Evaluation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for Assessing Sediment Quality in California Bays and Estuaries

Southern California Coastal Water Research Project

September 12, 2008

Background

The development of indices of chemical exposure for use in evaluating the Sediment Quality Objective (SQO) for protection of benthic communities included the evaluation of a variety of empirical and mechanistic approaches. The results of the initial phase of analysis were reported to the SQO Scientific Steering Committee in 2005 and served as part of the foundation for the Science Team's recommendation to focus on the development of empirical indices for the final indicator development. This document summarizes the results of those initial analyses, with an emphasis on the results for the mechanistic approaches based on the USEPA's recently developed equilibrium partitioning sediment benchmarks (ESBs).

ESBs are the numeric concentrations of individual chemicals that are intended to be protective of benthic aquatic life, and applicable to a range of marine and freshwater sediments (USEPA 2004). These benchmarks use equilibrium partitioning (EqP) theory to predict the biological effects of selected organic chemicals and metals on aquatic organisms (Di Toro *et al.* 1991). This approach has been created for the protection of both freshwater and marine organisms and is applicable to benthic and water column organisms. It is based on the premise that contaminant distributions are predictable among the different compartments of the sediment matrix based on the physical and chemical properties of the sediment components (e.g., sediment particles and interstitial water). This method assumes that there is equilibrium between sediment and interstitial water and that chemicals are partitioned between interstitial water and sediment particles. The partitioning is determined primarily by the organic carbon content of the sediment (for nonionic organics), the sulfide content (for metals) and the partitioning behavior of each particular chemical.

Like other approaches for evaluating sediment chemical concentrations, ESBs have limitations that influence their utility for assessing sediment quality in the context of California's SQO policy. The ESBs are single chemical values and do not intrinsically consider the antagonistic, additive or synergistic effects of other sediment contaminants. The predictive accuracy of the ESBs is dependent upon the quality of the toxicity and partitioning data used in their calculation. Development of ESBs for chemicals with limited information can result in increased uncertainty regarding their accuracy. Site specific variations in sediment characteristics, such as the presence of unusual forms of organic carbon, can affect contaminant partitioning and result in ESBs that are under or over protective.

Methods

ESBs for organics and metals were calculated using procedures described in U.S. EPA guidance documents (USEPA 2003, 2004, 2008). ESBs for organics were calculated for a range of PAHs, pesticides, and semivolatiles that are commonly measured in monitoring programs (Table 1). Two types of organics ESBs were calculated: Acute EqP, based on water quality criteria for acute toxicity, and chronic EqP, based on chronic toxicity values. ESBs for organics were calculated as follows:

ESB= Kp x TV
Where: ESB= Sediment benchmark concentration (µg/g organic carbon);
Kp= Partition coefficient for the chemical (L/kg); and,
TV= Toxicity Value (either Final Chronic Value or Final Acute Value (as µg/L)).

The ESBs were applied to individual sediment samples by dividing the chemical concentration by its respective ESB, resulting in a toxic unit value (TU). All samples contained data for the PAH compounds shown in Table 1. However, the samples usually contained data for only a few of the semivolatiles and pesticides. The TUs for the chemicals were summed to estimate mixture effects.

Table 1. Chemicals included in the organics ESB calculations.

Semivolatile	Pesticide	PAH
1,1,1-Trichloroethane	4,4'-DDT	Acenaphthene
1,1,2,2-Tetrachloroethane	Aldrin	Acenaphthylene
1,1,2-Trichloroethylene	Chlordane	Anthracene
1,2,4-Trichlorobenzene	Chlordane_Z	Benz(a)anthracene
1,2-Dichlorobenzene	delta-BHC	Benzo(a)pyrene
1,3-Dichlorobenzene	Diazinon	Benzo(b)fluoranthene
1,4-Dichlorobenzene	Dieldrin	Benzo(k)fluoranthene
4-Bromophenyl phenyl ether	Endosulfan I	Biphenyl
Benzene	Endosulfan II	Chrysene
Bromoform	Endrin	Fluoranthene
Butylbenzyl Phthalate	gamma-BHC	Fluorene
Chlorobenzene	Heptachlor	Naphthalene
Dibenzofuran	Heptachlor epoxide	Phenanthrene
Dibutyl phthalate	Lindane	Pyrene
Diethyl phthalate	Malathion	
Ethylbenzene	Methoxychlor	
Hexachloroethane	Pentachlorophenol	
Pentachlorobenzene		
Tetrachloroethylene		
Tetrachloromethane		
Toluene		
Toxaphene		
Xylene		

For metals, an ESB was calculated for a mixture of six elements: cadmium, copper, lead, nickel, silver, and zinc. This ESB is based on measurements of sediment acid volatile sulfides (AVS) and simultaneously extracted metals (SEM). The equilibrium model used to derive the $\mathrm{ESB}_{\mathrm{AVS}}$ for a mixture of the metals is presented below:

If the molar sum of SEM for the six metals is less than or equal to the AVS, that is,
if $\Sigma_i\,[\mathrm{SEM}_i] \leq [\mathrm{AVS}]$
where:

$$\Sigma_i[\mathrm{SEM}_i] = [\mathrm{SEMCd}] + [\mathrm{SEMCu}] + [\mathrm{SEMPb}] + [\mathrm{SEMNi}] + [\mathrm{SEMZn}] + 1/2[\mathrm{SEMAg}]$$

then the concentrations of the mixtures of metals in the sediment are acceptable for protection of benthic organisms from acute or chronic metal toxicity.

The utility of the ESBs described above for predicting the presence or absence of biological effects was evaluated by comparing the benchmarks to sediment toxicity measurements using the 10-day amphipod survival test. Comparisons were made using data from sediment samples collected from California bays and estuaries.

Two types of evaluations were conducted. The first evaluation consisted of calculating the nonparametric Spearman correlation coefficient between the ESB (organics TU or metals difference) and amphipod mortality. Correlations were also calculated for three types of empirical sediment quality guideline approaches: SQGQ1, ERM, and Consensus MEC.

The second evaluation consisted of using scatterplots to examine the distribution of the amphipod mortality data relative to ESB thresholds representing protection of benthic organisms: 1 TU (sum) for organics and $\Sigma_i\,[\mathrm{SEM}_i] - [\mathrm{AVS}] = 0$ for metals.

Results

The correlation analyses for the organics ESBs were conducted using three datasets: all available data (statewide), data from south of Pt. Conception (South), and north of Pt. Conception (North). The acute and chronic EqP ESBs showed essentially no correlation with variations in amphipod mortality (Table 2). Correlation coefficients were negative and ranged from -0.065 to -0.089. A negative correlation indicates a tendency for mortality to be higher at lower TU values, which is the opposite of the positive association that was expected. Correlations for each of the empirical SQG approaches were always higher than those for EqP and positive, ranging from 0.202 to 0.384. Similar results were obtained for each regional dataset.

Correlation analyses using the statewide dataset were also conducted for subsets of the organics ESBs grouped by contaminant type (Table 3). There was no statistically significant correlation for any of contaminant groups.

Far less data were available for calculation of the metals ESB as the SEM and AVS measurements are not components of most monitoring programs. All of the metals data were obtained from southern California bays and estuaries. Similar to the organics ESBs, the metals ESB correlation with toxicity was low, negative, and not statistically significant (Table 3).

Table 2. Spearman correlations of SQG approach with percent amphipod mortality. N=number of samples in analysis; r=correlation coefficient, p=probability that correlation is due to chance.

	Statewide			North			South		
Approach	N	r	p	N	r	p	N	r	p
Acute EqP Sum TU	1103	-0.086	0.004	392	-0.073	0.149	711	-0.089	0.018
Chronic EqP Sum TU	1103	-0.073	0.015	392	-0.077	0.128	711	-0.065	0.084
SGQ1 mean quotient	1186	0.202	0.000	401	0.335	0.000	785	0.231	0.000
ERM mean quotient	1186	0.282	0.000	401	0.389	0.000	785	0.266	0.000
Consensus MEC mean quotient	1304	0.206	0.000	504	0.324	0.000	800	0.204	0.000

Table 3. Spearman correlations of acute EqP by organics group or metals ESB with percent amphipod mortality. N=number of samples in analysis; r=correlation coefficient, p=probability that correlation is due to chance.

EqP Group	N	r	p
Acute EqP PAHs	1269	0.021	0.446
Acute EqP Pesticides	960	0.010	0.753
Acute EqP Semivolatiles	882	0.032	0.339
Acute EqP Metals (Dry wt)	238	-0.095	0.146

Scatterplots of the organics ESB TU sum against amphipod mortality showed no apparent relationship with amphipod mortality (Figure 1). There was no apparent difference in either the occurrence of toxicity (i.e., >20% mortality) or percent mortality in samples with a TU sum that was below the presumed protective threshold of 1 TU, relative to samples above the threshold.

Changes in the metals ESB_{avs} also did not show any apparent relationship to toxicity response (Figure 2). Most of the data had an ESB value of <0, indicating an expected lack of metal bioavailability, yet many of the samples were toxic. Few samples had an ESB value >0, which is expected to represent an increased potential for toxicity due to metals. Of those samples, most were nontoxic (i.e., less than 20% mortality).

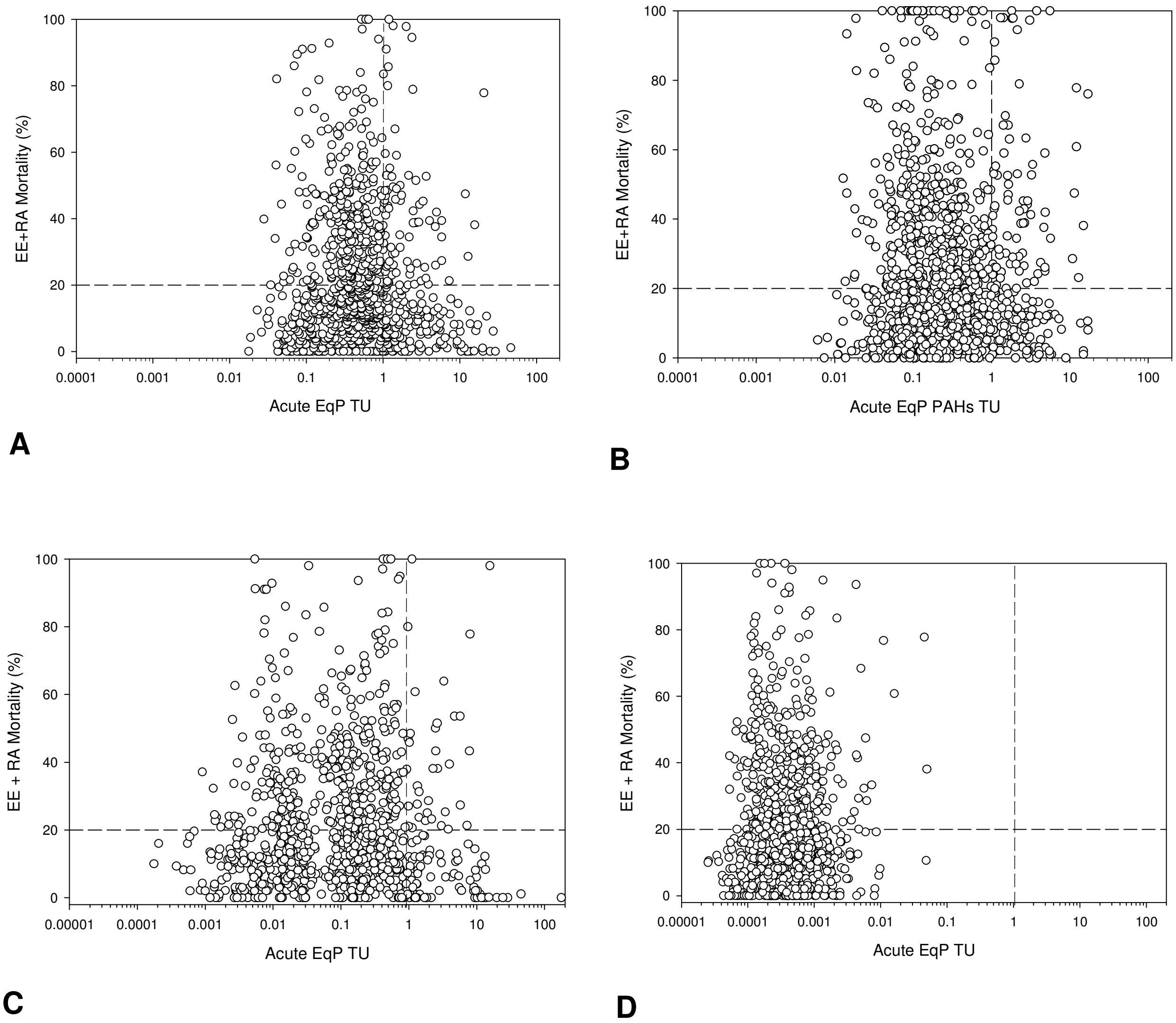

Figure 1. Plots of amphipod mortality (*Rhepoxynius abronius* or *Eohaustorius estuarius*) relative EqP toxic units. A. Sum of toxic units for all organics; B. Sum of PAH toxic units only; C. Sum of pesticide toxic units only; D. Sum of semivolatile toxic units only.

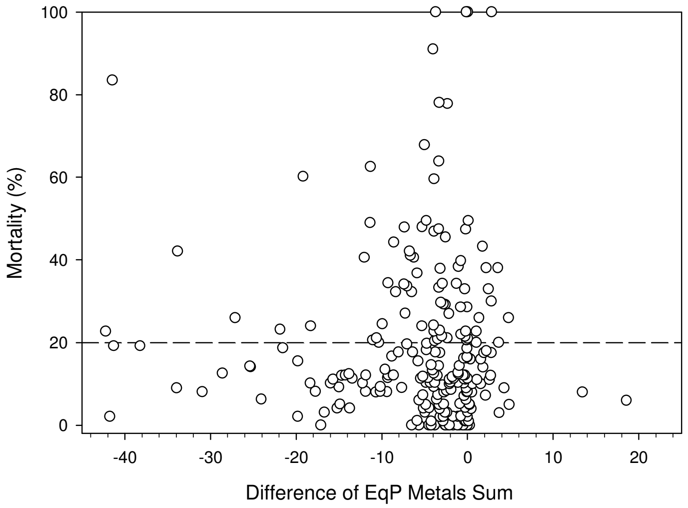

Figure 2. Figure 1. Plot of amphipod mortality (*Eohaustorius estuarius*) relative to the difference in sediment AVS and SEM concentration (umoles/g).

Summary

ESBs for organics and metals showed little or no relationship to sediment toxicity in the samples evaluated. Consequently, use of these ESBs as an index of chemical contamination for site assessment purposes would result in a high likelihood of errors and may not be protective of benthic communities. The reason for the poor correspondence of the ESBs to toxicity is not known at this time.

Literature Cited

Ankley G. T., Thomas N. A., Garrison A. W., Di Toro D. M., Allen H. E., Hansen D. J. Zarba, Ch. S., Mahony, John D., Berry W. J., Swartz R. C. and R. A. Hoke. 1994. Assessing potential bioavailability of metals in sediments: A proposed approach. Environ. Manag. 18: 331-337.

Di Toro D. M., Zarba C. S, Hansen D. J., Berry W. J., Swartz R. C., Cowan C. E., Pavlou S. P., Allen H. E., Thomas N. A., and P. R. Paquin.1991. Technical basis for establishing sediment quality criteria for non-ionic organic chemicals using equilibrium partitioning. Environ. Toxicol. Chem. 10: 1541-1583.

USEPA. 2003. Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: PAH Mixtures. EPA-600-R-02-013. Office of Research and Development. Washington, DC.

USEPA. 2004. Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: Metal Mixtures

(Cadmium, Copper, Lead, Nickel, Silver and Zinc). EPA-600-R-02-011. Office of Research and Development. Washington, DC

USEPA. 2008. Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: Compendium of Tier 2 Values for Nonionic Organics. EPA-600-R-02-016. Office of Research and Development. Washington, DC.