Thursday, August 25, 2011

Dear Dr. Fojut

At your request I have prepared the attached comments for the report

DRAFT
Methodology for Derivation of Pesticide Sediment Quality Criteria for the Protection of Aquatic Life
Phase I: Review of Existing Methodologies
Prepared for the Central Valley Regional Water Quality Control Board
Tessa L. Fojut, Ph.D., Martice Vasquez, Ph.D. and Ronald S. Tjeerdema, Ph.D.
Department of Environmental Toxicology
University of California, Davis

The report is very well done: clear, comprehensive, and useful. It was a pleasure reviewing it. The text that the comment refers to is highlighted in the pdf file that accompanies this report and reproduced below. The comments are in italic.

Thank you for the opportunity to review the report.

Sincerely yours

Dominic M. Di Toro

Edward C. Davis Professor of Civil and Environmental Engineering

Department of Civil and Environmental Engineering

University of Delaware

Department of Civil and Environmental Engineering
University of Delaware | Newark, DE 19716-3120
phone: 302-831-2442 | info@ce.udel.edu | fax: 302-831-3640

Comment #1 (p 2)

"The pesticides that are most likely to cause sediment toxicity are those that are nonpolar nonionic organic compounds because they have low aqueous solubilities and tend to sorb to solids and colloids in aqueous environments"

It's not because they have low solubilities but because they sorb to solids and settle. Polar chemicals that sorb and are toxic would also be a problem.

Comment #2 (p 7)

"The EqP approach assumes that the freely dissolved fraction of a chemical is in equilibrium between the sediment, biota and porewater (interstitial water between sediment particles)…"

EqP assumes that equilibrium between the sediment and the porewater but not the biota (see discussion of Fig 1 in Di Toro et al., 1991 p1543). This is a common miss understanding. In fact we went to some trouble to conduct the water only exposures and sediment exposures for the same length of time to match the exposures. For sediment ingesting organisms, however, it is likely that equilibrium with the biota would be necessary.

Comment #3 (p 7)

"The sediment concentration derived using EqP is predicted to cause the same biological effects in benthic organisms as water column organisms, which were used to derive the WQC (Wenning et al. 2005)."

A better way of describing this would be to say the the EqP method assumes that epibenthic and benthic organisms have the same species sensitivity distribution as water column organisms. This justifies the use of the FCV.

Comment #4 (p 9)

"1) degree of conservatism - they all tend toward under- or overprotection, "

I don't know what this means, or what is the evidence that this is true. Does he mean that they are inaccurate or have an uncertainty, which is of course true.

3) bioavailability - SQGs cannot be applied to all sediment conditions because bioavailability varies greatly depending on conditions

Of course, but the point of mechanistic criteria is that they attempt to correct for this problem.

It should be noted that the using pore water to predict sediment toxicity is a central tenant of EqP. Fig. 2 in Di Toro et al., 1991 p1544, is the data that backs up this claim.

Comment #5 (p 13)

“The methods that rely on equilibrium partitioning also do not have associated confidence limits, although they are based on water quality criteria derived using the species sensitivity distribution (SSD) methodology for which confidence limits can be generated (DiToro et al. 2002, OECD 1995, Rowlatt et al. 2002)

This is not the case. For example, from the Endrin SQC document (USEPA 2003b) Abstract

For endrin, this concentration is 5.4 µg endrin/gOC for freshwater sediments and 0.99 µg/ gOC for saltwater sediments. Confidence limits of 2.4 to 12 µg/gOC for freshwater sediments and 0.44 to 2.2 µg/ gOC for saltwater sediments were calculated using the uncertainty associated with the degree to which toxicity could be predicted by multiplying the K_{OC} and the water-only effects concentration.

Comment #6 (p 17)

“Newer experimental methodologies to determine the K_{ow}, such as the slow stir method (Tagatz and Ivey 1981) and the generator column method (Woodburn et al. 1984), should be used when finding literature-based K_{ow}s.”

I’m not familiar with the Tagatz ref. The reference I cite for slow stir is

de Bruijn, J., F. Busser, W. Seinen, and J. Hermens. "Determination of Octanol/Water Partition Coefficients for Hydrophobic Organic Chemicals with the "Slow-Stirring" Method." Environ. Toxicol. Chem 8 (1989): 499-512.

Comment #7 (p29)

“It has been noted that QSARs would not be useful in predicting toxicity for the compounds of greatest concern in the Sacramento and San Joaquin Rivers - pyrethroids and organophosphorus insecticides - since these classes of compounds have specific modes of action (TenBrook et al. 2009), and QSARs can only be used for compounds with a narcotic mode of action.”

There are QSARS that claim to be applicable to all modes of action, and some for a specific mode of action. But they are not restricted to only narcosis.

Comment #8 (p32)

“Frequency of exceedance has not been addressed by any of the existing methodologies, and determination of an appropriate frequency for compliance testing of bedded sediments could be problematic because sediment contaminants can accumulate over time, unlike water column contaminants. One way to address the problem of accumulation would be to test suspended particles in compliance monitoring, so that only new inputs would be monitored, rather than accumulated residues. “

It is a problem. However if EqP is used then the particles in the overlying water meet the criteria since the water column criteria and the sediment criteria are harmonized. Therefore the sediment would also always meet the criteria. However this argument ignores the possibility that particle properties change in the sediment.

Comment #9 (p32)

The EqP approach only considers exposure to freely dissolved residues in sediment porewater because toxicity is predicted using water-only exposures in which organisms were fed uncontaminated food."

EqP makes two claims: that pore water can be used to predict toxicity, and using partitioning theory to predict the sediment concentration that is in equilibrium with the pore water can be used to establish the SQC.

There is a final claim: that the route of exposure is not relevant. If the sediment particles are in equilibrium with the pore water, then the particles and the pore water are at the same chemical potential and exposure to either is equivalent. Thus EqP should apply to sediment ingesting organisms as well as epibenthic organisms.

This would not be the case if the ingesting organism changes the chemical potential of the particles: for example if the chemical is desorbed due to the acid in the gut of an animal. It should also be noted that the organic carbon fraction of particles ingested by worms does not materially change by passing through the gut. Only a small fraction of the OC is metabolized.

Sediment ingesting organisms have been tested for metals and EqP is predictive. I don't know of a specific test of organic chemicals with benthic animals but I would be surprised if EqP did not predict the results.

Comment #10 (p37)

This leads to the secondary assumption that the overall exposure is equivalent, no matter the exposure route, if the system is at equilibrium conditions between phases.

An important and mostly overlooked reference cited below sheds light on this question. It compares the BSAFs for benthic organisms with different feeding modes. They conclude (from the abstract)

"These analyses revealed similar BSAF values for various species both within and among habitat groups and indicated that the sum total exposures form all routes is similar across species. This similarity of chemical exposure across benthic species and species used to derive WQC FCVs supports the applicability of SQC for all benthic organisms as a group."

Tracey, G. A., and D. J. Hansen. "Use of Biota-Sediment Accumulation Factors to Assess Similarity of Nonionic Organic Chemical Exposure to Benthically-Coupled Organisms of Differing Trophic Mode." Archives of Environmental Contamination and Toxicology 30, no. 4 (1996): 467-75.

Comment #11 (p40)

.2) Assumes that porewater is the main uptake route, does not account for uptake via ingestion, through food chain, or directly from sediments (Persaud et al. 1993, Rowlatt et al. 2002)

See the discussion above. The food chain comment is correct since those food would not be in equilibrium with the porewater. However we would dispute the other claims.

5) Does not account for the presence of mixtures (Chapman 1989, Rowlatt et al. 2002).

The EqP for PAHs does account for mixtures. The others do not.

8) Assumes OC content of sediment is the most appropriate normalization procedure. For some HOCs, lipid content can be more important than OC content (Naf et al. 1996, Rowlatt et al. 2002). 9)

The most general EqP equation is Eq(2) of Di Toro et al 2002

$$SQC = K_p\, FCV$$

The use of K_{OC} is specifically restricted to chemicals for which it is appropriate.

Comment #12 p52

A more general approach to PAH mixtures and narcotic chemical mixtures was developed by DiToro and McGrath (2000).

It should be pointed out that this is a mixture criteria that has been officially issued by EPA, together with the single chemical ESBs

I would suggest that this type of criteria might be applicable to the pyrethroids as a class if they have the same mode of action. In fact any class with a similar mode of action might be modeled in this way.

One final remark
My name is spelled Di Toro, not DiToro.