Aquatic Pesticide Monitoring Program

Modeling Workgroup Final Report

Adrian Wadley
James R. Hunt
Tom M. Young
Karl Malamud-Roam
Daniel R. Oros

SFEI Contribution 104
December 2003

San Francisco Estuary Institute

This report should be cited as:

Wadley, A., Hunt, J., Young, T., Malamud-Roam, K., Oros, D., 2003. Aquatic Pesticide Monitoring Program Modeling Workgroup Final Report. SFEI Contribution 104. San Francisco Estuary Institute, Oakland, CA.

Aquatic Pesticide Monitoring Program

Modeling Workgroup
Final Report

Prepared by
Adrian Wadley, EMC Environmental Consulting
James R. Hunt, UC-Berkeley
Tom M. Young, UC-Davis
Karl Malamud-Roam, Contra Costa Mosquito Vector Control District
And
Daniel R. Oros, San Francisco Estuary Institute

San Francisco Estuary Institute
7770 Pardee Lane, 2nd Floor
Oakland, CA 94621

December 2003

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

Table 1. APMP Modeling Workgroup Participants.

Daniel R. Oros, Ph.D.
San Francisco Estuary Institute
7770 Pardee Lane, 2nd Floor
Oakland, CA 94621-2266
Email: daniel@sfei.org
Tel: (510) 746-7383
Fax: (510) 746-7300

James Hunt, Ph.D.
University of California
Department of Civil and Environmental Engineering
779 Davis Hall #1710
Berkeley, CA 94720-1710
Email: hunt@ce.berkeley.edu
Tel: (510) 642-0948
Fax: (510) 642-7483

Karl Malamud-Roam, Ph.D.
Environmental Projects Manager
Contra Costa Mosquito and Vector Control District
155 Mason Circle
Concord, CA 94520
Email: kmr@ccmvcd.net
Tel: (925) 685-9301 Ext. 107
Fax: (925) 685-0266

Tom Young, Ph.D.
University of California
Department of Civil and Environmental Engineering
2001 Engineering III
Davis, CA 95616
Email: tyoung@ucdavis.edu
Tel: (530) 754-9399
Fax: (530) 752-7872

Adrian Wadley
Eberhardt Meier Cassel
Environmental Consulting Services
700 Petal Court, Suite A
Vacaville, CA 95688-9289
Email: awadley@emcenviron.com
Tel: (510) 325-0935
Fax: (707) 455-7229

Geoff Siemering
Manager, Aquatic Pesticide Monitoring Program
San Francisco Estuary Institute
7770 Pardee Lane, 2nd Floor
Oakland, CA 9462199-2266
Email: geoff@sfei.org
Tel: (510) 746-7364
Fax: (510) 746-7300

EXECUTIVE SUMMARY

The Modeling Workgroup of the Aquatic Pesticide Monitoring Program (APMP) considered several publicly available screening and assessment models used for understanding the fate of pesticides applied to water bodies. One of these models, EXAMS II, was chosen and applied in two test cases, which were coordinated with the data collection efforts of the APMP monitoring program. Modeling was applied for two hydrodynamically simple systems, one a relatively static recreational pond (Costa Ponds, Porterville, CA) and the other a flowing irrigation canal (Byrnes Canal, Merced Irrigation District).

Results of the modeling effort for the two monitoring sites are presented. Planned and additionally requested characterization of the sites resulted in initial model input data sets and an understanding of the complexity of the environmental pesticide distributions. Further characterization may have enabled any uncertainty between model and real world findings to be resolved, however, both time and monitoring data were limited. In addition, the work conducted did not immediately suggest an application to predicting aquatic pesticide concentrations with certainty, certainly to the level that might be required for the support of permits. However, by considering the important factors in the fate and especially transport of the aquatic pesticide that is applied, the modeling could readily lead to useful guidance for when and where to monitor. For instance, the use of chemical tracers provided evidence of the location of the maximum extent of movement of a treated body of water as it dispersed below a possible threshold of concern.

The modeling that was done here was intended to inform the current regulatory proposal, which covers only direct and intentional applications to a water body, in this case static ponds and flowing irrigation canals. Though it may help illuminate other aquatic pesticide situations, other modeling approaches might be more appropriate. Thus, approaches to consider aquatic pesticide use in river and estuary systems that have more complex hydrology than the ponds and irrigation channels considered here were proposed. A short-term feasibility study with entities such as the U.S. Geological Survey and the California Department of Water Resources to examine suitable approaches

should also be considered if larger more complex hydrodynamic systems are to be included for modeling in the APMP.

BACKGROUND

Understanding the fate of pesticides intentionally applied to water is important for protecting human and ecosystem health. The State of California is starting a new process of regulating aquatic pesticide applications and has a number of possible approaches to that regulation. Two extremes are 1) to depend exclusively on various modeling efforts to anticipate adverse consequences or 2) to rely exclusively on monitoring programs for applicators. In all likelihood, there should be a combination of these approaches to reach some optimal level of environmental protection with a realistic expenditure of private and government funds. It is likely that the two-year time frame set aside for this effort by the Aquatic Pesticide Monitoring Program (APMP) will not completely resolve these issues. However there can be a concerted effort to achieve a balance.

In December 2002, the Aquatic Pesticide Monitoring Program (APMP) established a Modeling Workgroup. The charge of the Workgroup was to evaluate and demonstrate the use of existing models that assist in determining the fate, transport, persistence, and exposure concentrations of pesticides in surface waters. Several Tier 1 and Tier 2 surface water screening and assessment models have been developed by the U.S. EPA and others and are currently available to the public.

The Modeling Workgroup contributed by commenting and advising the APMP on the following management objectives: 1) Creation of an aquatic pesticide field data collection plan: The screening and assessment models that are evaluated should be incorporated into the field data collection program where appropriate. The modeling information may then contribute to the understanding of aquatic pesticide fate, transport, persistence, and exposure concentrations to biota in surface waters, and 2) Implementing field data collection and analysis such that the pesticide data (water concentrations and distributions) should be suitable for assessment modeling.

The models considered for evaluation in 2003 were GENEEC (Generic Expected Environmental Concentrations), WASP (the Water Quality Analysis Simulation Program), EXAMS II (the Exposure Analysis Modeling System), PRZM-EXAMS (the

Pesticide Root Zone Model linked to EXAMS II) and FIRST (the FQPA Index Reservoir Screening Tool).

These models have a common theme in that they all directly or indirectly address pesticides applied to water and handle the behavior of pesticides in water systems to varying extents. Their level of complexity varies from screening only in a defined scenario to fully user defined multi-compartment systems. However, their hydrology is often simple at best or has to be supplied externally. More complex hydrologic models were not considered at this stage since the workgroup felt that they would in general require modification to handle aquatic pesticide fate.

GENEEC is a US-EPA Tier 1 model used for screening pesticides. It assumes pesticide input from drift of pesticide from off-target applications as well as runoff from the site of application. Since this primarily is considering non – target exposure concentrations from regular agricultural field use, and because it is a Tier 1 screening tool only it was not considered suitable for further use with the APMP modeling exercises.

PRZM-EXAMS is a linked system of two separate models, PRZM, the Pesticide Root Zone Model predicts groundwater recharge from the root zone and runoff from surface and crop applied as well as soil incorporated pesticides. Off target movement of pesticides both dissolved in the runoff water as well as those adsorbed to eroded sediments are used as inputs to EXAMS and usually handled within a standard 2-compartment pond scenario. Since this model system is primarily designed to simulate agricultural applications and predict off target movement, and only then to consider fate in the aquatic system it was not felt suitable for further APMP work.

FIRST (FQPA Index Reservoir Screening Tool) was not considered suitable for two main reasons. Firstly the model is a screening tool, and the APMP modeling effort wished to go a little further than screening and secondly the model is designed to predict results of water concentrations in a reservoir from normal agricultural use, not from direct application of pesticides to water.

WASP, the Water Quality Analysis Simulation Program is a linked series of sub models handling water quality, eutrophication, sediment transport and toxic chemical transport and transformation. It can be run in 1,2 or 3 dimensional modes. This model requires extensive site-specific linkage efforts to couple with multi-dimensional hydrodynamic models. Also the model requires an extensive amount of data for calibration and verification. For these reasons it was considered too complex for initial use however it has many features that make it worthy of future consideration, especially the linkage possibilities to hydrodynamic models.

The choice for the modeling effort in 2003 was to concentrate on the potential use of the Exposure Analysis Modeling System II (EXAMS-II, or just EXAMS) as developed by U.S. EPA, which was judged a good test of equivalent models. Hydrodynamic models which did not include chemical transformations or exchanges with sediments were not considered appropriate at this stage.

At the February 2003 Science Advisory Committee (SAC) meeting several recommendations relating to the modeling effort were made, amongst many other useful recommendations. Specifically the SAC advocated the use of conservative tracers in field studies linked to the modeling, the close collaboration between the modeling and monitoring efforts, application of two dissimilar pesticides at the same time at a single site (along with a tracer) and several other very helpful suggestions.

Scope

The scope of any modeling efforts of this type must meet two essential criteria. First the model must be appropriate for the water bodies in question, or a subset of them. Secondly data must be available for those water bodies and the pesticides applied to them. The choice of the EXAMS model and the selection of the sites for field data collection resulted in several candidate sites for consideration. In addition available effort in 2003 for this exercise suggested an upper bound for the number of sites that could be initially considered. The EXAMS model choice allows the inclusion of hydrologically simple water bodies in the scope, which is where the field data collection effort has concentrated effort. In addition EXAMS is designed for screening of organic chemicals. Although site specific field data collection and associated modeling was considered for all sites for which field data collection was planned in 2003 the Modeling Workgroup felt that EXAMS was initially appropriate for the proposed modeling tasks only for hydrodynamically simple systems receiving direct pesticide application.

Modeling Approach

The APMP preliminary field monitoring efforts of 2002 and 2003 have wisely examined hydrologically simple systems of canals, streams, and reservoirs rather than the more complex and difficult to interpret water systems such as the San Francisco Bay and Delta and river reaches of the Sacramento and San Joaquin. The choices of sites for study were evidently opportunities to sample during normally scheduled operations and did not initially provide the opportunities to introduce a suite of tracers having simpler environmental behavior than the pesticides themselves. For example, once pesticides are introduced into the water body, the pesticide of interest likely undergoes a combination of volatilization, sorption, and chemical, biological, and photolytic changes. In addition, the water in these systems is being advected by flows and various dispersion processes are operating to mix the introduced fluid with surrounding waters. A few measurements of a single reactive pesticide under these conditions will not be able to resolve the multitude of processes that are likely controlling its fate. It was concluded that for modeling to play a significant role in the eventual permit process, then the actual field experiments will need to provide the data necessary to test models and lend some creditability to any modeling results used to evaluate pesticide choice and management options. Efforts to accomplish this are reported here.

The modeling work has been, and if continued will be, conducted using a phased approach:

<u>Phase I.</u>

Modeling will cover hydrodynamically simple systems such as short sections of irrigation canals. An existing unmodified model was identified and evaluated in a pilot modeling study. This work was completed using the EXAMS model and an example section of the Livingston canal monitored in 2002. It was reported to the APMP Science Advisory Committee in February 2003 and is summarized below in section 0.

<u>Phase II.</u>

Modeling was proposed to include other hydrodynamically simple systems such as small impoundments with simple hydrology, and perhaps other channelized flowing systems that can be characterized. Phase II will used an existing model and started to examine the steps necessary to apply this, or other perhaps yet to be developed models or linkages to more complex situations. This phase was the primary effort of the 2003 modeling and is reported here.

Phase III.

Modeling will be guided by the results of earlier phase modeling and by Modeling Workgroup input. Other models that address more hydrodynamically complex systems such as larger reservoirs and the San Francisco Delta might be considered for evaluation. This phase remains an objective and some commentary will be made in this report using the input of the Modeling Workgroup participants on the future steps necessary to achieve this.

Site-specific modeling of pesticide applications needs accurate reporting of pesticide application and the hydrodynamic conditions of the system. For canals, the inflows and outflows can usually be controlled and are readily measured. For streams and urban creeks, the inflows are less known, but should be measured along the reach of interest. Hydrodynamic mixing within reservoirs and lakes can become very complex and the level of detail needed for determining pesticide transport is likely pushing the state of the art in transport modeling given the short time scales of interest and the reactivity of the pesticides. While reservoirs, lakes and eventually estuaries will receive probably the most interest during the regulatory process, it was concluded that this two-year program has to concentrate on initially tractable problems and so the modeling approaches tried are applicable to a subset of the monitored locations.

SUMMARY OF INITIAL MODELING EFFORTS

In Phase I the major objective was to illustrate to the Modeling Workgroup what the EXAMS model required as input and what it potentially could deliver. In doing so the workgroup could learn how the model was structured and recommend, if appropriate, continued work with this model, or consider other approaches. Phase I was also used to develop the methods for setting up and running the model within the context of the type of systems the APMP would be considering and which were within the scope of this model.

EXAMS was used to simulate a short section of an irrigation canal, such as the Livingston Canal, following an application of acrolein. A simple idealized section of a small irrigation canal was set up consisting of a 300 m length of canal 2 m wide and 1m deep. In the model this was described as three sections, each section has a 1 m water depth segment 100 m long and a sediment segment with a depth of 5 cm. Flow into the system was varied as the various test scenarios were built.

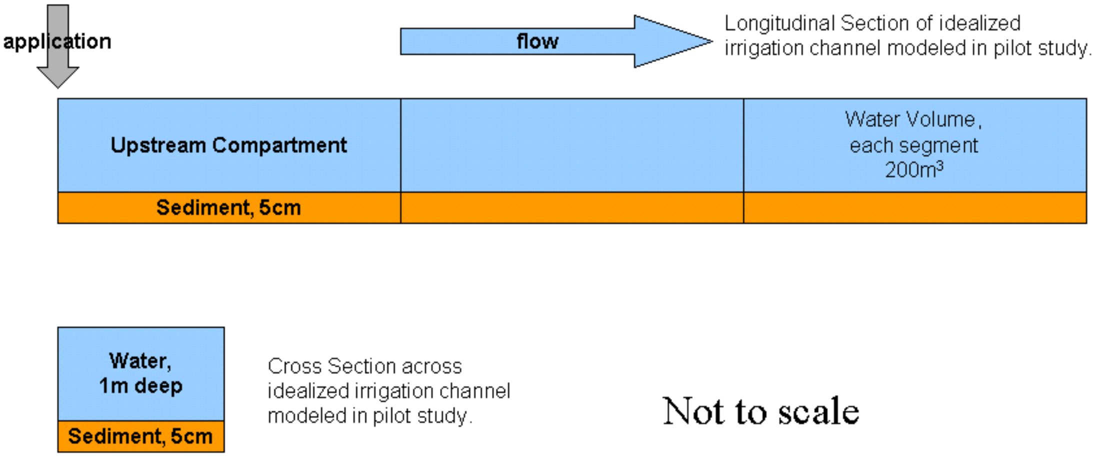

Figure 1. Sections of a simple irrigation canal used in test modeling.

Characterization of the water quality and sediment parameters for the initial pilot modeling was based on a mixture of available data and example datasets provided with the EXAMS II model.

Acrolein was chosen because it was used in the irrigation canal systems from which field data was collected in 2002. It is also of special interest to several participants in the APMP. The key inputs for modeling acrolein are shown in Table 1. Acrolein is hydrolyzed and volatilized in aquatic systems. Adsorption is very low and sediment binding is not likely to be important in removing acrolein from the water column. Microbial degradation is also implicated in the reported natural system half-lives of approximately 0.5 days.

Table 2. Key Inputs for modeling acrolein.

Input	Value	Source
Hydrolysis DT50	3.5 days (pH 5) 1.5 days (pH 7) 4 hours (pH 10)	APMP review from Tomlin (2000)
Molecular Weight	56.1 g $mole^{-1}$	California Air Resources Board Fact sheet
Henry's Law Constant[1]	Selected $3.0x10^{-5}$ atm m^3 mol^{-1} Range: $4.4x10^{-6}$ to $1.2x10^{-4}$ atm^{m3} mol^{-1}	World Health Organization Acrolein Fact sheet http://www.who.int/ pcs/cicad/full_text/ cicad43_acrolein.pdf
Partition Coefficient	Log P = 1.08	APMP review from Tomlin (2000)

This investigation of the use of EXAMS to produce useful outputs proceeded in stages. Initially EXAMS installation was confirmed with the provided test files. Then a conservative tracer was modeled and conservation of mass confirmed. Issues with weather data and precipitation were identified and resolved. Dissipation mechanisms were introduced. Since acrolein was being considered these were primarily hydrolysis and volatilization. When reliable model runs were achieved flow was introduced and the behavior of the model confirmed. This initial modeling exercise was presented to the workgroup in an interim report in February 2003.

This initial modeling was an entirely theoretical exercise for which field data was not available to perform either calibration or subsequent validation with an independent set of data. The field data collected represented samples take in a moderate sized irrigation system many miles apart. The total length of canal in the system and the number of extraction points for which water use information would have had to be collected precluded an easy initial exercise in which collected field data from 2002 could be readily modeled. Therefore, although the Livingston Canal and the use of acrolein in this system provided an idea from which to work, this initial exercise was not meant to simulate this real world system. Rather the initial modeling was used to demonstrate the

---

[1] Acrolein Henry's Law Constants reported have a very wide range. In practice this variability should be understood if predictive modeling of acrolein is undertaken. Sensitivity analysis would be very appropriate. Here, however, in the initial modeling efforts to understand how to apply EXAMS, a single value was arbitrarily selected and no sensitivity analysis was performed.

types of inputs the EXAMS model required, the methods of obtaining that data and to guide the field data collection portion in 2003 towards any additional data requirements.

The SAC commented that the choice of acrolein as a model chemical posed some special concerns that should be examined carefully if substantial effort was to be spent on modeling this chemical. Acrolein acts by rapidly destroying plant tissue which then detaches from the root systems and typically can be found floating downstream with the current 24 to 48 hours after application. The changes in water chemistry resulting from the additional organic matter burden as well as the need to handle transport of chemical adsorbed to the plant material at some point after application as it detaches were identified. The recommendation was to consider other aquatic pesticides before reconsidering acrolein. However, the workgroup acknowledged the special interest and significance of acrolein to APMP members and sponsors.

Irrigation canal systems seem initially attractive for modeling. They are enclosed and the water is the commodity that is being traded so records should be available for most water entering and leaving the system. However the example proposed of the Livingston Canal in the Merced Irrigation District was larger than initially believed. The canal system is many miles in length, is branched and looped with the potential for directional flow changes and serves many dozens of growers. Grower draw down of purchased water occurs at many points when suitable for the crop selected. Gathering of all the required hydrology data for a system of this size would likely have consumed more resource than was available. Hence although a chemical of considerable interest and in a very realistic larger irrigation system the conclusion was that Livingston Canal system was not suitable for further modeling effort in this next phase.

PHASE II MODEL SCENARIOS

The subset of monitored locations that are of interest, and that were considered for modeling with EXAMS in Phase II are channel flow systems with well characterized water flows such as small irrigation systems, and static or very low flow systems such as recreational ponds and impoundments. Two such situations were envisioned, one flowing, the other essentially static and site selection proceeded to find a suitable match between pesticide used, site characteristics, availability of data for both the site and the chemical, and level of interest in the chemical.

In order to investigate the use of EXAMS for different situations two contrasting scenarios were envisioned. One would be a flowing water scenario with well known water inputs to act as a model for applications to irrigation canals and where fate is dictated primarily by the flow, and the other would be a static or nearly static scenario such as a pond where modeling the chemical applied would allow us to investigate more the aspects of EXAMS treatment of the behavior of the compound over time.

In addition contrasting chemicals were chosen so that sediment binding or fate in the water column could be investigated.

Site Selection

Flowing Water Scenario

Two sites were considered. The Livingston Canal in the Merced Irrigation District that had been used in the pilot study with applications of acrolein in 2002 was considered along with the Byrnes Canal in the Solano Irrigation District. The Livingston Canal is a large system serving many thousands of acres with multiple laterals and delivery points. System size and complexity was high, with a very large data collection requirement in order to characterize even the water flows. In addition pesticide choice was questioned because of the expected behavior of acrolein in the system and its removal. The SAC comments advised that acrolein sequestration into the controlled aquatic plants and subsequent removal downstream as the plants succumbed and became detached would be a significant problem for a model that initially was trying to be relatively straightforward. Although there is significant interest in this chemical and its use it was felt that both the combination of size and complexity of the system and the non-standard chemical behavior characterization necessary would make this a poor choice at this stage.

The Byrnes Canal near Vacaville, CA is a relatively small system with a single source of water at the head and limited branching. The size of the canal and flow rates were well known and could be easily measured or taken from known recordings. The aquatic herbicide used is a copper formulation and although the selected model is designed for organic chemicals the very short timescales in this small system suggest simplifications in the treatment of the chemical behavior necessary would be acceptable.

Initial investigation of the Byrnes Canal showed that the canal was treated in two parts when the regular monthly copper applications were made. The downstream section of the canal was retreated because the concentration of the applied herbicide active ingredient declined below an efficacious level by the time the flow reached the fifth weir. The site chosen for study was therefore a subset of the whole length of canal, and consisted of the upper 2.1km section of the main canal. A site visit (May 1st 03) enabled the dimensions of the canal to be captured.

A site visit was carried out on May 1st 2003 to examine the site and measure the dimensions of the systems.

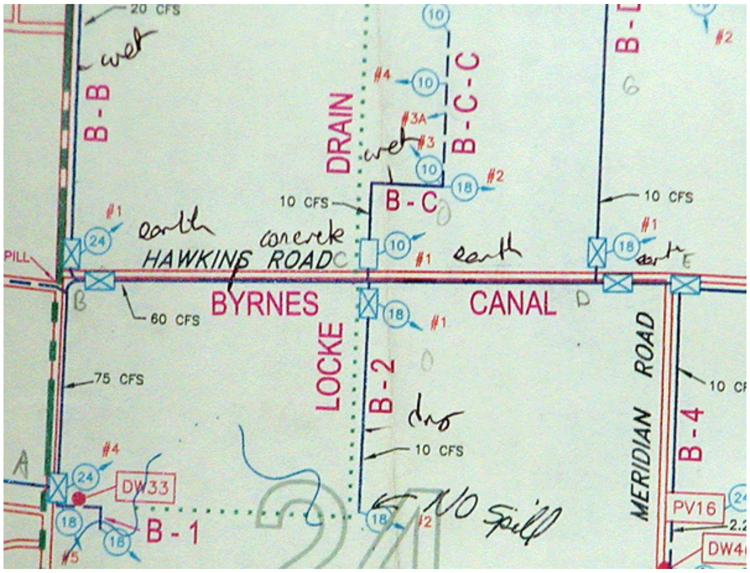

Figure 2. Section of the map supplied by Solano Irrigation District and on which is mapped the main Byrnes Canal and the laterals (designated B-x).

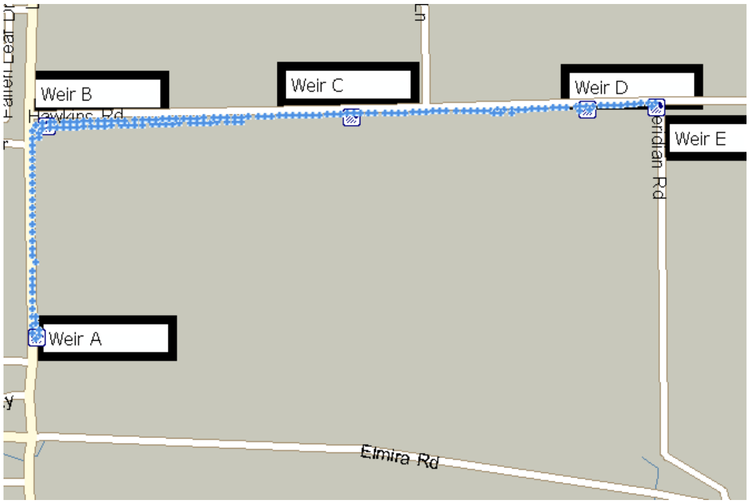

Figure 3. During the site visit the outline of the canal system was confirmed by the global positioning system and is shown here. Re-injection of the copper herbicide occurs at Weir E.

Figure 4. Byrnes Canal alongside Hawkins Road[2].

---

[2] Note mixture of earth sides and cement sides.

Figure 5. Byrnes Canal Weir A under low flow conditions on May 1st 2003. Site of normal applications.

Table 3. Byrnes Canal: Characterization of dimensions and flows[3].

Reach	Length (m)	Depth (m)	Average Width (m)
A (Below Weir A)	562	0.9	3.47
B	777	0.9	3.00
C	604	0.9	3.32
D	172	0.7	2.92

FLOWS	Flow rate at head weir (cfs)
Typical during application season[4]	20 - 30
Extremes during application season[2]	10 - 50
Actual during application 6/30/03[2]	23
Actual during site visit 5/1/03[1]	6.6

---

[3] Source: Measured during site visit of 5/1/03

[4] Source: Mark Veil, Solano Irrigation District

Static Water Scenario

In collaboration with the efforts of the monitoring group of the San Francisco Estuary Institute two static pond sites were proposed. A 2-acre (0.8 ha) shallow pond site "Sand Bay Isle" with applications of diquat and a 5 acre (2 ha) recreational pond "Costa Pond #5" where fluridone is regularly applied were put forward.

The small size and shallowness of the Sand Bay Isle site was attractive, however, the use of diquat with its specialized adsorption mechanism to clays in sediment and reported non-reversibility of that adsorption excluded this site. In addition February 2003 SAC comments suggested diquat should be of very low concern because of the very strong tendency for binding. The Costa Pond #5 site was therefore chosen and fluridone applications to the pond were considered.

At Costa Ponds weed control has been regularly achieved using the product Sonar, a 5% by weight formulation of fluridone. A history of 3 to 4 years use of three applications per year was recorded for this site with target application amounts used to achieve the labeled maximum of an annual total of 60 to 90ppb.

Figure 6. Costa Pond #5, a recreational facility near Porterville, CA.

Methods

EXAMS Parameterization
Byrnes Canal

System Geometry

The known system dimensions were used to derive a set of interconnected compartments within EXAMS that describe the Byrnes Canal. Each reach is divided into approximately 100m segments. Each section of a segment has a water column and sediment layer. There are 22 sections and 44 compartments. The sediment layer is modeled as being 2.5cm thick, representing the depth of the 2-3cm sediment grab samples.

Reach	**Number of sections**	**Dimensions (L x W x D, m)** **L= water column** **B= sediment**
A	6	L: 94 x 3.4 x 0.9 B: 94 x 3.4 x 0.025
B	8	L: 97 x 3.1 x 0.9 B: 97 x 3.1 x 0.025
C	6	L: 101 x 3.3 x 0.9 B: 101 x 3.3 x 0.025
D	2	L: 86 x 3.1 x 0.7 B: 86 x 3.1 x 0.025

EXAMS Input Data Justification

Since copper is not subject to biodegradation the degradation rate parameters affecting the applied chemical were set to zero. Loss from the water system will be primarily by adsorption and advection and these two processes are the major parameters controlling copper concentrations and distributions in the Byrnes canal. Exchange processes between the water column and the sediment result in copper being found in the sediment and lumped dispersion processes are used within EXAMS to simulate this.

EXAMS handles chemical binding to sediments as an equilibrium partition process. Although a gross simplification for copper an initial scenario will use a single adsorption constant, K_d, to define the partitioning of copper between the adsorbed and dissolved phases within each compartment. This does not imply instantaneous and fully reversible binding between sediments in a benthic layer and the overlying water column. This requires special treatment and is discussed below.

Copper binding and sequestration within sediments is beyond the scope of the EXAMS model to consider fully. In addition the timescales of interest for water column concentrations (the water that may be discharged into a receiving water body of interest) are very short – of the order of hours rather than days or months. Therefore, the simplified equilibrium partitioning approach that EXAMS uses is considered acceptable under these constraints. However literature values for binding of copper to sediments are highly variable and typically are complicated by consideration of all the different forms copper can take in aquatic systems. A simplified experimental approach considered by Grassi, Shi and Allen (2000) examined copper adsorption to Aluminum Oxide as an aquatic model phase. Potentially suitable values for copper adsorption from this source suggested a two order of magnitude range from 10^4 to 10^6 L/kg. Site-specific partition coefficients would be ideal, and although not explicitly measured, sediment samples were taken and concentrations of copper in the sediment pore water and the sediment dry matter were made separately. This is a suitable start to estimate site-specific adsorption for the sediment type found in the Byrnes Canal.

Two pre-application samples are available taken at two locations on May 1st 2003, the site evaluation visit. The first (BC01) is taken at approximately the same location of the dye sampling point 1 measurement from June 30th, i.e. ~60m downstream of the head weir. This sample has a duplicate analysis. The second sample was taken further downstream, presumed between weirs D and E. This sample has a single analysis.

Kd is estimated as Cs/Cw , where

Cs = concentration in sediment, dry weight basis, mg/kg, and

Cw = concentration dissolved in pore water, mg/L.

Site	**Copper in sediment (mg/kg dry wt)**	**Copper in pore-water (mg/l dissolved)**	**Kd estimate [l/kg]**
BC01	897 738 mean 817	0.161 0.061 mean 0.111	5600 12100 mean 8850
BC02	234	0.099	2364
Selected K_d value used			5600

The main unknown process is the extent of the mixing between bottom sediments and the overlying flowing water. Observations on both the initial site visit under low flow conditions and on June 30th for the June application didn't suggest any scouring or deposition of sediment. Thus re-suspension and settling / burial of sediments can be ruled out of consideration as a major factor at this site in the short term. However, some mixing must occur between the bottom sediments and the overlying water because there are known concentrations of copper in the sediments. This could be a result of some adsorption to suspended sediments that settle, or a little re-suspension and settling, or direct adsorption to the sediment. Diffusion could also occur into the sediment pore-water during an application when the water column concentration of copper is higher than the pore-water concentration.

In EXAMS all of these processes are lumped together and are considered as one overall dispersion term between the first benthic layer and the last water column layer. In our case we have one of each so this is dispersion between the water and sediment. There is little guidance to set this parameter within the EXAMS documentation. However, it is a useful parameter to use to calibrate the model behavior to the known situation; in this case the decline in concentration of copper along the length of the canal during the extended application period of 4 hours. It is surmised that adsorption to sediments is the primary reason for this decline and exchange between the sediment and the overlying water has to be driven by this dispersion term. However, another process or processes may drive the transfer of copper present in the water column to the sediment.

Modeling Process

A stepwise approach was taken, first using a conservative non-adsorbed solute to mimic the dye behavior followed by comparison to the dye results. Copper is then introduced to a "clean" system for the four-hour application window and the fate noted and compared to the reported behavior (decline over the 2km treatment length). Finally the initial conditions are set to mimic the already known values of copper in the sediment pre-application and a set of runs are made to examine the fate of the newly applied copper. For each set of runs consideration is given to adjusting the dispersion term between the bottom sediment and the overlying water to achieve the observed decline in water column concentrations that drives the need to make the repeat application at weir E (concentration drops below 0.7ppm and efficacy is lost).

EXAMS Parameterization
Costa Ponds #5

Costa Pond #5 is a small recreational pond of 5.22 acres (2.1 ha). Average depth measured on a site visit was 9'3" (2.8m). A small amount of inflow was measured at $6.8m^3hr^{-1}$. Measured outflow was about two-thirds of inflow. Application history and amounts suggest edge effects in the pond affect the average depth over the whole pond and this value is probably closer to 5' (1.5m).

Fluridone applications were made three times during the summer. The first application of 128oz Sonar product per acre was made on June 17th and two subsequent applications were made at lower amounts. Dates of subsequent applications are unrecorded. The site was sampled 1 day pre-application, on the day of application and 2 and 6 weeks after the first application.

EXAMS Input Data Justification

The pond is modeled in EXAMS as a simple two-compartment model – a single water compartment, which receives the inflow of clean water from an upstream source, and a single sediment compartment directly below. The sediment compartment was simulated to be 2.5cm deep to be consistent with the samples of sediment that were taken. Chemical is applied to the pond by a sub-surface method to achieve uniform application.

The water outflow was less than the inflow and due to the location in the Central Valley of California the difference on a pond of this size is likely to be due to evaporation. Therefore in the absence of any evidence of seepage out of or into the pond from other sources the pond is assumed to only have inputs of water from rain (very small to no rain typically during the study period) and from the estimated stream flow. This is a very small flow relative to the pond size and advection of chemical applied out of the system will be a small component, which is ideal for this scenario.

Literature review of pesticides in the APMP by SFEI (SFEI, 2002) summarized the parameters necessary for the EXAMS modeling. Specifically the reported sediment half-life can be as high as 9 months under anaerobic conditions. The water column dissipation half-life varies from 11 to 24 days – a value of 20 days was chosen, the recommended value in the literature review. Fluridone is moderately strongly adsorbed to sediments and this is related to the organic carbon content (and the fineness of the sediment). Thus using the K_{oc} model for adsorption in EXAMS and entering the measured organic carbon content of the sediment (average 5% OC) is appropriate. A K_{oc} value of 350,000 l/kg was employed.

Results

Byrnes Canal, Solano Irrigation District

Dye Study

Relative dye concentrations were measured during the June 30th application by fluorimetry. EPA Region IX laboratory in Richmond, CA provided the facility to conduct this analysis. An EXAMS run was conducted with a conservative non-adsorbed solute, and the longitudinal dispersion set as measured from the dye study. EXAMS finest timescale is hourly and for that reason and the problems noted with lack of mixing at the first dye measurement location 60m from the application point predictions at this location are not considered for comparison to the measured peak.

Comparisons are made between the predicted concentrations using EXAMS to those measured. The two sites where this comparison can be made are below weir B (compartment #13) and above weir E (#43).

Three runs were examined with the longitudinal dispersion term set to that predicted from the dye study and two lower values. When the longitudinal dispersion term is set to the lowest value the EXAMS model still appears to be including dispersion at a level above that expected. It predicts a broader and flatter peak at dye location 3 than that observed. This indicates that the model itself is mimicking longitudinal dispersion by the chosen model structure and that the calculated value of the dispersion from dye studies is higher than that necessary for the model: the model input value of the longitudinal dispersion term should use the dye study estimated value as an upper bound. Because the model structure is a set of interconnected compartments with direct flow from one to the other and because the chosen compartment size (approx 100m length) is larger than the length of the dye pulse this is the most likely explanation of the discrepancy between the modeled and observed results.

Copper Application: Clean sediment test run

A set of test runs were made to examine what value for the dispersive exchange term between the water and the sediment was necessary to predict a decline in concentration of copper in the canal from 1.0 to 0.7ppm over the 2.1 km length, as is known. Initially this is done without loading the sediment in the model with the pre-application measured values.

In order to achieve water column declines in peak copper concentration as observed the dispersive exchange term is in the range of 10^{-8} to 10^{-7} $m^2\,hr^{-1}$. Concentrations of copper in the initially clean sediment are predicted to rise to 0.02 to 0.2 $mg\,kg^{-1}$. Predicted sediment concentrations did not vary greatly along the canal, showing a slight decline with distance from the injection point.

Copper Application: Sediment with copper concentrations as measured.

Two pre-application sediment samples (BC01 and BC02) had copper concentrations of approximately 820 and 230 $mg\,kg^{-1}$ dry weight. EXAMS runs were conducted with sediment loaded with the measured burdens, assuming the two measured values represented the loading in the first and fourth reach of the system in the main canal, and using a sediment compartment depth of 2.5cm. Simple interpolated values were used as an approximation for the burdens in the second and third reaches.

Using a sediment dispersion value in the range as determined for the clean sediment runs was not sufficient to achieve the known decline in copper concentration over the length of the system. The value of the sediment dispersion term was increased to 6×10^{-6} $m^2\,hr^{-1}$ to match the 0.3ppm Cu decline.

Table 4. Byrnes Canal. Model results, pre- and post – application.

Pre-application	**Modeled Results**	**Observed Results**
Water column concentrations, mg/l	0.04 to 0.14 mg/l (reach D to A)	0.007 mg/l (Reach A)
Sediment concentrations, mg/kg dry wt	230 to 820 mg/kg dry weight (reach D to A)	230 to 820 mg/kg dry weight (reach D to A)
Post-application		
Water column concentrations, mg/l	Immediately 0.7 to 0.95 mg/l (reach D & A) Declining to 0.05 to 0.15 mg/l (reach D & A) after system is flushed.	Immediately 1.04 mg/l (n=4) reach A to 0.7 mg/l (n=1) reach D at 3.5hrs 0.1 mg/l as system is flushed (n=1)
Sediment concentrations, mg/kg dry wt	237 to 827 mg/kg dry weight i.e. increase 7 mg/kg (reach D to A)	210 to 620 mg/kg dry weight i.e. measured decrease (reach D to A)

A comparison of the measured vs. predicted copper values following the application shows that an approximate match to water column concentrations. A decline along the length of the canal was successfully simulated and this matches the known, and in this case observed decline.

Sediment predictions and measurements pose more of a challenge. Post-application copper results do not show a consistent pattern with the pre-application results, the earlier high value site (BC01) now has lower values — mean of 820 mg Cu/kg dry sediment prior to application, mean of 620 mg Cu/kg dry sediment after application. However, the downstream site (BC02) shows a similar, but still lower, value (mean of 230 mg Cu/kg dry sediment followed by mean of 210 mg Cu/kg dry sediment) – this suggests spatial inhomogeneity for copper in sediment or perhaps other changes with time that we are not considering – dredging, re-suspension & settling. Currently no valuable comparison appears to be possible between modeled and predicted sediment values.

Costa Pond #5 - Results

Costa pond #5 was sampled 1 day pre-application (sediment), on the day of application (water) and two and six weeks after application. Due to the uncertainty of subsequent applications the predicted and measured results are compared only for the sampling times up to two weeks after application, since the 2nd application scheduled for the year is unlikely to have been applied within this time.

Table 5 describes the actual measured, and EXAMS predicted, fluridone values at the times that samples were taken in the field. Comments on these are made in the footnotes.

There are no sediment sample concentrations yet available post application, either at two or six weeks to make model comparisons, which leaves this result set incomplete. However with the parameters selected sediment concentrations are predicted to decline (from a single application) to 3 mg kg^{-1} by year-end, and further by the start of the application season six months later. Measured values in sediment (see footnote) pre-application therefore seem very high.

Table 5. Predicted and measured fluridone levels at Costa Pond #5.

Date	Parameter	Measured	Predicted
Sediment			
6/16/03 (1 day pre app)	Fluridone, total in sediment [mg/kg]	71[5] ppm (n=6)	0[6]
7/2/03 (15 days post application)	Fluridone, total in sediment [mg/kg]	—	7.7
7/31/03 (6 weeks post application #1-03)	Fluridone, total in sediment [mg/kg]	—	6.7
Water			
6/17/03 (day of application, pre-app)	Fluridone, dissolved in water [µg/l]	0.05, <RL (n=2)	0
6/17/03 (day of application)	Fluridone, dissolved in water [µg/l]	4.3[7] (n=2: 1.3 & 7.2)	19
7/2/03 (15 days post application)	Fluridone, dissolved in water [µg/l]	1.4	1.4

---

[5] 71 ppm is a very high loading approximately 9 months after the last application. If valid then this suggests high levels of fluridone accumulation in sediment and very little degradation. Even with the longest reported aquatic sediment half-life (9 months) accumulation of these amounts seems unlikely. A check of this data seems warranted, especially the units.

[6] No sediment loading pre-application is simulated. Literature review of fluridone behavior in the environment does not suggest accumulation in sediment and that very low levels would be present from one season to the next. Hence at least initially no loading is presumed.

[7] Fluridone formulation is described on the Sonar Q product label as a pelleted formulation. Actual formulated product used maybe different, however, if Sonar Q was used a sample time of 1-hour post application would likely miss active ingredient that had yet to dissolve and was not available for analysis – assuming the water sample is filtered prior to testing.

Discussion

Two relatively simple systems were considered for EXAMS modeling. Site investigations, data gathering, and planned aquatic pesticide monitoring results showed that even in these simple systems there are interesting complexities and uncertainties.

At Byrnes canal the methods of sediment sample collection as a grab sample leaves a little uncertainty about depth representation of the sediment – does the sample accurately represent the estimated depth and was the model then set correctly to simulate that depth?

The change with time of the measured sediment concentrations, in fact a decline of sediment copper measured from before the application to a later sampling is strange. The expectation is that sediment copper concentrations would be higher after the application. We are led to this conclusion by the long history of copper use at this site and the elevated levels of copper found at the first sampling of the year, before this year's application season had started. Clearly copper does remain in the sediment at this site over the long term. The model would predict a slow decline of the copper in sediment because dispersion between the water and the sediment is simulated and this is a two way process. The flow will then carry away copper. However, accumulation has happened at this site and the reversibility of the adsorption of copper to sediments is too much of a simplification, and likely not accurate for long-term simulations. Hence these simulations attempted to handle what happened immediately pre and post application on a timescale of hours. In reality copper speciation and interaction with sediments and waters is more complex than can be handled by a model designed with organic chemicals in mind. The simplifications adopted here are reasonable for the short timescales, but longer-term simulation of copper based herbicide applications is probably unreasonable with EXAMS, without modification.

There are potentially other explanations of the behavior of copper in sediment and water at this site. Some of the sections of this canal were not lined, and it is possible that actual water flows were amended by seepage to groundwater and to the surrounding fields. The fields are gravity fed with their irrigation water and although no evidence was observed of any water leakage near the canal it is quite possible that water recharge to lower lying field surface and sub-surface soils does occur from the earth lined sections of the canal. Circumstantial evidence reported that an attempt to apply copper herbicide to this system under no-flow conditions was unsuccessful because water could not be adequately retained in the system for the length of time necessary for complete submerged weed and algal control. However, site conditions at that time are unknown and it could have been attempted after recently re-wetting previously dry sections of canal at which time recharge to the canal bed and surrounding soil could have been quite high (canal reaches are allowed to dry out if no water is being delivered through them). A more thorough characterization of water flow at multiple points in the system may have shed light on this possibility.

The static pond considered was a very simple system. However, even at this site uncertainties remained, for example surrounding the water depths. Even after careful site measurement and characterization of pond volume the reported application amounts to achieve the stated label recommended concentrations were lower than the volume would suggest. Concentrations of fluridone in the sediment before this season's applications started were very high suggesting either very extensive earlier use of this compound or a much slower degradation than literature reports.

Water column concentrations of fluridone show some agreement between observed and predicted values. The target application amount is designed to achieve 30ppb fluridone in the water column. The measured values are much less than this and the modeled 24-hour value of 19ppb agrees with the labeled use rate, but not with the measurement. The product is formulated for slow release and it is possible that un-dissolved but suspended herbicide is not included in the much lower measured mean value of 4.3ppb. Later predicted and observed values are the same at 1.4ppb. Sediment results for post-application sampling are not available. These would be very useful to re-confirm the very high pre-application sediment findings and to see if and increase in sediment concentrations similar to the model prediction was found.

The work conducted so far does not immediately suggest an application to predicting aquatic concentrations of herbicides with certainty, certainly to the level that might be required for the support of permits. However, by considering the important factors in the fate and especially transport of the compound modeling can readily lead to useful guidance for when and where to monitor.

Recommendations

The type of site-specific modeling attempted here requires rigorous development of, and adherence to, a site and application characterization protocol. Considerable effort was expended in checking units and confirming units of measurement and converting between US standard and metric (or SI) units. Standardization on SI units in recording and reporting protocols is recommended and this should include the records of applications of pesticides. For ease of explanation to all interested parties both units should be presented, but consistency and efficiency in data handling would be maintained if a consistent scheme were adopted throughout the program.

Generic modeling (using a non site specific screening approach) would be useful to illustrate the fate and transport of pesticides in water bodies and the impact of key environmental and chemical parameters. A valuable aid to defining relevant examples would be a GIS database of water body characteristics and their linkages to receiving water bodies associated with levels of concern for each water body.

Modeling of copper fate, especially in sediments, is more complex than EXAMS can readily handle and longer-term simulations should not use this model. Since copper based aquatic herbicides are extensively used in California guidance should be sought on more appropriate simulation approaches from relevant experts.

Many of the systems to which aquatic pesticides are applied discharge into receptor systems that are of more concern. Characterization of these discharges and their relation to timing of pesticide application and withholding periods is recommended. This analysis would enable a clearer picture of the most relevant systems to concentrate on. Irrigation systems that do not discharge to receiving water bodies but deliver all their water to agricultural uses are of less concern than those multi-purpose systems that deliver water for irrigation and other uses.

The use of a rhodamine tracer at the Byrnes Canal site was very helpful, and had immediate practical guidance in assisting with when to sample. The increased use of tracers (simple ions like bromide and fluorescent tracers like rhodamine) in additional studies is highly recommended. This could readily guide where and when to sample for potential peak residue in water (if that was of concern). It would also provide incontrovertible evidence of the location of the maximum extent of movement of a treated body of water as it disperses below a possible threshold of concern.

Other models should be considered for their utility in handling the fate and transport of pesticides in different and more complex water bodies within the areas of concern to the Aquatic Pesticide Monitoring Program. In particular more complex water bodies such as the San Francisco Estuary and Delta have complex hydrology and are far beyond most readily available aquatic fate and transport models. These systems probably require the development of specific modules to handle the chemicals of concern that can be run in conjunction with hydrology and sediment transport models that are more suited to these complex systems. Initially discussions should be established with the principle developers of relevant hydrology models of the Bay and Delta. These more complex hydrological models could be used to guide field data collection exercises in these larger water bodies where the question “where to sample” is both very important and difficult to answer. Within these models future enhancements could include more explicit treatment of aquatic pesticide introduction and fate. In particular the work of the U.S. Geological Survey at Menlo Park in modeling hydrology within the bay and the work of the California Department of Water Resources through models such as DSM2 (Delta Simulation Model II) should be considered.

Links with both USGS Menlo Park and California Department of Water Resources should be established to initiate short term feasibility studies on the application of their models and modeling approaches to understanding where and in what concentrations aquatic use pesticides might be found in the Sacramento/San Joaquin Delta and the San Francisco Bay system. If measurements of aquatic use pesticides are made in these systems it is these models which may most likely be able to help guide where and when to sample. The feasibility study should also address whether adaptations of these models, or new use methods for them, might also enable prediction of the potential, or lack of potential, for accumulation of aquatic use pesticides in the sediments and organisms of the major rivers, the delta and the bay.

Moderate complexity systems lie between the simple systems such as irrigation canals and lakes and ponds and the main discharge through the state via the Delta and the San Francisco Estuary. Models of these systems could be developed using already existing models of hydrodynamics and chemical fate. Ambrose (2003) neatly summarized these models and consideration of the Water Quality Simulation Program (WASP6, from U.S. EPA; AQUATOX, a simulation model linking water quality to aquatic life, from U.S. EPA), Hydroqual, Inc's offerings including ECOM/RCA, and models from the U.S. Army and Navy (CE-QUAL-ICM and CH3D, respectively), could also be considered.

It is worth echoing some final observations (Ambrose, 2003) from another review here: "Model applications in complex, dynamic systems can require several years of data collection and model development." These "applications are most effective with a core of technical specialists interacting regularly with the community of stakeholders" and "policy issues should be clearly distinguished from technical modeling issues for more effective resolution of both." For modeling to contribute effectively to the whole scope of water systems considered by the Aquatic Pesticide Monitoring Program within California consideration should be given to establishing a team to meet these challenges of successful modeling.

Acknowledgments

The author acknowledges the APMP Modeling Workgroup for guiding and overseeing the modeling effort. In addition members of staff at the San Francisco Estuary Institute (SFEI) and at participating study sites were essential in generating the information on which this report is based. In particular, I would like to thank Geoff Siemering (Aquatic Pesticide Monitoring Program Manager, SFEI), Jennifer Hayworth (Environmental Scientist, SFEI), Cristina Grosso (Data Manager, SFEI), Amy Franz (Intern, SFEI), Peter Husby (U.S. EPA, Region IX Laboratory, Richmond, CA), and Mark Veil (Solano Irrigation District),

References

Ambrose, R.B., 2003, Complex Dynamic Models to Predict Contaminant Fate Predict Contaminant Fate in Water in Water Bodies, presentation at Workshop on Environmental Stability of Chemicals in Sediments San Diego, California April 8 – 10, 2003.

Agricultural Research Service, 2001, ARS Pesticide Properties Database http://wizard.arsusda.gov/acsl/textfiles/ACROLEIN from Hornsby, *et al*., 1986.

Burns, L.A., 2000, Exposure Analysis Modeling System (EXAMS): User Manual and System Documentation. EPA/600/R-00/081 September 2000, Revision D. Ecosystems Research Division, US EPA, Athens, GA.

California Air Resources Board, 1997, Acrolein Fact Sheet http://www.arb.ca.gov/toxics/tac/factshts/acrolein.pdf

CDC Agency for Toxic Substances and Disease Registry, 1990, PB/91/180307/AS CDC Toxicity Profile, http://www.atsdr.cdc.gov/toxprofiles/tp124.html

Fischer, H.B., 1973, Longitudinal dispersion and turbulent mixing in open-channel flows, in Annual review of Fluid Mechanics: Palo Alto, Calif., Annual Review, Inc., v5 p. 59-78, quoted in Gurdak, J.J., Spahr, N.E. and Szmajter, R.J., 2002, U.S. Geological Survey Water-Resources Investigations Report 02-4037, Traveltime Characteristics of Gore Creek and Black Gore Creek, Upper Colorado River Basin, Colorado.

Grassi, M.T., Shi, B. and Allen, H.A., 2000, Partition of Copper between Dissolved and Particulate Phases Using Aluminum Oxide as an Aquatic Model Phase: Effects of pH, Solids and Organic Matter, J. Braz. Chem. Soc., Vol. 11, No. 5, 516-524.

SFEI, San Francisco Estuary Institute. 2002, Internal Review Document of APMP candidate pesticides.

WHO, World Health Organization Acrolein Fact Sheet
http://www.who.int/pcs/cicad/full_text/cicad43_acrolein.pdf

Appendix: Calculation of Longitudinal Dispersion Coefficient for Byrnes Canal

Following the method of Fischer (1973) the longitudinal dispersion of the Byrnes Canal at a flow rate of 23 $ft^3\ s^{-1}$ (2400 $m^3\ hr^{-1}$) during the time of application is calculated as follows.

$$K_x = (\bar{U}^2 / 2)\ d(\sigma_t^2)/(dt)$$

Where

K_x = longitudinal dispersion coefficient, in $m^2\ s^{-1}$

$\bar{U}$ = mean velocity of dye cloud, in $m\ s^{-1}$

σ_t^2 = variance of dye cloud concentration with respect to time in seconds squared
$\Delta\ \sigma_t^2$ = changed in variance of dye cloud concentration wrt time, from one location to next

t = time, in seconds
$\Delta\ t$ = change in time to peak from one location to the next

For the dispersion between dye measurement location 2 and dye measurement location 3

$\bar{U}$ = 0.168 $m\ s^{-1}$

$\Delta\ \sigma_t^2$ = 822600 s^2

$\Delta\ t$ = 9300 s

Resulting in K_x = 1.24 $m^2\ s^{-1}$
= 4470 $m^2\ hr^{-1}$