

Learned Discourses: Timely Scientific Opinions

Conclusion: A Well-Known Case Example

The development of equilibrium-based sediment quality guidelines (EQP-based SQGs) has been well covered in this column. While the shortcomings of these values in predicting toxicity are increasingly being recognized, their weaknesses, like those of water quality criteria, can be divided into two categories: 1) those that make the values under-protective, and 2) those that make the values over-protective. This goes back to the issue of error types. So far, much more attention has been focused on minimizing Type I errors, which can work against environmental protection.

Aspects of EQP-based SQGs that make them underprotective include their dependence on water quality criteria (WQC) which do not protect all species, do not consider additivity or synergy, and importantly, do not consider bioaccumulation (SETAC 1998). In addition, the fundamental data on which the WQC are based were mostly drawn from the literature in the 1980's. While some of these concerns could be addressed using additivity models, uncertainty factors, or bioaccumulation factors, very little of that has been done—despite the fact that many of these concerns were initially raised by credible parties many years ago (USEPA 1995, SETAC 1998). This is a model design problem.

On the flip side, aspects that could make criteria overprotective include various binding scenarios (AVS, TOC, ligand interactions), metal solubility, and pH. Provisions to address each of these factors already have been built into EQP-based SQGs to prevent over-protectiveness despite the fact that each is dependent on variable environmental conditions.

Decision-makers must interpret information to address societal needs, and scientists should provide an information base that objectively recognizes risks and balances the dangers of Type I and II errors. Yet without equal participation by the ENGO community, this cannot happen. In ten years working as an ENGO scientist I can say unequivocally that I have never seen equal participation between ENGOs and industry in a single policy decision, much less scientific debate. In spite of our best efforts, sediment quality guideline development is no exception. Until this situation is rectified it is safe to assume public health and the environment are not getting a fair shake.

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Comments on Eganhouse and Pontolillo: Assessing the Reliability of Physico-Chemical Property Data (K_{ow} , S_w) for Hydrophobic Organic Compounds: DDT and DDE as a Case Study

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The Learned Discourse by Eganhouse and Pontolillo (2002) presents what we believe is a distorted picture of the current scientific understanding and methods for the measurement of *n*-octanol/water partition coefficients (K_{ow}) and aqueous solubilities (S_w) for hydrophobic nonionic organic chemicals. These authors assembled data from more than 700 publications, and without censoring for measurement quality and/or technique, reported that data values span 2-4 orders of magnitude for DDT and DDE. They concluded with the statement that "... estimation of critical environmental parameters on the basis of S_w and K_{ow} is inadvisable because it will likely lead to incorrect environmental risk assessments." We disagree with their conclusion and the associated implications.

First, assembling data without censoring is a case of the "Garbage In - Garbage Out" phenomenon. Eganhouse and Pontolillo (2002) treat all methods as equal, which they are not, a fact known for some time (Brooke et al. 1990). The slow stir and generator column methods have been established by the field as methods of choice for measuring K_{ow} and S_w (respectively) of highly hydrophobic nonionic organic chemicals (Brooke et al. 1990), because they avoid or minimize measurement errors and biases caused by micelles, emulsions, and incomplete phase separations. Furthermore, research has shown that using impurity-free water, *n*-octanol, and test chemical, obtaining equilibrium conditions in the measurements, and maintaining temperature control are absolutely essential for highly quality measurements. Much of the older data for highly hydrophobic chemicals are of poor quality because the measurement techniques used didn't control or eliminate measurement errors and biases. Looking at Pontolillo and Eganhouse's (2001) report, generator column S_w measurements for DDT and DDE had ranges of 3x (5 measurements) and 13x (2 measurements), respectively, and slow-stir K_{ow} measurements had ranges of 15x (8 measurements) and 2x (1 measurement plus an unpublished value of 6.38), respectively. These ranges were obtained without censoring for data quality; with censoring, as suggested by the authors, DDT's K_{ow} range shrinks from 15x down to 4x. How much uncertainty is "acceptable" is application dependent, but it is clear that the true uncertainty is much, much less than the 2 to 4 orders of magnitude suggested.

Second, Eganhouse and Pontolillo's (2002) comments do not acknowledge the fact that measurement difficulties increase with increasing K_{ow} and decreasing S_w of the compound. Measurements for lower K_{ow} s (e.g., $< 10^5$) and more soluble compounds are much easier, and precision is good across several measure-

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ment techniques. For example, combining data for slow stir, generator column, and shake flask techniques, the average log K_{OW} for benzene is 2.14 with a standard deviation of only 0.03 ($n=4$) (de Bruijn et al. 1989). In general, differences among measurement methods become significant only for highly hydrophobic chemicals. Failing to acknowledge this leaves the implication that higher uncertainty exists for all nonionic organic chemicals.

Third, Eganhouse and Pontolillo (2002) remark with apparent trepidation that many assessments are relying on predicted, rather than measured, values. While properly measured values are always desirable, evaluation of current estimation models such as SPARC (Karickhoff et al. 1991) and ClogP (Hansch and Leo 1979) for K_{OW} shows excellent correspondence of modeled predictions with data from high quality measurements for most chemicals (Figure 1). For SPARC, 63%, 85%, and 95% of the SPARC predictions are within factors of 2x, 3x, and 5x, respectively, of their slow stir values for the 79 chemicals reported by de Bruijn et al. (1989) and de Haag et al. (1998). This convergence is particularly significant because SPARC predictions are from first principles only; there is no empirical training of the algorithm, hence no intrinsic bias toward a particular measurement technique. ClogP predictions are based on a chemical training set of empirical values; 76%, 84%, and 87% of ClogP predictions were within factors of 2x, 3x, and 5x of the 79 measured values. Although the predictive abilities are good overall, greater divergence is noticeable for highly hydrophobic chemicals ($\log K_{OW} > 8$) for both algorithms, and for bridged aliphatic molecules (dieldrin, endrin, and aldrin) with the ClogP algorithm.

Fourth, Eganhouse and Pontolillo (2002) mention in their conclusions that there is a need to "... create a mechanism for archiving reliable data for widespread use in the scientific/regulatory community." This is not a new idea, and there are already groups that warehouse and evaluate data, e.g., Drs. S.H. Yalkowsky (University of Arizona) and A.J. Leo (Pomona College) for S_w and K_{OW} , respectively.

Fifth, the assessment concludes with the statement that "...estimation of critical environmental parameters on the basis of S_w and K_{OW} is inadvisable because it will likely lead to incorrect environmental risk assessments." This conclusion is neither helpful nor appropriate—the sky is not falling. The past three decades of environmental research have brought tremendous advancement not only in methods to measure properties of hydrophobic chemicals, but the frameworks to use these properties to model and predict environmental behavior. The success of these efforts alone provides direct evidence that the situation is not as grievous as proposed by Eganhouse and Pontolillo (2002). A more appropriate conclusion would be that the use of high quality input data is required for high quality environmental risk assessments.

While the state of the science is not as confused as Eganhouse and Pontolillo (2002) assert, it is true that some "users" of K_{OW}

data may not be aware of the issues involved in selecting high quality K_{OW} data, particularly for highly hydrophobic chemicals. In this regard, we agree that the development of standards for selecting high quality values, and a quality-assured database of consensus K_{OW} values, would be of great benefit. Towards this end, U.S. Environmental Protection Agency (USEPA) has proposed methodologies for selecting K_{OW} based upon experimental data and estimation techniques (Appendix F of EPA 1998). OECD has a methodology for slow-stir K_{OW} determination currently under review.

To conclude, it is valid to observe that measurements of S_w and K_{OW} for highly hydrophobic chemicals are sensitive to methodology and experimental conditions, and that literature values should not be used without regard to these issues. However, to suggest that the uncertainty in S_w and K_{OW} for DDT, DDE, or other chemicals is 2 to 4 orders of magnitude ignores a wealth of scientific understanding and is unnecessarily alarmist. The convergence of data from high quality measurements with predictions from theoretical models suggests that we have the ability to estimate S_w and K_{OW} with both accuracy and precision far beyond that purported by Eganhouse and Pontolillo (2002). While it is important to acknowledge uncertainties in any assessment, exaggerating this uncertainty through the blind use of unscreened data is not helpful, and risks distracting from more pressing issues in environmental risk assessment.

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The Marine Biogeochemistry of Arsenic: 25 Years of Refinements

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In the late 1970s significant insights on the cycling of arsenic in the ocean were made by Andi Andreae (1979), Jim Sanders (Sanders and Windom 1980), and Dave Johnson (Johnson and Pilson 1975) that largely stand today. It is first important to realize that arsenic in the dissolved state can exist in several oxidation states (+3, +5) and many different forms within a given oxidation state (e.g., methylated forms of AsV). Moreover, the tri- and pentavalent oxidation states of arsenic are fully hydrolyzed and therefore exist as oxyanions whose behaviors are different than typical metal cations. As a consequence, analytical methods capable of determining arsenic speciation in a high ionic strength medium at nanomolar (low ppb) concentrations were essential for understanding the marine cycling of arsenic; these were largely perfected by Andreae, and his selective hydride generation procedures are still used today with minor modifications. Armed with this technique, Andreae demonstrated that arsenate (AsV) was the predominant form in seawater and displayed nutrient-like behavior (depletion in euphotic surface waters and enrichment in deeper waters) much like phosphate, but methylated arsenic (mono- and dimethyl As) and arsenite (AsIII) were present near the surface and appeared to be associated with phytoplankton productivity. Work by Sanders and by Andreae clearly showed that these forms are produced by phytoplankton under low phosphate concentrations to relieve arsenate stress/toxicity; the methyl species and arsenite are not toxic to phytoplankton (however, arsenite is more toxic to higher trophic level organisms like zooplankton and fish). Interestingly, these detoxification reactions provided an explanation of how a thermodynamically unstable form like arsenite could be found in oxygenated seawater, and the kinetic studies of Johnson and Pilson (1975) showed that it could persist in surface waters by slow rates of oxidation. So by the end of the 1970s we knew that the marine cycle of arsenic was truly "biogeochemical" in that there was a direct interaction between the element and biology (each affected the other) and that the rates of interconversion reactions played a key role in controlling the observed chemical speciation of the element.

What have we learned in the intervening 25 years? The essential analytical methodologies have remained the same, although using some different detectors, with some systems capable of being taken out on research vessels. This portability has shown that the speciation of As is not stable with storage, including quick freezing (e.g., oxidation of arsenite), and even total dissolved As (III+V) has storage problems. With respect to the latter, in anoxic waters this may be due to the oxidation of colloidal arsenic sulfides (As_2S_3), while in oxic waters higher molecular weight organic arsenic compounds (e.g., found in coastal waters; Howard and Comber

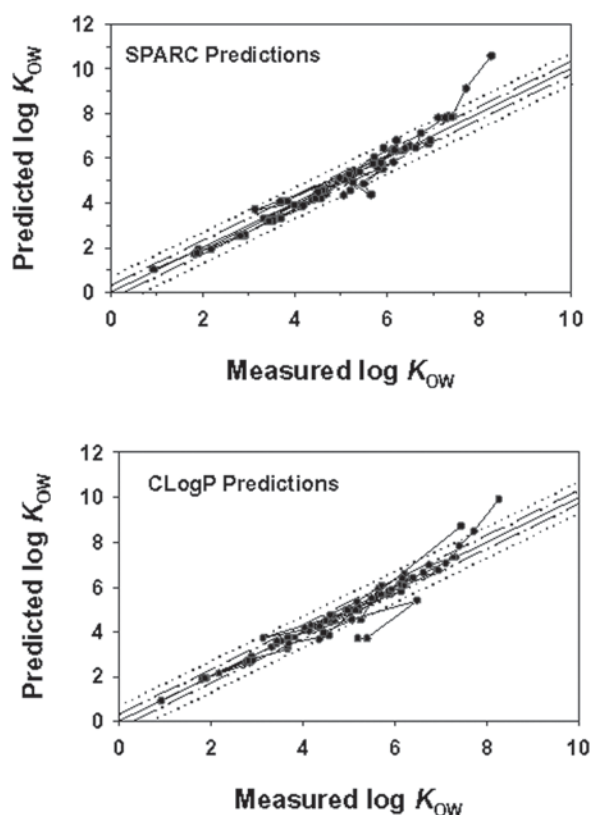


Figure 1. Slow-stir measured $\log K_{OW}$ s from de Bruijn et al. (1989) and de Haagd et al. (1998) plotted against $\log K_{OW}$ s predicted using the SPARC and ClogP algorithms. Solid line represents perfect agreement. Dashed and dotted lines represent deviations of 2x and 5x, respectively.