Lee, G. F. and Jones-Lee, A., "Equilibrium Partitioning-Based Values: Are They Reliable for Screening Contaminated Sediment?" Sediment Quality Criteria (SQO) - Letter to the editor of Environ. Sci. & Technol., 27:994 (1993).

Attached is the complete Letter to the Editor that was submitted to *Environmental Science & Technology*. The Editor chose to greatly reduce the space allowed for these comments. Further information on this topic is available from G. Fred Lee. www.gfredlee.com

Sediment quality criteria (SQC)

Dear Editors: In the February 1993 *ES&T* "Letters" department (pp. 205–6), William Adams asserted that while equilibrium partitioning (EqP)-based sediment quality criteria have many problems that diminish their reliability, they can be used for screening sediments for potential toxicity. As discussed by Lee and Jones-Lee in 1992 and 1993, such a claim is inappropriate; their unreliability is not equivalent to their being conservative. Use for "screening" is no justification for application of unreliable approaches especially in the regulatory arena. Unreliable water quality criteria and SQC trap public and private interests into massive waste of funds to "remediate" nonproblems signaled by administrative exceedances of the criteria, while effecting little or no improvement in the designated beneficial uses of the water body. EqP-based SQC for heavy metals and nonpolar organics tend to overestimate the actual aquatic life toxicity for the chemicals considered and fail to consider the aquatic life toxicity due to chemicals not considered, such as NH_3, H_2S and low DO, the most common causes of sediment toxicity. EqP-based SQC are not reliable for screening sediments for potential aquatic life toxicity.

Lee, G. F.; Jones-Lee, A. "Sediment Quality Criteria Development: Technical Difficulties with Current Approaches, and Suggested Alternatives," Report of G. Fred Lee & Associates, El Macero, CA, Jan. 1992.

Lee, G. F.; Jones-Lee, A. "Equilibrium Partitioning-Based Values: Are They Reliable for Screening Contaminated Sediment?" Report of G. Fred Lee & Associates, El Macero, CA, Feb. 1993.

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Equilibrium Partitioning-Based Values: Are They Reliable for Screening Contaminated Sediment?

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The February 1993 issue of *Environmental Science and Technology* contained an exchange of Letters-to-the-Editor by T. O'Connor and W. Adams regarding a feature article by W. Adams, R. Kimerle, and J. Barnett, Jr. on sediment quality issues (*ES&T* 1992, *26*(10), 1865-75). O'Connor pointed out some of the significant problems with the use of equilibrium partitioning (EqP) as a basis for evaluating and regulating sediment-associated contaminants. In response, Adams acknowledged that EqP approaches have many technical problems that affect their use as a basis for regulating contaminated sediments, but he also stated,

"My coauthors and I support the view that chemical criteria such as SQC [chemical concentration-based sediment quality criteria] *or sediment assessment values can be used as screening tools to determine whether or not sediment chemical contamination is likely to cause toxicity."*

It is our finding that Adams' argument for use of EqP is not consistent with cost-effective evaluation and management of chemical contaminants for regulatory purposes. Critical to the issue are the theoretical foundation and practical use aspects of values derived from application of equilibrium partitioning for screening sediments for potential water quality impacts of sediment-associated contaminants. Based on our experience, the following are key issues in the consideration of the use of equilibrium partitioning-based numeric values as a basis for screening contaminated sediments in water quality. These comments also have applicability to other, currently "fashionable," chemical concentration-based sediment screening approaches such as Apparent Effluent Threshold (AET) and "co-occurrence" approaches such as those of MacDonald and those based on the work of Long and Morgan.

Screening values based on EqP and "co-occurrence" approaches address only a limited number of chemicals present in aquatic sediments that could be adverse to the beneficial uses of a waterbody.

The most common causes of aquatic life toxicity in sediments (ammonia, hydrogen sulfide, and low dissolved oxygen) are not being considered by current EqP and "co-occurrence"-based values.

There is a wide variety of chemical processes that cause chemical contaminants in sediments to be non-toxic and unavailable to affect beneficial uses of waters.

EqP values derived from normalization of the concentrations of sediment-associated contaminants by such factors as TOC and acid volatile sulfides only consider a limited number of the chemical detoxification reactions and processes that normally occur in aquatic sediments to render potentially toxic chemicals non-toxic/unavailable.

EqP-based sediment screening values will be protective of a waterbody's beneficial uses for those specific chemicals considered, where the EqP numeric values developed for a sediment show the contaminants to be non-toxic/unavailable. However, the EqP analysis does not consider many of the reactions that can also render sediment-associated contaminants non-toxic/unavailable. Thus, when an EqP determination for a sediment shows that contaminants exceed allowable values (with the attendant presumption that the sediments contain contaminants that are toxic/available), there can readily be other chemical reactions or processes that occur in the sediments that lead to detoxification or reduction in availability beyond those predicted by EqP analysis. Therefore, for the parameters considered, exceedances of EqP values will be overly protective, i.e., they will predict problems that will not actually exist.

Therefore, EqP-based screening values can readily mischaracterize a sediment-associated contaminant as a problem for those contaminants it considers, and also fail to identify sediments that could cause real impacts on aquatic life since they do not consider key toxic chemicals that normally occur in many sediments.

In Adams' argument, there is a fundamental recognition of limitations of EqP values; out of that recognition, Adams recommended that the EqP values be used for "screening" purposes. That position inappropriately presumes that values used for "screening" can justifiably be less reliable than those used in subsequent evaluation. While values that are used to "screen" sediments or situations for inclusion in a group in need of further evaluation may be more inclusive, i.e., more conservative, than those which would serve as determiners of further action, they can be no less *reliable* technically. It is incorrect, indeed highly misleading, to assume that an *unreliable* value or approach is "conservative." To the contrary, an unreliable value or approach may well be under-protective, as can be the case with EqP values for reasons noted above.

Adams supported the suggested use of EqP values by noting that they would necessarily be used in conjunction with toxicity testing. Since proper toxicity testing can render meaningful and useful results for assessing the water quality significance of sediment-associated contaminants, and since there are significant technical deficiencies and limitations to the applicability of EqP values acknowledged by Adams, it would be duplicative, at best, to require the determination and application of the less-reliable EqP values. Since neither EqP nor "co-occurrence" values can be trusted, they would serve to confuse reliable toxicity test information. There are those who feel compelled to "use" any available value and consider it part of the "evidence" regarding a particular sediment, independent of the reliability of the value itself.

In the real world, improper screening of sediments for their potential water quality problems cannot be presumed to be rectified by further analysis. There are real ramifications of inappropriate screening of sediments whichever way the error is made, whether the screening flags a benign sediment as a potential problem, or fails to identify a sediment that could pose water quality problems; errors on either side can readily result in costly and time-consuming litigation. Failure to take "remediation" action on a sediment inappropriately screened "in" can lead to challenge from activists who view the retreat as relaxing concern or to claims of "backsliding." Failure to attribute real sediment-caused water quality problems to the right contaminant can lead to expensive remediation programs without effecting an improvement in the designated beneficial uses of a water. Further, it can incorrectly changes in NPDES discharge limitations for the waterbody. It is important that any sediment screening procedure be highly reliable for identifying those situations in which sediment-associated contaminants have real impacts on designated beneficial uses of the waterbody.

It has been our experience in seeing how numeric chemical concentration-based sediment screening and ranking procedures are being used today, that it is very difficult for a regulatory agency to reverse a decisions once a sediment has been designated as a potential problem area. Some environmental groups and members of the public will not accept the explanation that further study has shown that the sediment was incorrectly designated as a potentially toxic sediment owing to the use of unreliable screening procedures. This situation has already resulted in appeals/litigation by environmental groups to prohibit what they perceive to be a "relaxation" of designation of sediment toxic areas even though further studies have shown that the initial screening results were inaccurate.

For sediments that have been found, based on reliable and appropriately conducted toxicity testing, to cause toxicity to organisms of concern, EqP can possibly be used in the evaluation of the cause for the observed toxicity (i.e., as part of the toxicity identification evaluation (TIE)). While the EqP procedure is not reliable for defining what the toxicant *is*, it can be useful to eliminate certain chemicals considered in EqP review as the cause of the toxicity. If the EqP assessment predicts no toxicity due to the chemicals considered, then those chemicals can be screened out as a cause of toxicity.

Since "co-occurrence" values have no basis in the fundamental behavior of chemical contaminants, do not reliably consider contaminant availability, and do not portend to consider "cause and effect," they cannot be used in the assessment of the cause of toxicity observed in a sediment.

Many sediments that show toxicity to some test organisms come from waterbodies that have excellent fisheries in the overlying waters. While toxicity tests provide the most reliable basis upon which to make decisions about the potential impacts of sediment-associated contaminants, the results of toxicity tests cannot be directly applied to determining the need for sediment "remediation" or reduction in contaminant discharge. Simply finding toxicity in a sediment toxicity test, even one that is highly reliable, cannot be presumed to mean that the designated beneficial uses of the waterbody have been or will be impaired by sediment-associated contaminants. It is very important in the assessment of the impact of a sediment on beneficial uses of a water based on the most reliable approaches available, to consider the existing conditions. The greatest need in the area of sediment quality evaluation and management is to understand what the results of a sediment toxicity test measurement mean to the designated beneficial uses of a waterbody.

At this time there are no reliable laboratory methods for estimating the amount of bioaccumulation of contaminants of concern that will occur in aquatic organisms. EqP, "co-occurrence," and laboratory contaminant "uptake" tests are all unreliable for evaluating the potential degree of bioaccumulation of chemicals associated with sediments. The only reliable approach available is the measurement of the contaminants of concern in the flesh of edible organisms in the ambient waters. Even so, there is limited information available on the significance of the body burdens of many chemicals in the flesh of aquatic organisms upon which to interpret the water quality and public health significance of body burden data.

Considerable emphasis was placed in Adams' argument on the chemical character of pore water as an indicator of potential toxicity; indeed that is a argument for the EqP approach. It is important to note that the concentration of a chemical contaminant found in pore water is in large part dependent on the approach used to collect the pore water sample and separate out the dissolved components. It is well-discussed in the literature that few approaches can generate what can be considered to be a reliable assessment of the chemical character of the pore water as it is associated with the bedded sediment in a waterbody. Thus, most reportings of concentrations of chemicals in "pore water" are artifacts of the manner in which the sample was collected and analyzed. Therefore, irrespective of the role that chemical contaminants that actually exist in available forms in pore water in a bedded sediment in a waterway plays in causing toxicity to benthic or watercolumn organisms, it is very difficult to reliably determine the concentrations in such waters. It therefore follows that relationships developed between pore water character and predictions from the EqP approach are circumstantial and cannot be presumed to be translatable to any other situation or manner of determination. Adams appeared to acknowledge this later in his comments when he stated, *"Pore water is the operationally defined medium used to quantitate and identify toxicity."*

While the exercises and manipulations of the EqP development and evaluation are interesting, and researchers in their discussions can properly couch the findings within their scientific limitations, the key issue that has not been adequately considered by Adams and other advocates of the EqP approach is the implications of the use of the approach in water quality management decision-making. An overly conservative approach (which the EqP approach is for those contaminants that it considers, as acknowledged by Adams) can be recognized as such in scientific writing, but once it is consumed in the regulatory arena, that understanding is lost and its values become delimiters of acceptable conditions.

Adams noted that the EqP approach *"assumes the water chemical concentration is in equilibrium (at steady state) with the sediment chemical concentration."* This assumption is a fundamental deficiency in the EqP approach; the fact is that the chemical contaminants in pore water will not likely be in equilibrium with the solid phase chemicals in the sediment. This makes any relationships developed between solid phase concentrations of contaminants and dissolved phase concentrations (in the pore water - presuming that they could be reliably measured) operationally defined; while it may work for some situations, it will not have general applicability as a reliable approach.

It is important to note that not all dissolved-phase chemicals are toxic/available, especially those in pore water. Just as there are chemical reactions that detoxify many solid-phase contaminants, there is a wide variety of reactions, such as complexation and interactions with dissolved and colloidal organics, organic aggregates, and inorganics, that detoxify some dissolved-phase contaminants. The extent to which these reactions occur in a particular pore water is site-specific, depending on the character of the sediment. They cannot be predicted from information available today.

Adams stated, *"EqP methods do not assume that pore water is the primary route of exposure."* If the premise of the EqP approach is the estimation of the concentrations of selected contaminants in pore water in equilibrium with the sediment, and if the EqP approach is to be used to assess the potential toxicity impact of sediment-associated contaminants on aquatic organisms, it seems contradictory to then disclaim the necessary assumption that pore water is a primary route of exposure. If some other route is the primary route of exposure, that route of exposure should be the focus of assessment for water quality management purposes. Failure to focus on the primary route of exposure and to understand the factors that control it, can readily lead to inappropriate assessments of the significance of contaminants in sediment and the inappropriate "regulation" of sediment-associated contaminants and discharges.

Adams stated in his letter to the editor,

"Two major sources of evidence support the EqP approach. Chemicals measured in pore waters collected from the environment have been detected at levels that could be predicted from equilibrium theory, and laboratory experiments with real-world sediments (spiked and unspiked) have been used to predict, a priori, toxicity (and bioaccumulation)."

His statement should not be interpreted as a license to use the EqP approach without confirmation. The following should be considered.

With regard to the first source of "evidence," it is important to understand that relationships developed between pore water concentrations and equilibrium theory predictions for a specific system or limited set of conditions cannot be extrapolated to the environment at large. This was discussed to some extent above. While there are undoubtedly situations in which such predictions have been made, there are also situations in which simple EqP relationships have been found to be unreliable. Indeed, as noted above, the EqP approach does not consider all of the mechanisms for detoxification of chemicals associated with sediments or in the dissolved phase in pore water. There is a growing literature that reports that the simple EqP normalization (based on TOC and acid volatile sulfides) is unreliable for predicting concentrations of available forms of contaminants in pore water and impacts of sediment-associated contaminants on aquatic life.

With regard to the second source of "evidence," it is important to understand that the results of tests done on "spiked" sediment are highly operationally defined. The ability to "spike" a sediment with a chemical, run toxicity tests, and find a relationship between the concentration of the chemical in the sediment and the amount of toxicity does not address in any reliable way the potential impact of that contaminant in sediments in a waterbody. This is also the case for bioaccumulation of sediment-associated contaminants. The basic problem with sediment spiking approaches, which is well-known, is the failure of the spike to properly equilibrate with the native sediment-associated contaminants. Unless such equilibration is achieved (which for many chemicals will rarely occur in a laboratory testing system), the nature of the system being tested is unknown and the result therefore unreliable for predicting the behavior of chemicals that are or could become associated with the bedded ambient sediment.

The bottom line is that assessments made with EqP approaches always require confirmation with appropriate and reliable toxicity tests (or for bioaccumulation, the measurement of chemicals in edible flesh of ambient organisms). If it is necessary to confirm the EqP-based assessment with such evaluations, why should it be used in a regulatory program? It is more reliable and more cost-effective to do the toxicity testing (that would be required anyway to confirm EqP assessments) up-front. As discussed above, the problems in reliability of the EqP approach does not justify its relegation to "screening level" evaluation.

The work that has been done in developing the EqP approach has made a significant contribution as a research tool. This approach should not be used for any regulatory purpose, including the screening of sediments for potential water quality impacts of sediment-associated contaminants.

It has been our conclusion from many years of work on the topic and review of the current literature and findings of others that EqP and "co-occurrence" values are not reliable for screening sediments to identify those in need of more detailed evaluation, or for ranking of sediments with regard to their potential impacts on beneficial uses of water. Additional discussions of these issues are presented in Lee and Jones (1992a,b)(1993), and Jones-Lee and Lee (1993).

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