish tissue consumed to 3%

FM = food chain multiplier (from Table 3-1)

BCF = bioconcentration factor (mg toxicant/kg fish divided by mg toxicant/L water) for fish with 3% lipid content

Exhibit 3-1. Equation for Deriving Human Health Criteria Based on Noncarcinogenic Effects

• adequacy of the cancer data base (i.e., human vs. animal data); and

• limited information regarding the mechanism of cancer causation.

Risk levels of 10^{-5}, 10^{-6}, and 10^{-7} are often used by States as minimal risk levels in interpreting their standards. EPA considers risks to be additive, i.e., the risk from individual chemicals is not necessarily the overall risk from exposure to water. For example, an individual risk level of 10^{-6} may yield a higher overall risk level if multiple carcinogenic chemicals are present.

For carcinogenic effects, the criterion can be determined by using the equation in Exhibit 3-2.

If the receiving water body is not designated as a drinking water source, the factor WI can be deleted.

Deriving Quantitative Risk Assessments in the Absence of IRIS Values

The RfDs or cancer potency estimates comprise the existing dose-response factors for developing criteria. When IRIS data are unavailable, quantitative risk level information may be developed according to a State's own procedures. Some States have established their own procedures whereby dose-response factors can be developed based upon extrapolation of acute and/or chronic animal data to concentrations of exposure protective of fish consumption by

$$C \ (mg/l) \ = \ \frac{(RL \times WT)}{q_1{}^* \ [WI + FC \times L \times (FM \times BCF)]}$$

where:

C   =   updated water quality criterion (mg/l)

RL   =   risk level (10^x) where x is usually in the range of 4 to 6

WT   =   weight of an average human adult (70 kg)

$q_1{}^*$ =   carcinogenic potency factor (kg day/mg)

WI   =   average human adult water intake (2 l/day)

FC   =   daily fish consumption (kg fish/day)

L   =   ratio of lipid fraction of fish tissue consumed to 3% assumed by EPA

FM   =   food chain multiplier (from Table 3-1)

BCF   =   bioconcentration factor (mg toxicant/kg fish divided by mg toxicant/L water) for fish with 3% lipid content

Exhibit 3-2. Equation for Deriving Human Health Criteria Based on Carcinogenic Effects

humans.

3.2 Relationship of Section 304(a) Criteria to State Designated Uses

The section 304(a)(1) criteria published by EPA from time to time can be used to support the designated uses found in State standards. The following sections briefly discuss the relationship between certain criteria and individual use classifications. Additional information on this subject also can be found in the "Green Book" (FWPCA, 1968); the "Blue Book" (NAS/NAE, 1973); the "Red Book" USEPA, 1976); the EPA *Water Quality Criteria Documents* (see Appendix I); the "Gold Book" (USEPA, 1986a); and future EPA section 304(a)(1) water quality criteria publications.

Where a water body is designated for more than one use, criteria necessary to protect the most sensitive use must be applied. The following four sections discuss the major types of use categories.

3.2.1 Recreation

Recreational uses of water include activities such as swimming, wading, boating, and fishing. Often insufficient data exist on the human health effects of physical and chemical pollutants, including most toxics, to make a determination of criteria for recreational uses. However, as a general guideline, recreational waters that contain chemicals in concentrations toxic or otherwise harmful to man if ingested, or irritating to the skin or mucous membranes of the human body

upon brief immersion, should be avoided. The section 304(a)(1) human health effects criteria based on direct human drinking water intake and fish consumption might provide useful guidance in these circumstances. Also, section 304(a)(1) criteria based on human health effects may be used to support this designated use where fishing is included in the State definition of "recreation." In this latter situation, only the portion of the criterion based on fish consumption should be used. Section 304(a)(1) criteria to protect recreational uses are also available for certain physical, microbiological, and narrative "free from" aesthetic criteria.

Research regarding bacteriological indicators has resulted in EPA recommending that States use *Escherichia coli* or enterococci as indicators of recreational water quality (USEPA, 1986b) rather than fecal coliform because of the better correlation with gastroenteritis in swimmers.

The "Green Book" and "Blue Book" provide additional information on protecting recreational uses such as pH criteria to prevent eye irritation and microbiological criteria based on aesthetic considerations.

3.2.2 Aquatic Life

The section 304(a)(1) criteria for aquatic life should be used directly to support this designated use. If subcategories of this use are adopted (e.g., to differentiate between coldwater and warmwater fisheries), then appropriate criteria should be set to reflect the varying needs of such subcategories.

3.2.3 Agricultural and Industrial Uses

The "Green Book" (FWPCA, 1968) and "Blue Book" (NAS/NAE, 1973) provide some information on protecting agricultural and industrial uses. Section 304(a)(1) criteria for protecting these uses have not been specifically developed for numerous parameters pertaining to these uses, including most toxics.

Where criteria have not been specifically developed for these uses, the criteria developed for human health and aquatic life are usually sufficiently stringent to protect these uses. States may also establish criteria specifically designed to protect these uses.

3.2.4 Public Water Supply

The drinking water exposure component of the section 304(a)(1) criteria based on human health effects can apply directly to this use classification. The criteria also may be appropriately modified depending upon whether the specific water supply system falls within the auspices of the Safe Drinking Water Act's (SDWA) regulatory control and the type and level of treatment imposed upon the supply before delivery to the consumer. The SDWA controls the presence of contaminants in finished ("at-the-tap") drinking water.

A brief description of relevant sections of the SDWA is necessary to explain how the Act will work in conjunction with section 304(a)(1) criteria in protecting human health from the effects of toxics due to consumption of water. Pursuant to section 1412 of the SDWA, EPA has promulgated "National Primary Drinking Water Standards" for certain radionuclide, microbiological, organic, and inorganic substances. These standards establish maximum contaminant levels (MCLs), which specify the maximum permissible level of a contaminant in water that may be delivered to a user of a public water system now defined as serving a minimum of 25 people. MCLs are established based on consideration of a range of factors including not only the health effects of the contaminants but also treatment capability, monitoring availability, and costs. Under section 1401(1)(D)(i) of the SDWA, EPA is also allowed to establish the minimum quality criteria for water that may be taken into a public water supply system.

Section 304(a)(1) criteria provide estimates of pollutant concentrations protective of human health, but do not consider treatment technology, costs, and other feasibility factors. The section

304(a)(1) criteria also include fish bioaccumulation and consumption factors in addition to direct human drinking water intake. These numbers were not developed to serve as "at-the-tap" drinking water standards, and they have no regulatory significance under the SDWA. Drinking water standards are established based on considerations, including technological and economic feasibility, not relevant to section 304(a)(1) criteria. Section 304(a)(1) criteria are more analogous to the maximum contaminant level goals (MCLGs) (previously known as RMCLs) under section 1412(b)(1)(B) of the SDWA in which, based upon a report from the National Academy of Sciences, the Administrator should set target levels for contaminants in drinking water at which "no known or anticipated adverse effects occur and which allow an adequate margin of safety." MCLGs do not take treatment, cost, and other feasibility factors into consideration. Section 304(a)(1) criteria are, in concept, related to the health-based goals specified in the MCLGs.

MCLs of the SDWA, where they exist, control toxic chemicals in finished drinking water. However, because of variations in treatment, ambient water criteria may be used by the States as a supplement to SDWA regulations. When setting water quality criteria for public water supplies, States have the option of applying MCLs, section 304(a)(1) human health effects criteria, modified section 304(a)(1) criteria, or controls more stringent than these three to protect against the effects of contaminants by ingestion from drinking water.

For treated drinking water supplies serving 25 people or greater, States must control contaminants down to levels at least as stringent as MCLs (where they exist for the pollutants of concern) in the finished drinking water. However, States also have the options to control toxics in the ambient water by choosing section 304(a)(1) criteria, adjusted section 304(a)(1) criteria resulting from the reduction of the direct drinking water exposure component in the criteria calculation to the extent that the treatment process reduces the level of pollutants, or a more stringent contaminant level than the former three options.

3.3 State Criteria Requirements

Section 131.11(a)(1) of the Regulation requires States to adopt water quality criteria to protect the designated use(s). The State criteria must be based on sound scientific rationale and must contain sufficient parameters or constituents to protect the designated use(s). For waters with multiple use designations, the criteria must support the most sensitive use.

In section 131.11, States are encouraged to adopt both numeric and narrative criteria. Aquatic life criteria should protect against both short-term (acute) and long-term (chronic) effects. Numeric criteria are particularly important where the cause of toxicity is known or for protection against pollutants with potential human health impacts or bioaccumulation potential. Numeric water quality criteria may also be the best way to address nonpoint source pollution problems. Narrative criteria can be the basis for limiting toxicity in waste discharges where a specific pollutant can be identified as causing or contributing to the toxicity but where there are no numeric criteria in the State standards. Narrative criteria also can be used where toxicity cannot be traced to a particular pollutant.

Section 131.11(a)(2) requires States to develop implementation procedures which explain how the State will ensure that narrative toxics criteria are met.

To more fully protect aquatic habitats, it is EPA's policy that States fully integrate chemical-specific, whole-effluent, and biological assessment approaches in State water quality programs (see Appendix R). Specifically, each of these three methods can provide a valid assessment of non-attainment of designated aquatic life uses but can rarely demonstrate use attainment separately. Therefore, EPA supports a policy of independent application of these three water quality assessment

approaches. Independent application means that the validity of the results of any one of the approaches does not depend on confirmation by one or both of the other methods. This policy is based on the unique attributes, limitations, and program applications of each of the three approaches. Each method alone can provide valid and independently sufficient evidence of non-attainment of water quality standards, irrespective of any evidence, or lack thereof, derived from the other two approaches. The failure of one method to confirm impacts identified by another method does not negate the results of the initial assessment.

It is also EPA's policy that States should designate aquatic life uses that appropriately address biological integrity and adopt biological criteria necessary to protect those uses (see section 3.5.3 and Appendices C, K, and R).

3.4 Criteria for Toxicants

Applicable requirements for State adoption of water quality criteria for toxicants vary depending upon the toxicant. The reason for this is that the 1983 Water Quality Standards Regulation (Appendix A) and the Water Quality Act of 1987 which amended the Clean Water Act (Public Law 100-4) include more specific requirements for the particular toxicants listed pursuant to CWA section 307(a). For regulatory purposes, EPA has translated the 65 compounds and families of compounds listed pursuant to section 307(a) into 126 more specific substances, which EPA refers to as "priority toxic pollutants." The 126 priority toxic pollutants are listed in the WQS regulation and in Appendix P of this Handbook. Because of the more specific requirements for priority toxic pollutants, it is convenient to organize the requirements applicable to State adoption of criteria for toxicants into three categories:

- requirements applicable to priority toxic pollutants that have been the subject of CWA section 304(a)(1) criteria guidance (see section 3.4.1);

- requirements applicable to priority toxic pollutants that have not been the subject of CWA section 304(a)(1) criteria guidance (see section 3.4.1); and

- requirements applicable to all other toxicants (e.g., non-conventional pollutants like ammonia and chlorine) (see section 3.4.2).

3.4.1 Priority Toxic Pollutant Criteria

The criteria requirements applicable to priority toxic pollutants (i.e., the first two categories above) are specified in CWA section 303(c)(2)(B). Section 303(c)(2)(B), as added by the Water Quality Act of 1987, provides that:

Whenever a State reviews water quality standards pursuant to paragraph (1) of this subsection, or revises or adopts new standards pursuant to this paragraph, such State shall adopt criteria for all toxic pollutants listed pursuant to section 307(a)(1) of this Act for which criteria have been published under section 304(a), the discharge or presence of which in the affected waters could reasonably be expected to interfere with those designated uses adopted by the State, as necessary to support such designated uses. Such criteria shall be specific numerical criteria for such toxic pollutants. Where such numerical criteria are not available, whenever a State reviews water quality standards pursuant to paragraph (1), or revises or adopts new standards pursuant to this paragraph, such State shall adopt criteria based on biological monitoring or assessment methods consistent with information published pursuant to section 304(a)(8). Nothing in this section shall be construed to limit or delay the use of effluent limitations or other permit conditions based on or involving biological monitoring or assessment

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methods or previously adopted numerical criteria.

EPA, in devising guidance for section 303(c)(2)(B), attempted to provide States with the maximum flexibility that complied with the express statutory language but also with the overriding congressional objective: prompt adoption and implementation of numeric toxics criteria. EPA believed that flexibility was important so that each State could comply with section 303(c)(2)(B) and to the extent possible, accommodate its existing water quality standards regulatory approach.

General Requirements

To carry out the requirements of section 303(c)(2)(B), whenever a State revises its water quality standards, it must review all available information and data to first determine whether the discharge or the presence of a toxic pollutant is interfering with or is likely to interfere with the attainment of the designated uses of any water body segment.

If the data indicate that it is reasonable to expect the toxic pollutant to interfere with the use, or it actually is interfering with the use, then the State must adopt a numeric limit for the specific pollutant. If a State is unsure whether a toxic pollutant is interfering with, or is likely to interfere with, the designated use and therefore is

unsure that control of the pollutant is necessary to support the designated use, the State should undertake to develop sufficient information upon which to make such a determination. Presence of facilities that manufacture or use the section 307(a) toxic pollutants or other information indicating that such pollutants are discharged or will be discharged strongly suggests that such pollutants could be interfering with attaining designated uses. If a State expects the pollutant not to interfere with the designated use, then section 303(1)(2)(B) does not require a numeric standard for that pollutant.

Section 303(c)(2)(B) addresses only pollutants listed as "toxic" pursuant to section 307(a) of the Act, which are codified at 40 CFR 131.36(b). The section 307(a) list contains 65 compounds and families of compounds, which potentially include thousands of specific compounds. The Agency has interpreted that list to include 126 "priority" toxic pollutants for regulatory purposes. Reference in this guidance to toxic pollutants or section 307(a) toxic pollutants refers to the 126 priority toxic pollutants unless otherwise noted. Both the list of priority toxic pollutants and recommended criteria levels are subject to change.

The national criteria recommendations published by EPA under section 304(a) (see section 3.1, above) of the Act include values for both acute and chronic aquatic life protection; only chronic criteria recommendations have been established to

protect human health. To comply with the statute, a State needs to adopt aquatic life and human health criteria where necessary to support the appropriate designated uses. Criteria for the protection of human health are needed for water bodies designated for public water supply. When fish ingestion is considered an important activity, then the human health-related water quality criteria recommendation developed under section 304(a) of the CWA should be used; that is, the portion of the criteria recommendation based on fish consumption. For those pollutants designated as carcinogens, the recommendation for a human health criterion is generally more stringent than the aquatic life criterion for the same pollutant. In contrast, the aquatic life criteria recommendations for noncarcinogens are generally more stringent than the human health recommendations. When a State adopts a human health criterion for a carcinogen, the State needs to select a risk level. EPA has estimated risk levels of 10^{-5}, 10^{-6}, and 10^{-7} in its criteria documents under one set of exposure assumptions. However, the State is not limited to choosing among the risk levels published in the section 304(a) criteria documents, nor is the State limited to the base case exposure assumptions; it must choose the risk level for its conditions and explain its rationale.

EPA generally regulates pollutants treated as carcinogens in the range of 10^{-6} to 10^{-4} to protect average exposed individuals and more highly exposed populations. However, if a State selects a criterion that represents an upper bound risk level less protective than 1 in 100,000 (e.g., 10^{-5}), the State needs to have substantial support in the record for this level. This support focuses on two distinct issues. First, the record must include documentation that the decision maker considered the public interest of the State in selecting the risk level, including documentation of public participation in the decision making process as required by the Water Quality Standards Regulation at 40 CFR 131.20(b). Second, the record must include an analysis showing that the risk level selected, when combined with other risk assessment variables, is a balanced and reasonable

estimate of actual risk posed, based on the best and most representative information available. The importance of the estimated actual risk increases as the degree of conservatism in the selected risk level diminishes. EPA carefully evaluates all assumptions used by a State if the State chose to alter any one of the standard EPA assumption values (57 F.R. 60864, December 22, 1993).

EPA does not intend to propose changes to the current requirements regarding the bases on which a State can adopt numeric criteria (40 CFR 131.11(b)(1)). Under EPA's regulation, in addition to basing numeric criteria on EPA's section 304(a) criteria documents, States may also base numeric criteria on site-specific determinations or other scientifically defensible methods.

EPA expects each State to comply with the new statutory requirements in any section 303(c) water quality standards review initiated after enactment of the Water Quality Act of 1987. The structure of section 303(c) is to require States to review their water quality standards at least once each 3 year period. Section 303(c)(2)(B) instructs States to include reviews for toxics criteria whenever they initiate a triennial review. Therefore, even if a State has complied with section 303(c)(2)(B), the State must review its standards each triennium to ensure that section 303(c)(2)(B) requirements continue to be met, considering that EPA may have published additional section 304(a) criteria documents and that the State will have new information on existing water quality and on pollution sources.

It should be noted that nothing in the Act or in the *Water Quality Standards Regulation restricts the* right of a State to adopt numeric criteria for any pollutant not listed pursuant to section 307(a)(1), and that such criteria may be expressed as concentration limits for an individual pollutant or for a toxicity parameter itself as measured by whole-effluent toxicity testing. However, neither numeric toxic criteria nor whole-effluent toxicity

should be used as a surrogate for, or to supersede the other.

State Options

States may meet the requirements of CWA section 303(c)(2)(B) by choosing one of three scientifically and technically sound options (or some combination thereof):

(1) Adopt statewide numeric criteria in State water quality standards for all section 307(a) toxic pollutants for which EPA has developed criteria guidance, regardless of whether the pollutants are known to be present;

(2) Adopt specific numeric criteria in State water quality standards for section 307(a) toxic pollutants as necessary to support designated uses where such pollutants are discharged or are present in the affected waters and could reasonably be expected to interfere with designated uses;

(3) Adopt a "translator procedure" to be applied to a narrative water quality standard provision that prohibits toxicity in receiving waters. Such a procedure is to be used by the State in calculating derived numeric criteria, which shall be used for all purposes under section 303(c) of the CWA. At a minimum, such criteria need to be developed for section 307(a) toxic pollutants, as necessary to support designated uses, where these pollutants are discharged or present in the affected waters and could reasonably be expected to interfere with designated uses.

Option 1 is consistent with State authority to establish water quality standards. Option 2 most directly reflects the CWA requirements and is the option recommended by EPA. Option 3, while meeting the requirements of the CWA, is best suited to supplement numeric criteria from option 1 or 2. The three options are discussed in more detail below.

OPTION 1

Adopt statewide numeric criteria in State water quality standards for all section 307(a) toxic pollutants for which EPA has developed criteria guidance, regardless of whether the pollutants are known to be present.

Pro:

- simple, straightforward implementation

- ensures that States will satisfy statute

- makes maximum uses of EPA recommendations

- gets specific numbers into State water quality standards fast, at first

Con:

- some priority toxic pollutants may not be discharged in State

- may cause unnecessary monitoring by States

- might result in "paper standards"

Option 1 is within a State's legal authority under the CWA to adopt broad water quality standards. This option is the most comprehensive approach to satisfy the statutory requirements because it would include all of the priority toxic pollutants for which EPA has prepared section 304(a) criteria guidance for either or both aquatic life protection and human health protection. In addition to a simple adoption of EPA's section 304(a) guidance as standards, a State must select a risk level for those toxic pollutants which are carcinogens (i.e., that cause or may cause cancer in humans).

Many States find this option attractive because it ensures comprehensive coverage of the priority toxic pollutants with scientifically defensible criteria without the need to conduct a resource-intensive evaluation of the particular segments and

pollutants requiring criteria. This option also would not be more costly to dischargers than other options because permit limits would be based only on the regulation of the particular toxic pollutants in their discharges and not on the total listing in the water quality standards. Thus, actual permit limits should be the same under any of the options.

The State may also exercise its authority to use one or more of the techniques for adjusting water quality standards:

- establish or revise designated stream uses based on use attainability analyses (see section 2.9);

- develop site-specific criteria; or

- allow short-term variances (see section 5.3) when appropriate.

All three of these techniques may apply to standards developed under any of the three options discussed in this guidance. It is likely that States electing to use option 1 will rely more on variances because the other two options are implemented with more site-specific data being available. It should be noted, however, that permits issued pursuant to such water quality variances still must comply with any applicable antidegradation and antibacksliding requirements.

OPTION 2

Adopt specific numeric criteria in State water quality standards for section 307(a) toxic pollutants as necessary to support designated uses where such pollutants are discharged or are present in the affected waters and could reasonably be expected to interfere with designated uses.

Pro:

- directly reflects statutory requirement

- standards based on demonstrated need to control problem pollutants

- State can use EPA's section 304(a) national criteria recommendations or other scientifically acceptable alternative, including site-specific criteria

- State can consider current or potential toxic pollutant problems

- State can go beyond section 307(a) toxics list, as desired

Con:

- may be difficult and time consuming to determine if, and which, pollutants are interfering with the designated use

- adoption of standards can require lengthy debates on correct criteria limit to be included in standards

- successful State toxic control programs based on narrative criteria may be halted or slowed as the State applies its limited resources to developing numeric standards

- difficult to update criteria once adopted as part of standards

- to be absolutely technically defensible, may need site-specific criteria in many situations, leading to a large workload for regulatory agency

EPA recommends that a State use this option to meet the statutory requirement. It directly reflects all the Act's requirements and is flexible, resulting in adoption of numeric water quality standards as needed. To assure that the State is capable of dealing with new problems as they arise, EPA also recommends that States adopt a translator procedure the same as, or similar to, that described in option 3, but applicable to all chemicals causing toxicity and not just priority pollutants as is the case for option 3.

Beginning in 1988, EPA provided States with candidate lists of priority toxic pollutants and water bodies in support of CWA section 304(l) implementation. These lists were developed because States were required to evaluate existing and readily available water-related data to comply with section 304(l), 40 CFR 130.10(d). A similar "strawman" analysis of priority pollutants potentially requiring adoption of numeric criteria under section 303(c)(2)(B) was furnished to most States in September or October of 1990 for their use in ongoing and subsequent triennial reviews. The primary differences between the "strawman" analysis and the section 304(l) candidate lists were that the "strawman" analysis (1) organized the results by chemical rather than by water body, (2) included data for certain STORET monitoring stations that were not used in constructing the candidate lists, (3) included data from the Toxics Release Inventory database, and (4) did not include a number of data sources used in preparing the candidate lists (e.g., those, such as fish kill information, that did not provide chemical-specific information).

EPA intends for States, at a minimum, to use the information gathered in support of section 304(l) requirements as a starting point for identifying (1) water segments that will need new and/or revised water quality standards for section 307(a) toxic pollutants, and (2) which priority toxic pollutants require adoption of numeric criteria. In the longer term, EPA expects similar determinations to occur during each triennial review of water quality standards as required by section 303(c).

In identifying the need for numeric criteria, EPA is encouraging States to use information and data such as:

- presence or potential construction of facilities that manufacture or use priority toxic pollutants;

- ambient water monitoring data, including those for sediment and aquatic life (e.g., fish tissue data);

- NPDES permit applications and permittee self-monitoring reports;

- effluent guideline development documents, many of which contain section 307(a)(1) priority pollutant scans;

- pesticide and herbicide application information and other records of pesticide or herbicide inventories;

- public water supply source monitoring data noting pollutants with Maximum Contaminant Levels (MCLs); and

- any other relevant information on toxic pollutants collected by Federal, State, interstate agencies, academic groups, or scientific organizations.

States are also expected to take into account newer information as it became available, such as information in annual reports from the Toxic Chemical Release Inventory requirements of the Emergency Planning and Community Right-To-Know Act of 1986 (Title III, Public Law 99-499).

Where the State's review indicates a reasonable expectation of a problem from the discharge or presence of toxic pollutants, the State should identify the pollutant(s) and the relevant segment(s). In making these determinations, States should use their own EPA-approved criteria or existing EPA water quality criteria for purposes of segment identification. After the review, the State may use other means to establish the final criterion as it revises its standards.

As with option 1, a State using option 2 must follow all its legal and administrative requirements for adoption of water quality standards. Since the resulting numeric criteria are part of a State's water quality standards, they are required to be submitted by the State to EPA for review and either approval or disapproval.

EPA believes this option offers the State optimum flexibility. For section 307(a) toxic pollutants

adversely affecting designated uses, numeric criteria are available for permitting purposes. For other situations, the State has the option of defining site-specific criteria.

OPTION 3

Adopt a procedure to be applied to the narrative water quality standard provision that prohibits toxicity in receiving waters. Such a procedure would be used by a State in calculating derived numeric criteria to be used for all purposes of water quality criteria under section 303(c) of the CWA. At a minimum such criteria need to be derived for section 307(a) toxic pollutants where the discharge or presence of such pollutants in the affected waters could reasonably be expected to interfere with designated uses, as necessary to support such designated uses.

Pro:

- allows a State flexibility to control priority toxic pollutants

- reduces time and cost required to adopt specific numeric criteria as water quality standards regulations

- allows immediate use of latest scientific information available at the time a State needs to develop derived numeric criteria

- revisions and additions to derived numeric criteria can be made without need to revise State law

- State can deal more easily with a situation where it did not establish water quality standards for the section 307(a) toxic pollutants during the most recent triennial review

- State can address problems from non-section 307(a) toxic pollutants

Con:

- EPA is currently on notice that a derived numeric criterion may invite legal challenge

- once the necessary procedures are adopted to enhance legal defensibility (e.g., appropriate scientific methods and public participation and review), actual savings in time and costs may be less than expected

- public participation in development of derived numeric criteria may be limited when such criteria are not addressed in a hearing on water quality standards

EPA believes that adoption of a narrative standard along with a translator mechanism as part of a State's water quality standard satisfies the substantive requirements of the statute. These criteria are subject to all the State's legal and administrative requirements for adoption of standards plus review and either approval or disapproval by EPA, and result in the development of derived numeric criteria for specific section 307(a) toxic pollutants. They are also subject to an opportunity for public participation. Nevertheless, EPA believes the most appropriate use of option 3 is as a supplement to either option 1 or 2. Thus, a State would have formally adopted numeric criteria for toxic pollutants that occur frequently; that have general applicability statewide for inclusion in NPDES permits, total maximum daily loads, and waste load allocations; and that also would have a sound and predictable method to develop additional numeric criteria as needed. This combination of options provides a complete regulatory scheme.

Although the approach in option 3 is similar to that currently allowed in the Water Quality Standards Regulation (40 CFR 131.11(a)(2)), this guidance discusses several administrative and scientific requirements that EPA believes are necessary to comply with section 303(c)(2)(B).

(1) The Option 3 Procedure Must Be Used To Calculate Derived Numeric Water Quality Criteria

States must adopt a specific procedure to be applied to a narrative water quality criterion. To satisfy section 303(c)(2)(B), this procedure shall be used by the State in calculating derived numeric criteria, which shall be used for all purposes under section 303(c) of the CWA. Such criteria need to be developed for section 307(a) toxic pollutants as necessary to support designated uses, where these pollutants are discharged or are present in the affected waters and could reasonably be expected to interfere with the designated uses.

To assure protection from short-term exposures, the State procedure should ensure development of derived numeric water quality criteria based on valid acute aquatic toxicity tests that are lethal to half the affected organisms (LC50) for the species representative of or similar to those found in the State. In addition, the State procedure should ensure development of derived numeric water quality criteria for protection from chronic exposure by using an appropriate safety factor applicable to this acute limit. If there are saltwater components to the State's aquatic resources, the State should establish appropriate derived numeric criteria for saltwater in addition to those for freshwater.

The State's documentation of the tests should include a detailed discussion of its quality control and quality assurance procedures. The State should also include a description (or reference existing technical agreements with EPA) of the procedure it will use to calculate derived acute and chronic numeric criteria from the test data, and how these derived criteria will be used as the basis for deriving appropriate TMDLs, WLAs, and NPDES permit limits.

As discussed above, the procedure for calculating derived numeric criteria needs to protect aquatic life from both acute and chronic exposure to specific chemicals. Chronic aquatic life criteria

are to be met at the edge of the mixing zone. The acute criteria are to be met (1) at the end-of-pipe if mixing is not rapid and complete and a high rate diffuser is not present; or (2) after mixing if mixing is rapid and complete or a high rate diffuser is present. (See EPA's *Technical Support Document for Water Quality-based Toxics Control*, USEPA 1991a.)

EPA has not established a national policy specifying the point of application in the receiving water to be used with human health criteria. However, EPA has approved State standards that apply human health criteria for fish consumption at the mixing zone boundary and/or apply the criteria for drinking water consumption, at a minimum, at the point of use. EPA has also proposed more stringent requirements for the application of human health criteria for highly bioaccumulative pollutants in the *Water Quality guidance for the Great Lakes System* (50 F.R. 20931, 21035, April 16, 1993) including elimination of mixing zones.

In addition, the State should also include an indication of potential bioconcentration or bioaccumulation by providing for:

- laboratory tests that measure the steady-state bioconcentration rate achieved by a susceptible organism; and/or

- field data in which ambient concentrations and tissue loads are measured to give an appropriate factor.

In developing a procedure to be used in calculating derived numeric criteria for the protection of aquatic life, the State should consider the potential impact that bioconcentration has on aquatic and terrestrial food chains.

The State should also use the derived bioconcentration factor and food chain multiplier to calculate chronically protective numeric criteria for humans that consume aquatic organisms. In calculating this derived numeric criterion, the State should indicate data requirements to be met

when dealing with either threshold (toxic) or non-threshold (carcinogenic) compounds. The State should describe the species and the minimum number of tests, which may generally be met by a single mammalian chronic test if it is of good quality and if the weight of evidence indicates that the results are reasonable. The State should provide the method to calculate a derived numeric criterion from the appropriate test result.

Both the threshold and non-threshold criteria for protecting human health should contain exposure assumptions, and the State procedure should be used to calculate derived numeric criteria that address the consumption of water, consumption of fish, and combined consumption of both water and fish. The State should provide the assumptions regarding the amount of fish and the quantity of water consumed per person per day, as well as the rationale used to select the assumptions. It needs to include the number of tests, the species necessary to establish a dose-response relationship, and the procedure to be used to calculate the derived numeric criteria. For non-threshold contaminants, the State should specify the model used to extrapolate to low dose and the risk level. It should also address incidental exposure from other water sources (e.g., swimming). When calculating derived numeric criteria for multiple exposure to pollutants, the State should consider additive effects, especially for carcinogenic substances, and should factor in the contribution to the daily intake of toxicants from other sources (e.g., food, air) when data are available.

(2) The State Must Demonstrate That the Procedure Results in Derived Numeric Criteria Are Protective

The State needs to demonstrate that its procedures for developing criteria, including translator methods, yield fully protective criteria for human health and for aquatic life. EPA's review process will proceed according to EPA's regulation of 40 CFR 131.11, which requires that criteria be based on sound scientific rationale and be protective of all designated uses. EPA will use the expertise and experience it has gained in developing section 304(a) criteria for toxic pollutants by application of its own translator method (USEPA, 1980b; USEPA, 1985b).

Once EPA has approved the State's procedure, the Agency's review of derived numeric criteria, for example, for pollutants other than section 307(a) toxic pollutants resulting from the State's procedure, will focus on the adequacy of the data base rather than the calculation method. EPA also encourages States to apply such a procedure to calculate derived numeric criteria to be used as the basis for deriving permit limitations for nonconventional pollutants that also cause toxicity.

(3) The State Must Provide Full Opportunity for Public Participation in Adoption of the Procedure

The Water Quality Standards Regulation requires States to hold public hearings to review and revise water quality standards in accordance with provisions of State law and EPA's Public Participation Regulation (40 CFR 25). Where a State plans to adopt a procedure to be applied to the narrative criterion, it must provide full opportunity for public participation in the development and adoption of the procedure as part of the State's water quality standards.

While it is not necessary for the State to adopt each derived numeric criterion into its water quality standards and submit it to EPA for review and approval, EPA is very concerned that all affected parties have adequate opportunity to participate in the development of a derived

numeric criterion even though it is not being adopted directly as a water quality standard.

A State can satisfy the need to provide an opportunity for public participation in the development of derived numeric criteria in several ways, including:

- a specific hearing on the derived numeric criterion;

- the opportunity for a public hearing on an NPDES permits as long as public notice is given that a criterion for a toxic pollutant as part of the permit issuance is being contemplated; or

- a hearing coincidental with any other hearing as long as it is made clear that development of a specific criterion is also being undertaken.

For example, as States develop their lists and individual control strategies (ICSs) under section 304(1), they may seek full public participation. NPDES regulations also specify public participation requirements related to State permit issuance. Finally, States have public participation requirements associated with Water Quality Management Plan updates. States may take advantage of any of these public participation requirements to fulfill the requirement for public review of any resulting derived numeric criteria. In such cases, the State must give prior notice that development of such criteria is under consideration.

(4) The Procedure Must Be Formally Adopted and Mandatory

Where a State elects to supplement its narrative criterion with an accompanying implementing procedure, it must formally adopt such a procedure as a part of its water quality standards. The procedure must be used by the State to calculate derived numeric criteria that will be used as the basis for all standards' purposes, including the following: developing TMDLs, WLAs, and

limits in NPDES permits; determining whether water use designations are being met; and identifying potential nonpoint source pollution problems.

(5) The Procedure Must Be Approved by EPA as Part of the State's Water Quality Standards Regulation

To be consistent with the requirements of the Act, the State's procedure to be applied to the narrative criterion must be submitted to EPA for review and approval, and will become a part of the State's water quality standards. (See 40 CFR 131.21 for further discussion.) This requirement may be satisfied by a reference in the standards to the procedure, which may be contained in another document, which has legal effect and is binding on the State, and all the requirements for public review, State implementation, and EPA review and approval are satisfied.

Criteria Based on Biological Monitoring

For priority toxic pollutants for which EPA has not issued section 304(a)(1) criteria guidance, CWA section 303(c)(2)(B) requires States to adopt criteria based on biological monitoring or assessment methods. The phrase "biological monitoring or assessment methods" includes:

- whole-effluent toxicity control methods;

- biological criteria methods; or

- other methods based on biological monitoring or assessment.

The phrase "biological monitoring or assessment methods" in its broadest sense also includes criteria developed through translator procedures. This broad interpretation of that phrase is consistent with EPA's policy of applying chemical-specific, biological, and whole-effluent toxicity methods independently in an integrated toxics control program. It is also consistent with the intent of Congress to expand State standards programs beyond chemical-specific approaches.

States should also consider developing protocols to derive and adopt numeric criteria for priority toxic pollutants (or other pollutants) where EPA has not issued section 304(a) criteria guidance. The State should consider available laboratory toxicity test data that may be sufficient to support derivation of chemical-specific criteria. Existing data need not be as comprehensive as that required to meet EPA's 1985 guidelines in order for a State to use its own protocols to derive criteria. EPA has described such protocols in the proposed *Water Quality Guidance for the Great Lakes System* (58 F.R. 20892, at 21016, April 16, 1993.) This is particularly important where other components of a State's narrative criterion implementation procedure (e.g., WET controls or biological criteria) may not ensure full protection of designated uses. For some pollutants, a combination of chemical-specific and other approaches is necessary (e.g., pollutants where bioaccumulation in fish tissue or water consumption by humans is a primary concern).

Biologically based monitoring or assessment methods serve as the basis for control where no specific numeric criteria exist or where calculation or application of pollutant-by-pollutant criteria appears infeasible. Also, these methods may serve as a supplemental measurement of attainment of water quality standards in addition to numeric and narrative criteria. The requirement for both numeric criteria and biologically based methods demonstrates that section 303(c)(2)(B) contemplates that States develop a comprehensive toxics control program regardless of the status of EPA's section 304(a) criteria.

The whole-effluent toxicity (WET) testing procedure is the principal biological monitoring guidance developed by EPA to date. The purpose of the WET procedure is to control point source dischargers of toxic pollutants. The procedure is particularly useful for monitoring and controlling the toxicity of complex effluents that may not be well controlled through chemical-specific numeric criteria. As such, biologically based effluent testing procedures are a necessary component of

a State's toxics control program under section 303(c)(2)(B) and a principal means for implementing a State's narrative "free from toxics" standard.

Guidance documents EPA considers to serve the purpose of section 304(a)(8) include the *Technical Support Document for Water Quality-based Toxics Control* (USEPA, 1991a; *Guidelines for Deriving National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses* (Appendix H); *Guidelines and Methodology Used in the Preparation of Health Effect Assessment Chapters of the Consent Decree Water Criteria Documents* (Appendix J); *Methods for Measuring Acute Toxicity of Effluents to Freshwater and Marine Organisms* (USEPA, 1991d); *Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms* (USEPA, 1991e); and *Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms* (USEPA, 1991f).

3.4.2 Criteria for Nonconventional Pollutants

Criteria requirements applicable to toxicants that are not priority toxic pollutants (e.g., ammonia and chlorine), are specified in the 1983 Water Quality Standards Regulation (see 40 CFR 131.11). Under these requirements, States must adopt criteria based on sound scientific rationale that cover sufficient parameters to protect designated uses. Both numeric and narrative criteria (discussed in sections 3.5.1 and 3.5.2, below) may be applied to meet these requirements.

3.5 Forms of Criteria

States are required to adopt water quality criteria, based on sound scientific rationale, that contain sufficient parameters or constituents to protect the designated use. EPA believes that an effective State water quality standards program should include both parameter-specific (e.g., ambient numeric criteria) and narrative approaches.

3.5.1 Numeric Criteria

Numeric criteria are required where necessary to protect designated uses. Numeric criteria to protect aquatic life should be developed to address both short-term (acute) and long-term (chronic) effects. Saltwater species, as well as freshwater species, must be adequately protected. Adoption of numeric criteria is particularly important for toxicants known to be impairing surface waters and for toxicants with potential human health impacts (e.g., those with high bioaccumulation potential). Human health should be protected from exposure resulting from consumption of water and fish or other aquatic life (e.g., mussels, crayfish). Numeric water quality criteria also are useful in addressing nonpoint source pollution problems.

In evaluating whether chemical-specific numeric criteria for toxicants that are not priority toxic pollutants are required, States should consider whether other approaches (such as whole-effluent toxicity criteria or biological controls) will ensure full protection of designated uses. As mentioned above, a combination of independent approaches may be required in some cases to support the designated uses and comply with the requirements of the Water Quality Standards Regulation (e.g., pollutants where bioaccumulation in fish tissue or water consumption by humans is a primary concern).

3.5.2 Narrative Criteria

To supplement numeric criteria for toxicants, all States have also adopted narrative criteria for toxicants. Such narrative criteria are statements that describe the desired water quality goal, such as the following:

> All waters, including those within mixing zones, shall be free from substances attributable to wastewater discharges or other pollutant sources that:

(1) Settle to form objectional deposits;

(2) Float as debris, scum, oil, or other matter forming nuisances;

(3) Produce objectionable color, odor, taste, or turbidity;

(4) Cause injury to, or are toxic to, or produce adverse physiological responses in humans, animals, or plants; or

(5) Produce undesirable or nuisance aquatic life (54 F.R. 28627, July 6, 1989).

EPA considers that the narrative criteria apply to all designated uses at all flows and are necessary to meet the statutory requirements of section 303(c)(2)(A) of the CWA.

Narrative toxic criteria (No. 4, above) can be the basis for establishing chemical-specific limits for waste discharges where a specific pollutant can be identified as causing or contributing to the toxicity and the State has not adopted chemical-specific numeric criteria. Narrative toxic criteria are cited as a basis for establishing whole-effluent toxicity controls in EPA permitting regulations at 40 CFR 122.44(d)(1)(v).

To ensure that narrative criteria for toxicants are attained, the Water Quality Standards Regulation requires States to develop implementation procedures (see 40 CFR 131.11(a)(2)). Such implementation procedures (Exhibit 3-3) should address all mechanisms to be used by the State to ensure that narrative criteria are attained. Because implementation of chemical-specific numeric criteria is a key component of State toxics control programs, narrative criteria implementation procedures must describe or reference the State's procedures to implement such chemical-specific numeric criteria (e.g., procedures for establishing chemical-specific permit limits under the NPDES permitting

State implementation procedures for narrative toxics criteria should describe the following:

- Specific, scientifically defensible methods by which the State will implement its narrative toxics standard for all toxicants, including:

    - methods for chemical-specific criteria, including methods for applying chemical-specific criteria in permits, developing or modifying chemical-specific criteria via a "translator procedure" (defined and discussed below), and calculating site-specific criteria based on local water chemistry or biology);

    - methods for developing and implementing whole-effluent toxicity criteria and/or controls; and

    - methods for developing and implementing biological criteria.

- How these methods will be integrated in the State's toxics control program (i.e., how the State will proceed when the specified methods produce conflicting or inconsistent results).

- Application criteria and information needed to apply numerical criteria, for example:

    - methods the State will use to identify those pollutants to be regulated in a specific discharge;

    - an incremental cancer risk level for carcinogens;

    - methods for identifying compliance thresholds in permits where calculated limits are below detection;

    - methods for selecting appropriate hardness, pH, and temperature variables for criteria expressed as functions;

    - methods or policies controlling the size and in-zone quality of mixing zones;

    - design flows to be used in translating chemical-specific numeric criteria for aquatic life and human health into permit limits; and

    - other methods and information needed to apply standards on a case-by-case basis.

Exhibit 3-3.   Components of a State Implementation Procedure for Narrative Toxics Criteria

program). Implementation procedures must also address State programs to control whole-effluent toxicity (WET) and may address programs to implement biological criteria, where such programs have been developed by the State. Implementation procedures therefore serve as umbrella documents that describe how the State's various toxics control programs are integrated to ensure adequate protection for aquatic life and human health and attainment of the narrative toxics criterion. In essence, the procedure should apply the "independent application" principle, which provides for independent evaluations of attainment of a designated use based on chemical-specific, whole-effluent toxicity, and biological criteria methods (see section 3.5.3 and Appendices C, K, and R).

EPA encourages, and may ultimately require, State implementation procedures to provide for implementation of biological criteria. However, the regulatory basis for requiring whole-effluent toxicity (WET) controls is clear. EPA regulations at 40 CFR 122.44(d)(1)(v) require NPDES permits to contain WET limits where a permittee has been shown to cause, have the reasonable potential to cause, or contribute to an in-stream excursion of a narrative criterion. Implementation of chemical-specific controls is also required by EPA regulations at 40 CFR 122.44(d)(1). State implementation procedures should, at a minimum, specify or reference methods to be used in implementing chemical-specific and whole-effluent toxicity-based controls, explain how these methods are integrated, and specify needed application criteria.

In addition to EPA's regulation at 40 CFR 131, EPA has regulations at 40 CFR 122.44 that cover the National Surface Water Toxics Control Program. These regulations are intrinsically linked to the requirements to achieve water quality standards, and specifically address the control of pollutants both with and without numeric criteria. For example, section 122.44(d)(1)(vi) provides the permitting authority with several options for establishing effluent limits when a State does not have a chemical-specific

numeric criterion for a pollutant present in an effluent at a concentration that causes or contributes to a violation of the State's narrative criteria.

3.5.3 Biological Criteria

The Clean Water Act of 1972 directs EPA to develop programs that will evaluate, restore, and maintain the chemical, physical, and biological integrity of the Nation's waters. In response to this directive, States and EPA have implemented chemically based water quality programs that address significant water pollution problems. However, over the past 20 years, it has become apparent that these programs alone cannot identify and address all surface water pollution problems. To help create a more comprehensive program, EPA is setting a priority for the development of biological criteria as part of State water quality standards. This effort will help States and EPA (1) achieve the biological integrity objective of the CWA set forth in section 101, and (2) comply with the statutory requirements under sections 303 and 304 of the Act (see Appendices C and K).

Regulatory Bases for Biocriteria

The primary statutory basis for EPA's policy that States should develop biocriteria is found in sections 101(a) and 303(c)(2)(B) of the Clean Water Act. Section 101(a) of the CWA gives the general goal of biological criteria. It establishes as the objective of the Act the restoration and maintenance of the chemical, physical, and biological integrity of the Nation's waters. To meet this objective, water quality criteria should address biological integrity. Section 101(a) includes the interim water quality goal for the protection and propagation of fish, shellfish, and wildlife.

Section 304(a) of the Act provides the legal basis for the development of informational criteria, including biological criteria. Specific directives for the development of regulatory biocriteria can be found in section 303(c), which requires EPA to develop criteria based on biological assessment

methods when numerical criteria are not established.

Section 304(a) directs EPA to develop and publish water quality criteria and information on methods for measuring water quality and establishing water quality criteria for toxic pollutants on bases other than pollutant-by-pollutant, including biological monitoring and assessment methods that assess:

- the effects of pollutants on aquatic community components (". . . plankton, fish, shellfish, wildlife, plant life . . .") and community attributes (". . . biological community diversity, productivity, and stability . . .") in any body of water; and

- factors necessary " . . . to restore and maintain the chemical, physical, and biological integrity of all navigable waters . . ." for " . . . the protection of shellfish, fish, and wildlife for classes and categories of receiving waters . . . ."

Once biocriteria are formally adopted into State standards, biocriteria and aquatic life use designations serve as direct, legal endpoints for determining aquatic life use attainment/non-attainment. CWA section 303(c)(2)(B) provides that when numeric criteria are not available, States shall adopt criteria for toxics based on biological monitoring or assessment methods; biocriteria can be used to meet this requirement.

Development and Implementation of Biocriteria

Biocriteria are numerical values or narrative expressions that describe the expected reference biological integrity of aquatic communities inhabiting waters of a designated aquatic life use. In the most desirable scenario, these would be waters that are either in pristine condition or minimally impaired. However, in some areas these conditions no longer exist and may not be attainable. In these situations, the reference biological communities represent the best attainable conditions. In either case, the reference

conditions then become the basis for developing biocriteria for major surface water types (streams, rivers, lakes, wetlands, estuaries, or marine waters).

Biological criteria support designated aquatic life use classifications for application in State standards (see chapter 2). Each State develops its own designated use classification system based on the generic uses cited in the Act (e.g., protection and propagation of fish, shellfish, and wildlife). Designated uses are intentionally general. However, States may develop subcategories within use designations to refine and clarify the use class. Clarification of the use class is particularly helpful when a variety of surface waters with distinct characteristics fit within the same use class, or do not fit well into any category.

For example, subcategories of aquatic life uses may be on the basis of attainable habitat (e.g., coldwater versus warmwater stream systems as represented by distinctive trout or bass fish communities, respectively). Special uses may also be designated to protect particularly unique, sensitive, or valuable aquatic species, communities, or habitats.

Resident biota integrate multiple impacts over time and can detect impairment from known and unknown causes. Biological criteria can be used to verify improvement in water quality in response to regulatory and other improvement efforts and to detect new or continuing degradation of waters. Biological criteria also provide a framework for developing improved best management practices and management measures for nonpoint source impacts. Numeric biological criteria can provide effective monitoring criteria for more definitive evaluation of the health of an aquatic ecosystem.

The assessment of the biological integrity of a water body should include measures of the structure and function of the aquatic community within a specified habitat. Expert knowledge of the system is required for the selection of

appropriate biological components and measurement indices. The development and implementation of biological criteria requires:

- selection of surface waters to use in developing reference conditions for each designated use;

- measurement of the structure and function of aquatic communities in reference surface waters to establish biological criteria;

- measurement of the physical habitat and other environmental characteristics of the water resource; and

- establishment of a protocol to compare the biological criteria to biota in comparable test waters to determine whether impairment has occurred.

These elements serve as an interactive network that is particularly important during early development of biological criteria where rapid accumulation of information is effective for refining both designated uses and developing biological criteria values and the supporting biological monitoring and assessment techniques.

3.5.4 Sediment Criteria

While ambient water quality criteria are playing an important role in assuring a healthy aquatic environment, they alone have not been sufficient to ensure appropriate levels of environmental protection. Sediment contamination, which can involve deposition of toxicants over long periods of time, is responsible for water quality impacts in some areas.

EPA has authority to pursue the development of sediment criteria in streams, lakes and other waters of the United States under sections 104 and 304(a)(1) and (2) of the CWA as follows:

- section 104(n)(1) authorizes the Administrator to establish national programs

that study the effects of pollution, including sedimentation, in estuaries on aquatic life;

- section 304(a)(1) directs the Administrator to develop and publish criteria for water quality, including information on the factors affecting rates of organic and inorganic sedimentation for varying types of receiving waters;

- section 304(a)(2) directs the Administrator to develop and publish information on, among other issues, "the factors necessary for the protection and propagation of shellfish, fish, and wildlife for classes and categories of receiving waters. . . ."

To the extent that sediment criteria could be developed that address the concerns of the section 404(b)(1) Guidelines for discharges of dredged or fill material under the CWA or the Marine Protection, Research, and Sanctuaries Act, they could also be incorporated into those regulations.

EPA's current sediment criteria development effort, as described below, focuses on criteria for the protection of aquatic life. EPA anticipates potential future expansion of this effort to include sediment criteria for the protection of human health.

Chemical Approach to Sediment Criteria Development

Over the past several years, sediment criteria development activities have centered on evaluating and developing the Equilibrium Partitioning Approach for generating sediment criteria. The Equilibrium Partitioning Approach focuses on predicting the chemical interaction between sediments and contaminants. Developing an understanding of the principal factors that influence the sediment/contaminant interactions will allow predictions to be made regarding the level of contaminant concentration that benthic and other organisms may be exposed to. Chronic water quality criteria, or possibly other toxicological endpoints, can then be used to

predict potential biological effects. In addition to the development of sediment criteria, EPA is also working to develop a standardized sediment toxicity test that could be used with or independently of sediment criteria to assess chronic effects in fresh and marine waters.

> *Equilibrium Partitioning (EqP) Sediment Quality Criteria (SQC) are the U.S. Environmental Protection Agency's best recommendation of the concentration of a substance in sediment that will not unacceptably affect benthic organisms or their uses.*

Methodologies for deriving effects-based SQC vary for different classes of compounds. For non-ionic organic chemicals, the methodology requires normalization to organic carbon. A methodology for deriving effects-based sediment criteria for metal contaminants is under development and is expected to require normalization to acid volatile sulfide. EqP SQC values can be derived for varying degrees of uncertainty and levels of protection, thus permitting use for ecosystem protection and remedial programs.

Application of Sediment Criteria

SQC would provide a basis for making more informed decisions on the environmental impacts of contaminated sediments. Existing sediment assessment methodologies are limited in their ability to identify chemicals of concern, responsible parties, degree of contamination, and zones of impact. To make the most informed decisions, EPA believes that a comprehensive approach using SQC and biological test methods is preferred.

Sediment criteria will be particularly valuable in site-monitoring applications where sediment contaminant concentrations are gradually approaching a criterion over time or as a preventive tool to ensure that point and nonpoint sources of contamination are controlled and that uncontaminated sediments remain uncontaminated.

Also comparison of field measurements to sediment criteria will be a reliable method for providing early warning of a potential problem. An early warning would provide an opportunity to take corrective action before adverse impacts occur. For the reasons mentioned above, it has been identified that SQC are essential to resolving key contaminated sediment and source control issues in the Great Lakes.

Specific Applications

Specific applications of sediment criteria are under development. The primary use of EqP-based sediment criteria will be to assess risks associated with contaminants in sediments. The various offices and programs concerned with contaminated sediment have different regulatory mandates and, thus, have different needs and areas for potential application of sediment criteria. Because each regulatory need is different, EqP-based sediment quality criteria designed specifically to meet the needs of one office or program may have to be implemented in different ways to meet the needs of another office or program.

One mode of application of EqP-based numerical sediment quality criteria would be in a tiered approach. In such an application, when contaminants in sediments exceed the sediment quality criteria the sediments would be considered as causing unacceptable impacts. Further testing may or may not be required depending on site-specific conditions and the degree in which a criterion has been violated. (In locations where contamination significantly exceeds a criterion, no additional testing would be required. Where sediment contaminant levels are close to a criterion, additional testing might be necessary.) Contaminants in a sediment at concentrations less than the sediment criterion would not be of concern. However, in some cases the sediment could not be considered safe because it might contain other contaminants above safe levels for which no sediment criteria exist. In addition, the synergistic, antagonistic, or additive effects of

several contaminants in the sediments may be of concern.

Additional testing in other tiers of an evaluation approach, such astoxicity tests, could be required to determine if the sediment is safe. It is likely that such testing would incorporate site-specific considerations. Examples of specific applications of sediment criteria after they are developed include the following:

- Establish permit limits for point sources to ensure that uncontaminated sediments remain uncontaminated or sediments already contaminated have an opportunity to cleanse themselves. Of course, this would occur only after criteria and the means to tie point sources to sediment contamination are developed.

- Establish target levels for nonpoint sources of sediment contamination.

- For remediation activities, SQC would be valuable in identifying:

  - need for remediation,

  - spatial extent of remediation area,

  - benefits derived from remediation activities,

  - responsible parties,
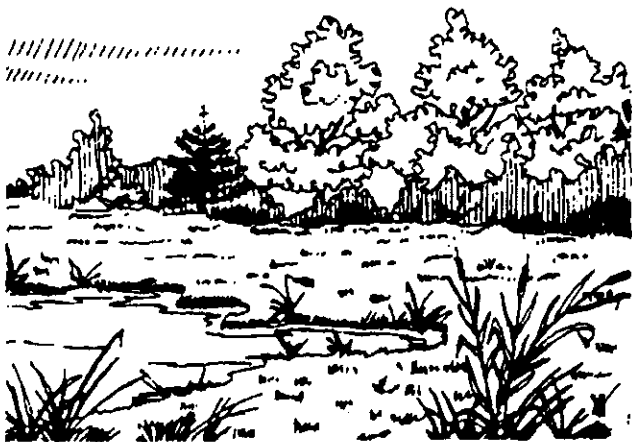
- impacts of depositing contaminated sediments in water environments, and

- success of remediation activities.

In tiered testing sediment evaluation processes, sediment criteria and biological testing procedures work very well together.

Sediment Criteria Status

Science Advisory Board Review

The Science Advisory Board has completed a second review of the EqP approach to deriving sediment quality criteria for non-ionic contaminants. The November 1992 report (USEPA, 1992c) endorses the EqP approach to deriving criteria as ". . . sufficiently valid to be used in the regulatory process if the uncertainty associated with the method is considered, described, and incorporated," and that "EPA should . . . establish criteria on the basis of present knowledge within the bounds of uncertainty. . . ."

The Science Advisory Board also identified the need for ". . . a better understanding of the uncertainty around the assumptions inherent in the approach, including assumptions of equilibrium, bioavailability, and kinetics, all critical to the application of the EqP."

Sediment Criteria Documents and Application Guidance

EPA efforts at producing sediment criteria documents are being directed first toward phenanthrene, fluoranthene, dieldrin, acenaphthene, and endrin. Efforts are also being directed towards producing a guidance document on the derivation and interpretation of sediment quality criteria. The criteria documents were announced in the *Federal Register* in January 1994; the public comment period ended June 1994. Final documents and implementation guidance should be available in early 1996.

Methodology for Developing Sediment Criteria for Metal Contaminants

EPA is proceeding to develop a methodology for calculating sediment criteria for benthic toxicity to metal contaminants, with key work focused on identifying and understanding the role of acid volatile sulfides (AVS), and other binding factors, in controlling the bioavailability of metal contaminants. A variety of field and laboratory verification studies are under way to add additional support to the methodology. Standard AVS sampling and analytical procedures are under development. Presentation of the metals methodology to the SAB for review is anticipated for Fall 1994.

Biological Approach to Sediment Criteria Development

Under the Contaminated Sediment Management Strategy, EPA programs have committed to using consistent biological methods to determine if sediments are contaminated. In the water program, these biological methods will be used as a complement to the sediment-chemical criteria under development. The biological methods consist of both toxicity and bioaccumulation tests. Freshwater and saltwater benthic species, selected to represent the sensitive range of species' responses to toxicity, are used in toxicity tests to measure sediment toxicity. Insensitive freshwater and saltwater benthic species that form the base of the food chain are used in toxicity tests to measure the bioaccumulation potential of sediment. In FY 1994, acute toxicity tests and bioaccumulation tests selected by all the Agency programs should be standardized and available for use. Training for States and EPA Regions on these methods is expected to begin in FY 1995.

In the next few years, research will be conducted to develop standardized chronic toxicity tests for sediment as well as toxicity identification evaluation (TIE) methods. The TIE approach will be used to identify the specific chemicals in a sediment causing acute or chronic toxicity in the test organisms. Under the Contaminated

Sediment Management Strategy, EPA's programs have also agreed to incorporate these chronic toxicity and TIE methods into their sediment testing when they are available.

3.5.5 Wildlife Criteria

Terrestrial and avian species are useful as sentinels for the health of the ecosystem as a whole. In many cases, damage to wildlife indicates that the ecosystem itself is damaged. Many wildlife species that are heavily dependent on the aquatic food web reflect the health of aquatic systems. In the case of toxic chemicals, terminal predators such as otter, mink, gulls, terns, eagles, ospreys, and turtles are useful as integrative indicators of the status or health of the ecosystem.

Statutory and Regulatory Authority

Section 101(a)(2) of the CWA sets, as an interim goal of,

> . . . wherever attainable . . . water quality which provides for the protection and propagation of fish, shellfish, and wildlife . . . (emphasis added).

Section 304(a)(1) of the Act also requires EPA to:

> . . . develop and publish . . . criteria for water quality accurately reflecting . . . the kind and extent of all identifiable effects on health and welfare including . . . wildlife.

The Water Quality Standards Regulation reflect the statutory goals and requirements by requiring States to adopt, where attainable, the CWA section 101(a)(2) goal uses of protection and propagation of fish, shellfish, and wildlife (40 CFR 131.10), and to adopt water quality criteria sufficient to protect the designated use (40 CFR 131.11).

Wildlife Protection in Current Aquatic Criteria

Current water quality criteria methodology is designed to protect fish, benthic invertebrates, and zooplankton; however, there is a provision in the current aquatic life criteria guidelines (Appendix H) that is intended to protect wildlife that consume aquatic organisms from the bioaccumulative potential of a compound. The final residue value can be based on either the FDA Action Level or a wildlife feeding study. However, if maximum permissible tissue concentration is not available from a wildlife feeding study, a final residue value cannot be derived and the criteria quantification procedure continues without further consideration of wildlife impacts. Historically, wildlife have been considered only after detrimental effects on wildlife populations have been observed in the environment (this occurred with relationship to DDT, selenium, and PCBs).

Wildlife Criteria Development

EPA's national wildlife criteria effort began following release of a 1987 Government Accounting Office study entitled *Wildlife Management - National Refuge Contamination Is Difficult To Confirm and Clean Up* (GAO, 1987). After waterfowl deformities observed at Kesterson Wildlife Refuge were linked to selenium contamination in the water, Congress requested this study and recommended that "the Administrator of EPA, in close coordination with the Secretary of the Interior, develop water quality criteria for protecting wildlife and their refuge habitat."

In November of 1988, EPA's Environmental Research Laboratory in Corvallis sponsored a workshop entitled *Water Quality Criteria To Protect Wildlife Resources*, (USEPA, 1989g) which was co-chaired by EPA and the Fish and Wildlife Service (FWS). The workshop brought together 26 professionals from a variety of institutions, including EPA, FWS, State governments, academia, and consultants who had

expertise in wildlife toxicity, aquatic toxicity, ecology, environmental risk assessment, and conservation. Efforts at he workshop focused on evaluating the need for, and developing a strategy for production of wildlife criteria. Two recommendations came out of that workshop:

(1) The process by which ambient water quality criteria are established should be modified to consider effects on wildlife; and

(2) chemicals should be prioritized based on their potential to adversely impact wildlife species.

Based on the workshop recommendations, screening level wildlife criteria (SLWC) were calculated for priority pollutants and chemicals of concern submitted by the FWS to gauge the extent of the problem by:

(1) evaluating whether existing water quality criteria for aquatic life are protective of wildlife, and

(2) prioritizing chemicals for their potential to adversely impact wildlife species.

There were 82 chemicals for which EPA had the necessary toxicity information as well as ambient water quality criteria, advisories, or lowest-observed-adverse-effect levels (LOAELs) to compare with the SLWC values. As would be expected, the majority of chemicals had SLWC larger than existing water quality criteria, advisories, or LOAELs for aquatic life. However, the screen identified classes of compounds for which current ambient water quality criteria may not be adequately protective of wildlife: chlorinated alkanes, benzenes, phenols, metals, DDT, and dioxins. Many of these compounds are produced in very large amounts and have a variety of uses (e.g., solvents, flame retardants, organic syntheses of fungicides and herbicides, and manufacture of plastics and textiles. The manufacture and use of
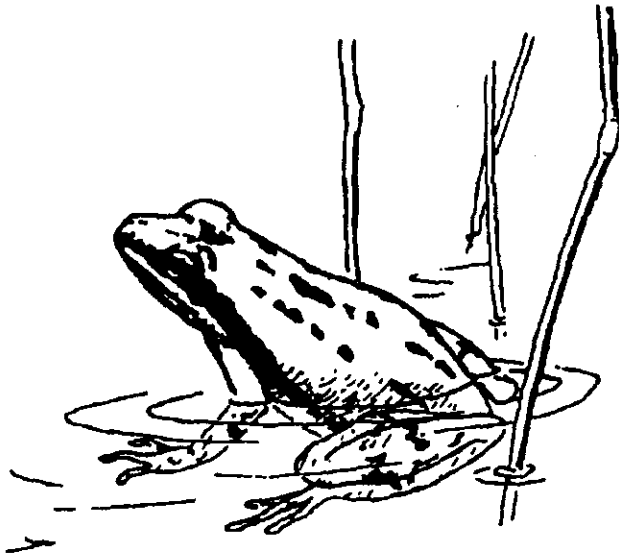
these materials produce waste byproduct). Also, 5 of the 21 are among the top 25 pollutants identified at Superfund sites in 1985 (3 metals, 2 organics).

Following this initial effort, EPA held a national meeting in April 1992[1] to constructively discuss and evaluate proposed methodologies for deriving wildlife criteria to build consensus among the scientific community as to the most defensible scientifically approach(es) to be pursued by EPA in developing useful and effective wildlife criteria.

The conclusions of this national meeting were as follows:

- wildlife criteria should have a tissue-residue component when appropriate;

- peer-review of wildlife criteria and data sets should be used in their derivation;

- wildlife criteria should incorporate methods to establish site-specific wildlife criteria;

- additional amphibian and reptile toxicity data are needed;

- further development of inter-species toxicological sensitivity factors are needed; and

- criteria methods should measure biomarkers in conjunction with other studies.

On April 16, 1993, EPA proposed wildlife criteria in the *Water Quality Guidance for the Great Lakes System* (58 F.R. 20802). The proposed wildlife criteria are based on the current EPA noncancer human health criteria approach. In this proposal, in addition to requesting comments on the proposed Great Lakes criteria and methods, EPA also requested comments on possible modifications of the proposed Great Lakes approach for consideration in the development of national wildlife criteria.

3.5.6 Numeric Criteria for Wetlands

Extension of the EPA national 304(a) numeric aquatic life criteria to wetlands is recommended as part of a program to develop standards and criteria for wetlands. Appendices D and E provide an overview of the need for standards and criteria for wetlands. The 304(a) numeric aquatic life criteria are designed to be protective of aquatic life for surface waters and are generally applicable to most wetland types. Appendix E provides a possible approach, based on the site-specific guidelines, for detecting wetland types that might not be protected by direct application of national 304(a) criteria. The evaluation can be simple and inexpensive for those wetland types for which sufficient water chemistry and species assemblage data are available, but will be less useful for wetland types for which these data are not readily available. In Appendix E, the site-specific approach is described and recommended for wetlands for which modification of the 304(a) numeric criteria are considered necessary. The results of this type of evaluation, combined with information on local or regional environmental threats, can be used to prioritize wetland types (and individual criteria) for further site-specific evaluations and/or additional data collection. Close coordination among regulatory agencies, wetland scientists, and criteria experts will be required.

3.6 Policy on Aquatic Life Criteria for Metals

It is the policy of the Office of Water that the use of dissolved metal to set and measure compliance with water quality standards is the recommended approach, because dissolved metal more closely approximates the bioavailable fraction of metal in the water column than does total recoverable metal. This conclusion regarding metals bioavailability is supported by a majority of the scientific community within and outside EPA. One reason is that a primary mechanism for water column toxicity is adsorption at the gill surface which requires metals to be in the dissolved form.

Until the scientific uncertainties are better resolved, a range of different risk management decisions can be justified by a State. EPA recommends that State water quality standards be based on dissolved metal--a conversion factor must be used in order to express the EPA criteria articulated as total recoverable as dissolved. (See the paragraph below for technical details on developing dissolved criteria.) EPA will also approve a State risk management decision to adopt standards based on total recoverable metal, if those standards are otherwise approvable as a matter of law. (*Office of Water Policy and Technical Guidance on Interpretation and Implementation of Aquatic Life Metals Criteria* USEPA, 1993f)

3.6.1 Background

The implementation of metals criteria is complex due to the site-specific nature of metals toxicity. This issue covers a number of areas including the expression of aquatic life criteria; total maximum daily loads (TMDLs), permits, effluent monitoring, and compliance; and ambient monitoring. The following Sections, based on the policy memorandum referenced above, provide additional guidance in each of these areas. Included in this Handbook as Appendix J are three guidance documents issued along with the Office of Water policy memorandum with

additional technical details. They are: *Guidance Document on Expression of Aquatic Life Criteria as Dissolved Criteria* (Attachment #2), *Guidance Document on Dynamic Modeling and Translators* (Attachment #3), and *Guidance Document on Monitoring* (Attachment #4). These will be supplemented as additional information becomes available.

Since metals toxicity is significantly affected by site-specific factors, it presents a number of programmatic challenges. Factors that must be considered in the management of metals in the aquatic environment include: toxicity specific to effluent chemistry; toxicity specific to ambient water chemistry; different patterns of toxicity for different metals; evolution of the state of the science of metals toxicity, fate, and transport; resource limitations for monitoring, analysis, implementation, and research functions; concerns regarding some of the analytical data currently on record due to possible sampling and analytical contamination; and lack of standardized protocols for clean and ultraclean metals analysis. The States have the key role in the risk management process of balancing these factors in the management of water programs. The site-specific nature of this issue could be perceived as requiring a permit-by-permit approach to implementation. However, EPA believes that this guidance can be effectively implemented on a broader level, across any waters with roughly the same physical and chemical characteristics, and recommends that States work with the EPA with that perspective in mind.

3.6.2 Expression of Aquatic Life Criteria

Dissolved vs. Total Recoverable Metal

A major issue is whether, and how, to use dissolved metal concentrations ("dissolved metal") or total recoverable metal concentrations ("total recoverable metal") in setting State water quality standards. In the past, States have used both approaches when applying the same EPA Section 304(a) criteria guidance. Some older criteria documents may have facilitated these different

approaches to interpretation of the criteria because the documents were somewhat equivocal with regards to analytical methods. The May 1992 interim guidance continued the policy that either approach was acceptable.

The position that the dissolved metals approach is more accurate has been questioned because it neglects the possible toxicity of particulate metal. It is true that some studies have indicated that particulate metals appear to contribute to the toxicity of metals, perhaps because of factors such as desorption of metals at the gill surface, but these same studies indicate the toxicity of particulate metal is substantially less than that of dissolved metal.

Furthermore, any error incurred from excluding the contribution of particulate metal will generally be compensated by other factors which make criteria conservative. For example, metals in toxicity tests are added as simple salts to relatively clean water. Due to the likely presence of a significant concentration of metals binding agents in many discharges and ambient waters, metals in toxicity tests would generally be expected to be more bioavailable than metals in discharges or in ambient waters.

If total recoverable metal is used for the purpose of specifying water quality standards, the lower bioavailability of particulate metal and lower bioavailability of sorbed metals as they are discharged may result in an overly conservative water quality standard. The use of dissolved metal in water quality standards gives a more accurate result in the water column. However, total recoverable measurements in ambient water have value, in that exceedences of criteria on a total recoverable basis are an indication that metal loadings could be a stress to the ecosystem, particularly in locations other than the water column (*e.g.*, in the sediments).

The reasons for the potential consideration of total recoverable measurements include risk management considerations not covered by evaluation of water column toxicity alone. The ambient water quality criteria are neither designed nor intended to protect sediments, or to prevent effects in the food webs containing sediment dwelling organisms. A risk manager, however, may consider sediments and food chain effects and may decide to take a conservative approach for metals, considering that metals are very persistent chemicals. This conservative approach could include the use of total recoverable metal in water quality standards. However, since consideration of sediment impacts is not incorporated into the criteria methodology, the degree of conservatism inherent in the total recoverable approach is unknown. The uncertainty of metal impacts in sediments stem from the lack of sediment criteria and an imprecise understanding of the fate and transport of metals. EPA will continue to pursue research and other activities to close these knowledge gaps.

Dissolved Criteria

In the toxicity tests used to develop EPA metals criteria for aquatic life, some fraction of the metal is dissolved while some fraction is bound to particulate matter. The present criteria were developed using total recoverable metal measurements or measures expected to give equivalent results in toxicity tests, and are articulated as total recoverable. Therefore, in order to express the EPA criteria as dissolved, a total recoverable to dissolved conversion factor must be used. Attachment #2 in Appendix J provides guidance for calculating EPA dissolved criteria from the published total recoverable criteria. The data expressed as percentage metal dissolved are presented as recommended values and ranges. However, the choice within ranges is a State risk management decision. EPA has recently supplemented the data for copper and is proceeding to further supplement the data for copper and other metals. As testing is completed, EPA will make this information available and this is expected to reduce the magnitude of the ranges for some of the conversion factors provided. EPA also strongly encourages the application of dissolved criteria across a watershed or

waterbody, as technically sound and the best use of resources.

Site-Specific Criteria Modifications

While the above methods will correct some site-specific factors affecting metals toxicity, further refinements are possible. EPA has issued guidance for three site-specific criteria development methodologies: recalculation procedure, water-effect ratio (WER) procedure (called the indicator species procedure in previous guidance) and resident species procedure. (See Section 3.7 of this Chapter.)

In the National Toxics Rule (57 FR 60848, December 22, 1992), EPA recommended the WER as an optional method for site-specific criteria development for certain metals. EPA committed in the NTR preamble to provide additional guidance on determining the WERs. The *Interim Guidance on the Determination and Use of Water-Effect Ratios for Metals* was issued by EPA on February 22, 1994 and is intended to fulfill that commitment. This interim guidance supersedes all guidance concerning water-effect ratios and the recalculation procedure previously issued by EPA. This guidance is included as Appendix L to this Handbook.

In order to meet current needs, but allow for changes suggested by protocol users, EPA issued the guidance as "interim." EPA will accept WERs developed using this guidance, as well as by using other scientifically defensible protocols.

3.6.3 Total Maximum Daily Loads (TMDLs) and National Pollutant Discharge Elimination System (NPDES) Permits

Dynamic Water Quality Modeling

Although not specifically part of the reassessment of water quality criteria for metals, dynamic or probabilistic models are another useful tool for implementing water quality criteria, especially for those criteria protecting aquatic life. These models provide another way to incorporate site-specific data. The *Technical Support Document for Water Quality-based Toxics Control* (TSD) (USEPA, 1991a) describes dynamic, as well as static (steady-state) models. Dynamic models make the best use of the specified magnitude, duration, and frequency of water quality criteria and, therefore, provide a more accurate representation of the probability that a water quality standard exceedence will occur. In contrast, steady-state models frequently apply a number of simplifying, worst case assumptions which makes them less complex but also less accurate than dynamic models.

Dynamic models have received increased attention over the last few years as a result of the widespread belief that steady-state modeling is over-conservative due to environmentally conservative dilution assumptions. This belief has led to the misconception that dynamic models will always lead to less stringent regulatory controls (e.g., NPDES effluent limits) than steady-state models, which is not true in every application of dynamic models. EPA considers dynamic models to be a more accurate approach to implementing water quality criteria and continues to recommend their use. Dynamic modeling does require a commitment of resources to develop appropriate data. (See Appendix J, Attachment #3 and the USEPA, 1991a for details on the use of dynamic models.)

Dissolved-Total Metal Translators

Expressing ambient water quality criteria for metals as the dissolved form of a metal poses a

need to be able to translate from dissolved metal to total recoverable metal for TMDLs and NPDES permits. TMDLs for metals must be able to calculate: (1) dissolved metal in order to ascertain attainment of water quality standards, and (2) total recoverable metal in order to achieve mass balance necessary for permitting purposes.

EPA's NPDES regulations require that limits of metals in permits be stated as total recoverable in most cases (see 40 CFR §122.45(c)) except when an effluent guideline specifies the limitation in another form of the metal, the approved analytical methods measure only dissolved metal, or the permit writer expresses a metals limit in another form (e.g., dissolved, valent specific, or total) when required to carry out provisions of the Clean Water Act. This is because the chemical conditions in ambient waters frequently differ substantially from those in the effluent, and there is no assurance that effluent particulate metal would not dissolve after discharge. The NPDES rule does not require that State water quality standards be expressed as total recoverable; rather, the rule requires permit writers to translate between different metal forms in the calculation of the permit limit so that a total recoverable limit can be established. Both the TMDL and NPDES uses of water quality criteria require the ability to translate between dissolved metal and total recoverable metal. Appendix J, Attachment #3 provides guidance on this translation.

3.6.4 Guidance on Monitoring

Use of Clean Sampling and Analytical Techniques

In assessing waterbodies to determine the potential for toxicity problems due to metals, the quality of the data used is an important issue. Metals data are used to determine attainment status for water quality standards, discern trends in water quality, estimate background loads for TMDLs, calibrate fate and transport models, estimate effluent concentrations (including effluent variability), assess permit compliance, and conduct research. The quality of trace level metal data, especially

below 1 ppb, may be compromised due to contamination of samples during collection, preparation, storage, and analysis. Depending on the level of metal present, the use of "clean" and "ultraclean" techniques for sampling and analysis may be critical to accurate data for implementation of aquatic life criteria for metals.

The significance of the sampling and analysis contamination problem increases as the ambient and effluent metal concentration decreases and, therefore, problems are more likely in ambient measurements. "Clean" techniques refer to those requirements (or practices for sample collection and handling) necessary to produce reliable analytical data in the part per billion (ppb) range. "Ultraclean" techniques refer to those requirements or practices necessary to produce reliable analytical data in the part per trillion (ppt) range. Because typical concentrations of metals in surface waters and effluents vary from one metal to another, the effect of contamination on the quality of metals monitoring data varies appreciably.

EPA plans to develop protocols on the use of clean and ultra-clean techniques and is coordinating with the United States Geological Survey (USGS) on this project, because USGS has been doing work on these techniques for some time, especially the sampling procedures. Draft protocols for clean techniques were presented at the Norfolk, VA analytical methods conference in the Spring of 1994 and final protocols are expected to be available in early 1995. The development of comparable protocols for ultra-clean techniques is underway and are expected to be available in late 1995. In developing these protocols, we will consider the costs of these techniques and will give guidance as to the situations where their use is necessary. Appendix L, pp. 98-108 provide some general guidance on the use of clean analytical techniques. We recommend that this guidance be used by States and Regions as an interim step, while the clean and ultra-clean protocols are being developed.

Use of Historical Data

The concerns about metals sampling and analysis discussed above raise corresponding concerns about the validity of historical data. Data on effluent and ambient metal concentrations are collected by a variety of organizations including Federal agencies (e.g., EPA, USGS), State pollution control agencies and health departments, local government agencies, municipalities, industrial dischargers, researchers, and others. The data are collected for a variety of purposes as discussed above.

Concern about the reliability of the sample collection and analysis procedures is greatest where they have been used to monitor very low level metal concentrations. Specifically, studies have shown data sets with contamination problems during sample collection and laboratory analysis, that have resulted in inaccurate measurements. For example, in developing a TMDL for New York Harbor, some historical ambient data showed extensive metals problems in the harbor, while other historical ambient data showed only limited metals problems. Careful resampling and analysis in 1992/1993 showed the latter view was correct. The key to producing accurate data is appropriate quality assurance (QA) and quality control (QC) procedures. EPA believes that most historical data for metals, collected and analyzed with appropriate QA and QC at levels of 1 ppb or higher, are reliable. The data used in development of EPA criteria are also considered reliable, both because they meet the above test and because the toxicity test solutions are created by adding known amounts of metals.

With respect to effluent monitoring reported by an NPDES permittee, the permittee is responsible for collecting and reporting quality data on a Discharge Monitoring Report (DMR). Permitting authorities should continue to consider the information reported to be true, accurate, and complete as certified by the permittee. Where the permittee becomes aware of new information specific to the effluent discharge that questions the quality of previously submitted DMR data, the

permittee must promptly submit that information to the permitting authority. The permitting authority will consider all information submitted by the permittee in determining appropriate enforcement responses to monitoring/reporting and effluent violations. (See Appendix J, Attachment #4 for additional details.)

3.7 Site-Specific Aquatic Life Criteria

The purpose of this section is to provide guidance for the development of site-specific water quality criteria which reflect local environmental conditions. Site-specific criteria are allowed by regulation and are subject to EPA review and approval. The Federal water quality standards regulation at section 131.11(b)(1)(ii) provides States with the opportunity to adopt water quality criteria that are "...modified to reflect site-specific conditions." Site-specific criteria, as with all water quality criteria, must be based on a sound scientific rationale in order to protect the designated use. Existing guidance and practice are that EPA will approve site-specific criteria developed using appropriate procedures.

A site-specific criterion is intended to come closer than the national criterion to providing the intended level of protection to the aquatic life at the site, usually by taking into account the biological and/or chemical conditions (i.e., the species composition and/or water quality characteristics) at the site. The fact that the U.S. EPA has made these procedures available should not be interpreted as implying that the agency advocates that states derive site-specific criteria before setting state standards. Also, derivation of a site-specific criterion does not change the intended level of protection of the aquatic life at the site.

3.7.1 History of Site-Specific Criteria Guidance

National water quality criteria for aquatic life may be under- or over-protective if:

(1) the species at the site are more or less sensitive than those included in the national criteria data set (*e.g.*, the national criteria data set contains data for trout, salmon, penaeid shrimp, and other aquatic species that have been shown to be especially sensitive to some materials), or

(2) physical and/or chemical characteristics of the site alter the biological availability and/or toxicity of the chemical (*e.g.*, alkalinity, hardness, pH, suspended solids and salinity influence the concentration(s) of the toxic form(s) of some heavy metals, ammonia and other chemicals).

Therefore, it is appropriate that site-specific procedures address each of these conditions separately as well as the combination of the two. In the early 1980's, EPA recognized that laboratory-derived water quality criteria might not accurately reflect site-specific conditions and, in response, created three procedures to derive site-specific criteria. This Handbook contains the details of these procedures, referenced below.

1. The Recalculation Procedure is intended to take into account relevant differences between the sensitivities of the aquatic organisms in the national dataset and the sensitivities of organisms that occur at the site (see Appendix L, pp. 90-97).

2. The Water-Effect Ratio Procedure (called the Indicator Species Procedure in USEPA, 1983a; 1984f) provided for the use of a water-effect ratio (WER) that is intended to take into account relevant differences between the toxicities of the chemical in laboratory dilution water and in site water (see Appendix L).

3. The Resident Species Procedure intended to take into account both kinds of differences simultaneously (see Section 3.7.6).

These procedures were first published in the 1983 *Water Quality Standards Handbook* (USEPA,

1983a) and expanded upon in the *Guidelines for Deriving Numerical Aquatic Site-Specific Water Quality Criteria by Modifying National Criteria* (USEPA, 1984f). Interest has increased in recent years as states have devoted more attention to chemical-specific water quality criteria for aquatic life. In addition, interest in water-effect ratios increased when they were integrated into some of the aquatic life criteria for metals that were promulgated for several states in the National Toxics Rule (57 FR 60848, December 22, 1992). The *Office of Water Policy and Technical Guidance on Interpretation and Implementation of Aquatic Life Criteria for Metals* (USEPA, 1993f) (see Section 3.6 of this Handbook) provided further guidance on site-specific criteria for metals by recommending the use of dissolved metals for setting and measuring compliance with water quality standards.

The early guidance concerning WERs (USEPA, 1983a; 1984f) contained few details and needed revision, especially to take into account newer guidance concerning metals. To meet this need, EPA issued *Interim Guidance on the Determination and Use of Water-Effect Ratios for Metals* in 1994 (Appendix L). Metals are specifically addressed in Appendix L because of the National Toxics Rule and because of current interest in aquatic life criteria for metals; although most of this guidance also applies to other pollutants, some obviously applies only to metals. Appendix L supersedes all guidance concerning water-effect ratios and the Indicator Species Procedure given in Chapter 4 of the *Water Quality Standards Handbook* (USEPA, 1983a) and in *Guidelines for Deriving Numerical Aquatic Site-Specific Water Quality Criteria by Modifying National Criteria* (USEPA, 1984f). Appendix L (p. 90-98) also supersedes the guidance in these earlier documents for the Recalculation Procedure for performing site-specific criteria modifications. The Resident Species Procedure remains essentially unchanged since 1983 (except for changes in the averaging periods to conform to the 1985 aquatic life criteria guidelines (USEPA, 1985b) and is presented in Section 3.7.6, below.

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The previous guidance concerning site-specific procedures did not allow the Recalculation Procedure and the WER procedure to be used together in the derivation of a site-specific aquatic life criterion; the only way to take into account both species composition and water quality characteristics in the determination of a site-specific criterion was to use the Resident Species Procedure. A specific change contained Appendix L is that, except in jurisdictions that are subject to the National Toxics Rule, the Recalculation Procedure and the WER Procedure may now be used together provided that the recalculation procedure is performed first. Both the Recalculation Procedure and the WER Procedure are based directly on the guidelines for deriving national aquatic life criteria (USEPA 1985) and, when the two are used together, use of the Recalculation Procedure must be performed first because the Recalculation Procedure has specific implications concerning the determination of the WER.

3.7.2 Preparing to Calculate Site-Specific Criteria

Adopting site-specific criteria in water quality standards is a State option--not a requirement. Moreover, EPA is not advocating that States use site-specific criteria development procedures for setting all aquatic life criteria as opposed to using the National Section 304(a) criteria recommendations. Site-specific criteria are not needed in all situations. When a State considers the possibility of developing site-specific criteria, it is essential to involve the appropriate EPA Regional office at the start of the project.

This early planning is also essential if it appears that data generation and testing may be conducted by a party other than the State or EPA. The State and EPA need to apply the procedures judiciously and must consider the complexity of the problem and the extent of knowledge available concerning the fate and effect of the pollutant under consideration. If site-specific criteria are developed without early EPA involvement in the planning and design of the task, the State may

expect EPA to take additional time to closely scrutinize the results before granting any approval to the formally adopted standards.

The following sequence of decisions need to be made before any of the procedures are initiated:

◆ verify that site-specific criteria are actually needed (*e.g.*, that the use of clean sampling and/or analytical techniques, especially for metals, do not result in attainment of standards.)

◆ Define the site boundaries.

◆ Determine from the national criterion document and other sources if physical and/or chemical characteristics are known to affect the biological availability and/or toxicity of a material of interest.

◆ If data in the national criterion document and/or from other sources indicate that the range of sensitivity of the selected resident species to the material of interest is different from the range for the species in the national criterion document, and variation in physical and/or chemical characteristics of the site water is not expected to be a factor, use the *Recalculation Procedure* (Section 3.7.4).
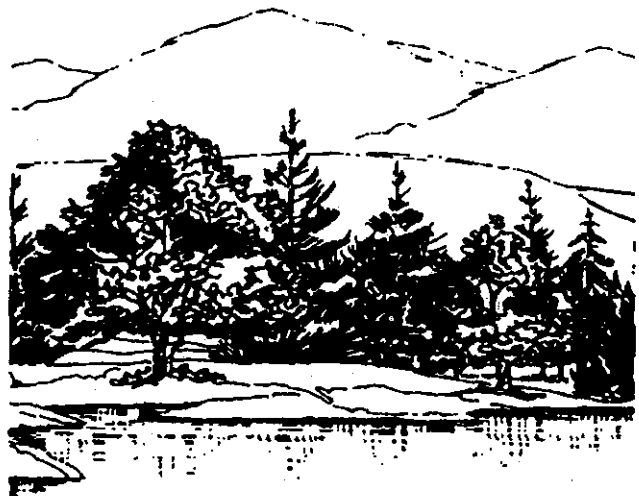
♦ If data in the national criterion document and/or from other sources indicate that physical and/or chemical characteristics of the site water may affect the biological availability and/or toxicity of the material of interest, and the selected resident species range of sensitivity is <u>similar</u> to that for the species in the national criterion document, use the *Water-Effect Ratio Procedure* (Section 3.7.5).

♦ If data in the national criterion document and/or from other sources indicated that physical and/or chemical characteristics of the site water may affect the biological availability and/or toxicity of the material of interest, and the selected resident species range of sensitivity is <u>different</u> from that for the species in the national criterion document, and if both these differences are to be taken into account, use the *Recalculation Procedure in conjunction with the Water-Effect Ratio Procedure* or use the *Resident Species Procedure* (Section 3.7.6).

3.7.3 Definition of a Site

Since the rationales for site-specific criteria are usually based on potential differences in species sensitivity, physical and chemical characteristics of the water, or a combination of the two, the concept of site must be consistent with this rationale.

In the general context of site-specific criteria, a "site" may be a state, region, watershed, waterbody, or segment of a waterbody. The site-specific criterion is to be derived to provide adequate protection for the entire site, however the site is defined.

If water quality effects on toxicity are not a consideration, the site can be as large as a generally consistent biogeographic zone permits. For example, large portions of the Chesapeake Bay, Lake Michigan, or the Ohio River may be considered as one site if their respective aquatic communities do not vary substantially. However,

when a site-specific criterion is derived using the Recalculation Procedure, all species that "occur at the site" need to be taken into account when deciding what species, if any, are to be deleted from the dataset. Unique populations or less sensitive uses within sites may justify a designation as a distinct site.

If the species of a site are toxicologically comparable to those in the national criteria data set for a material of interest, and physical and/or chemical water characteristics are the only factors supporting modification of the national criteria, then the site can be defined on the basis of expected changes in the material's biological availability and/or toxicity due to physical and chemical variability of the site water. However, when a site-specific criterion is derived using a WER, the WER is to be adequately protective of the entire site. If, for example, a site-specific criterion is being derived for an estuary, WERs could be determined using samples of the surface water obtained from various sampling stations, which, to avoid confusion, should not be called "sites". If all the WERs were sufficiently similar, one site-specific criterion could be derived to apply to the whole estuary. If the WERs were sufficiently different, either the lowest WER could be used to derive a site-specific criterion for the whole estuary, or the data might indicate that the estuary should be divided into two or more sites, each with its own criterion.

3.7.4 The Recalculation Procedure

The Recalculation Procedure is intended to cause a site-specific criterion to appropriately differ from a national aquatic life criterion if justified by demonstrated pertinent toxicological differences between the aquatic species that occur at the site and those that were used in the derivation of the national criterion. There are at least three reasons why such differences might exist between the two sets of species.

♦ First, the national dataset contains aquatic species that are sensitive to many pollutants,

but these and comparably sensitive species might not occur at the site.

♦ Second, a species that is critical at the site might be sensitive to the pollutant and require a lower criterion. (A critical species is a species that is commercially or recreationally important at the site, a species that exists at the site and is listed as threatened or endangered under section 4 of the Endangered Species Act, or a species for which there is evidence that the loss of the species from the site is likely to cause an unacceptable impact on a commercially or recreationally important species, a threatened or endangered species, the abundances of a variety of other species, or the structure or function of the community.)

♦ Third, the species that occur at the site might represent a narrower mix of species than those in the national dataset due to a limited range of natural environmental conditions.

The procedure presented in Appendix L, pp. 90-98 is structured so that corrections and additions can be made to the national dataset without the deletion process being used to take into account taxa that do not occur at the site; in effect, this procedure makes it possible to update the national aquatic life criterion. All corrections and

additions that have been approved by EPA are required, whereas use of the deletion process is optional. The deletion process may not be used to remove species from the criterion calculation that are not currently present at a site due to degraded conditions.

The Recalculation Procedure is more likely to result in lowering a criterion if the net result of addition and deletion is to decrease the number of genera in the dataset, whereas the procedure is more likely to result in raising a criterion if the net result of addition and deletion is to increase the number of genera in the dataset.

For the lipid soluble chemicals whose national Final Residue Values are based on Food and Drug Administration (FDA) action levels, adjustments in those values based on the percent lipid content of resident aquatic species is appropriate for the derivation of site-specific Final Residue Values. For lipid-soluble materials, the national Final Residue Value is based on an average 11 percent lipid content for edible portions for the freshwater chinook salmon and lake trout and an average of 10 percent lipids for the edible portion for saltwater Atlantic herring. Resident species of concern may have higher (e.g., Lake Superior siscowet, a race of lake trout) or lower (e.g., many sport fish) percent lipid content than used for the national Final Residue Value.
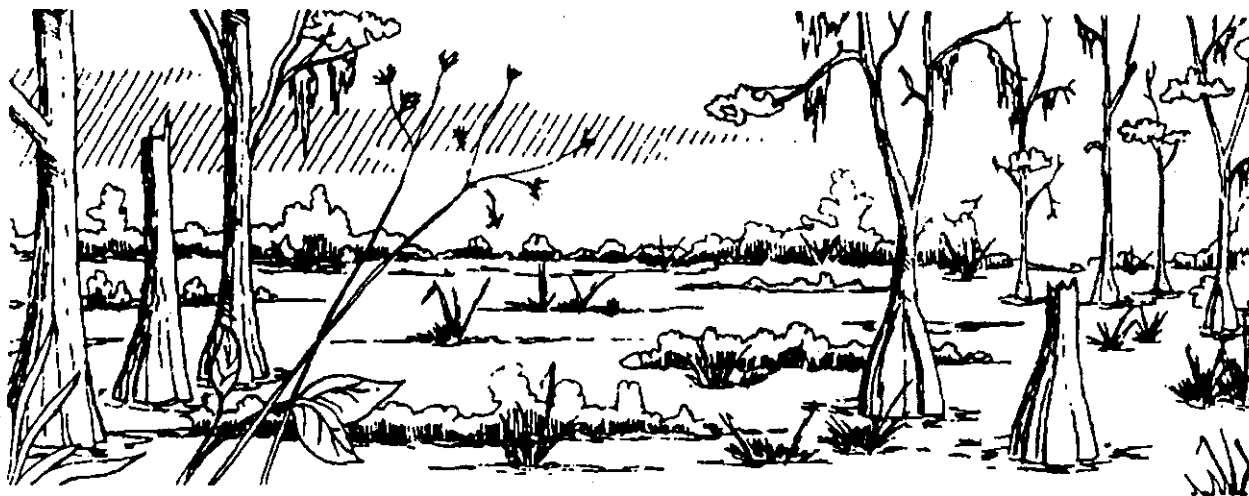
For some lipid-soluble materials such as polychlorinated biphenyls (PCB) and DDT, the national Final Residue Value is based on wildlife consumers of fish and aquatic invertebrate species rather than an FDA action level because the former provides a more stringent residue level. See the National Guidelines (USEPA, 1985b) for details.

For the lipid-soluble materials whose national Final Residue Values are based on wildlife effects, the limiting wildlife species (mink for PCB and brown pelican for DDT) are considered acceptable surrogates for resident avian and mammalian species (e.g., herons, gulls, terns, otter, etc.) Conservatism is appropriate for those two chemicals, and no less restrictive modification of the national Final Residue Value is appropriate. The site-specific Final Residue Value would be the same as the national value.

3.7.5 The Water-Effect Ratio (WER) Procedure

The guidance on the Water-Effect Ratio Procedure presented in Appendix L is intended to produce WERs that may be used to derive site-specific aquatic life criteria from most national and state aquatic life criteria that were derived from laboratory toxicity data.

As indicated in Appendix L, the determination of a water-effect ratio may require substantial resources. A discharger should consider cost-effective, preliminary measures described in this Appendix L (e.g., use of "clean" sampling and chemical analytical techniques especially for metals, or in non-NTR States, a recalculated criterion) to determine if an indicator species site-specific criterion is really needed. In many instances, use of these other measures may eliminate the need for deriving water-effect ratios. The methods described in the 1994 interim guidance (Appendix L) should be sufficient to develop site-specific criteria that resolve concerns of dischargers when there appears to be no instream toxicity but, where (a) a discharge appears to exceed existing or proposed water

quality-based permit limits, or (b) an instream concentration appears to exceed an existing or proposed water quality criterion.

WERs obtained using the methods described in Appendix L should only be used to adjust aquatic life criteria that were derived using laboratory toxicity tests. WERs determined using the methods described herein cannot be used to adjust the residue-based mercury Criterion Continuous Concentration (CCC) or the field-based selenium freshwater criterion.

Except in jurisdictions that are subject to the NTR, the WERs may also be used with site-specific aquatic life criteria that are derived using the Recalculation Procedure described in Appendix L (p.90).

Water-Effect Ratios in the Derivation of Site-Specific Criteria

A central question concerning WERs is whether their use by a State results in a site-specific criterion subject to EPA review and approval under Section 303(c) of the Clean Water Act?

Derivation of a water-effect ratio by a State is a site-specific criterion adjustment subject to EPA review and approval/disapproval under Section 303(c). There are two options by which this review can be accomplished.

Option 1:

A State may derive and submit each individual water-effect ratio determination to EPA for review and approval. This would be accomplished through the normal review and revision process used by a State.

Option 2:

A State can amend its water quality standards to provide a formal procedure which includes derivation of water-effect ratios, appropriate definition of sites, and enforceable monitoring provisions to assure that designated uses are

protected. Both this procedure and the resulting criteria would be subject to full public participation requirements. EPA would review and approve/disapprove this protocol as a revised standard as part of the State's triennial review/revision. After adoption of the procedure, public review of a site-specific criterion could be accomplished in conjunction with the public review required for permit issuance. For public information, EPA recommends that once a year the State publish a list of site-specific criteria.

An exception to this policy applies to the waters of the jurisdictions included in the National Toxics Rule. The EPA review is not required for the jurisdictions included in the National Toxics Rule where EPA established the procedure for the State for application to the criteria promulgated. The National Toxics Rule was a formal rulemaking process (with notice and comment) in which EPA pre-authorized the use of a correctly applied water-effect ratio. That same process has not yet taken place in States not included in the National Toxics Rule.

However, the National Toxics Rule does not affect State authority to establish scientifically defensible procedures to determine Federally authorized WERs, to certify those WERs in NPDES permit proceedings, or to deny their application based on the State's risk management analysis.

As described in Section 131.36(b)(iii) of the water quality standards regulation (the official regulatory reference to the National Toxics Rule), the water-effect ratio is a site-specific calculation. As indicated on page 60866 of the preamble to the National Toxics Rule, the rule was constructed as a rebuttable presumption. The water-effect ratio is assigned a value of 1.0 until a different water-effect ratio is derived from suitable tests representative of conditions in the affected waterbody. It is the responsibility of the State to determine whether to rebut the assumed value of 1.0 in the National Toxics Rule and apply another value of the water-effect ratio in order to establish a site-specific criterion. The site-specific criterion

is then used to develop appropriate NPDES permit limits. The rule thus provides a State with the flexibility to derive an appropriate site-specific criterion for specific waterbodies.

As a point of emphasis, although a water-effect ratio affects permit limits for individual dischargers, it is the State in all cases that determines if derivation of a site-specific criterion based on the water-effect ratio is allowed and it is the State that ensures that the calculations and data analysis are done completely and correctly.

3.7.6 The Resident Species Procedure

The resident Species Procedure for the derivation of a site-specific criterion accounts for differences in resident species sensitivity and differences in biological availability and/or toxicity of a material due to variability in physical and chemical characteristics of a site water. Derivation of the site-specific criterion maximum concentration (CMC) and site-specific criterion continuous concentration (CCC) are accomplished after the complete acute toxicity minimum data set requirements have been met by conducting tests with resident species in site water. Chronic tests may also be necessary. This procedure is designed to compensate concurrently for any real differences between the sensitivity range of species represented in the national data set and for site water which may markedly affect the biological availability and/or toxicity of the material of interest.

Certain families of organisms have been specified in the National Guidelines acute toxicity minimum data set (e.g., Salmonidae in fresh water and Penaeidae or Mysidae in salt water); if this or any other requirement cannot be met because the family or other group (e.g., insect or benthic crustacean) in fresh water is not represented by resident species, select a substitute(s) from a sensitive family represented by one or more resident species and meet the 8 family minimum data set requirement. If all the families at the site have been tested and the minimum data set requirements have not been met, use the most

sensitive resident family mean acute value as the site-specific Final Acute Value.

To derive the criterion maximum concentration divide the site-specific Final Acute Value by two. The site-specific Final Chronic Value can be obtained as described in the Appendix L. The lower of the site-specific Final Chronic Value (as described in the recalculation procedure - Appendix L, p. 90) and the recalculated site-specific Final Residue Value becomes the site-specific criterion continuous concentration unless plant or other data (including data obtained from the site-specific tests) indicates a lower value is appropriate. If a problem is identified, judgment should be used in establishing the site-specific criterion.

The frequency of testing (e.g., the need for seasonal testing) will be related to the variability of the physical and chemical characteristics of site water as it is expected to affect the biological availability and/or toxicity of the material of interest. As the variability increases, the frequency of testing will increase. Many of the limitations discussed for the previous two procedures would also apply to this procedure.

Endnotes

1. Proceedings in production.

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CHAPTER 4

ANTIDEGRADATION

(40 CFR 131.12)

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