

## **Sediment Quality Criteria: Numeric Chemical– vs. Biological Effects–Based Approaches**

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### **ABSTRACT**

The US EPA and state regulatory agencies are developing sediment quality criteria and standards for the protection of water quality from sediment-associated contaminants. Many of the approaches being pursued rely in whole or substantive part on the bulk concentrations of selected chemical contaminants in the sediment as a basis for determining those sediments sufficiently contaminated to warrant remedial action. Principles of aqueous environmental chemistry and toxicology of chemical contaminants and practical experience demonstrate that such an approach is an unreliable basis for assessing potential water quality impacts of sediment-associated contaminants. Instead, assessments should be made on the basis of biological effects that are related to beneficial uses of the receiving water. This paper summarizes technical deficiencies with current approaches for sediment quality criteria and standards development and suggests an alternative, biological effects-based approach that utilizes existing well-established procedures for the evaluation and management of contaminated sediments.

Keywords: Sediments, Water quality, Biological effects, Chemical concentrations

### **INTRODUCTION**

Some aquatic sediments in the US, especially those near urban and industrial areas, have been found to be highly contaminated with a variety of potentially toxic or otherwise deleterious chemicals such as heavy metals, chlorinated hydrocarbon and other pesticides, PCB's, aquatic plant nutrients (N and P), polynuclear aromatic compounds, and petroleum hydrocarbons. The US EPA and water quality regulatory agencies in several states are developing sediment quality criteria and standards to be used to survey sediments, judge the water quality significance of sediment-associated contaminants, and establish sediment clean-up objectives for the protection of beneficial uses of the associated waters. Those criteria and standards would also be used as a basis for regulating the amounts of chemical contaminants discharged in municipal and industrial point-source discharges as well as in non-point-source runoff from urban, agricultural and rural areas, so they would not lead to "excessive" accumulations of contaminants in downstream aquatic sediments that could adversely affect water quality.

The key to developing technically valid, cost-effective management programs for sediment-associated contaminants is the proper implementation of technically reliable sediment quality criteria and standards. From the work that has been done toward the development of sediment quality criteria (US EPA, 1991; DiToro *et al.*, 1991), it is becoming increasingly evident that the criteria and standards being developed at the federal and state levels have serious technical

deficiencies such that their implementation could unnecessarily and greatly increase the costs of municipal and industrial wastewater treatment, management of contaminants in urban and rural land runoff and of contaminated dredged sediments. The criteria and standards are being based in whole or substantive part on the chemical composition of sediments and disregard of fundamental principles of aqueous environmental chemistry and aquatic toxicology of chemical contaminants. These deficiencies are recognized and discussed by other groups within the US EPA (Ankley *et al.*, 1991), as well as in previous writings of the authors (Lee and Jones, 1992a; Lee and Jones-Lee, 1993a). This paper is a condensed update of Lee and Jones (1992a) and summarizes technical deficiencies in chemical composition-based sediment quality criteria and standards, with particular reference to equilibrium partitioning (EqP), Long and Morgan, MacDonald apparent effects threshold (AET), "Triad" co-occurrence-based indices, and spiked bioassay approaches. Alternative, biological effects-based approaches that have proven reliable for assessing the water quality significance of sediment-associated contaminants are also discussed. The reader is referred to Lee and Jones (1992a), Lee and Jones-Lee (1993a,b), and Lee (1993) (available from the authors) for expanded discussion of many aspects of this topic.

## CRITERIA AND STANDARDS FOR SEDIMENT-ASSOCIATED CONTAMINANTS

In furtherance of the goals of the Clean Water Act, sediment quality criteria and standards have the purpose of contributing to the protection of beneficial uses of the Nation's waters from chemical pollutants. By convention and in keeping with the Clean Water Act, the general phrase "protection of water quality" means the protection of the beneficial uses designated by the state for those waters. Beneficial uses may include fish and aquatic life, domestic water supply, recreation, wildlife habitat, navigation, agricultural water supply, industrial water supply, waste-heat dissipation, wastewater dilution, etc. Thus, it is fundamental to technically valid, cost-effective water quality management that sediment quality criteria and standards be developed and implemented based on reliable assessment of the real impacts that the sediment-associated contaminants could have on water quality in a waterbody.

In order for a sediment-associated contaminant to have an adverse impact on aquatic life it must be available to the aquatic organisms within the sediments, at the sediment/water interface, or in the watercolumn above the sediments. It is generally found that dissolved, uncomplexed contaminants are available to aquatic life and, therefore, could be toxic to them, provided that organisms are in contact with sufficient amounts of the dissolved chemical species for a sufficient period of time. Particulate forms of many contaminants, on the other hand, are generally not available and are therefore non-toxic to aquatic life (see also Tessier and Campbell, 1987; Ankley *et al.*, 1991; Lee and Jones, 1992a).

A significant and recurrent problem associated with the development of programs for control of sediment-associated contaminants has been the failure to recognize that concentrations of contaminants in sediments do not carry the same meaning as the concentrations of contaminants in water. In water, the background matrix (H<sub>2</sub>O) is of known, constant composition. In sediments, however, the background matrix is a solid phase that is of highly variable composition. A sediment can be composed of widely variable proportions of constituents from both natural and anthropogenic sources, such as organic and inorganic erosional materials, clays, detrital material, carbonate precipitates, calcareous organism remains, plant material, etc. Each of

the different types of matrices in a sediment has its own ability to bind-detoxify chemical contaminants through chemical interactions with the chemical species in the solid phase. Furthermore, sediments are often highly heterogeneous; their nature, composition, and contaminant characteristics can vary greatly within small areas.

Mancini and Plummer (1993) and Coates and Delfino (1993) have recently discussed the potential significance of the highly heterogeneous character of aquatic sediments in implementing sediment regulatory programs. The typical approach that is used for sampling sediments, in which a single grab sample is taken at one location, often has limited reliability in characterizing the area from which the sample was taken. It is the authors' experience (Lee and Jones-Lee; 1992c) that in order to obtain a statistically valid assessment of the concentration and/or potential impacts of sediment-associated contaminants, a preliminary study must be done at each location to be evaluated in order to establish the statistical variability of the parameters of interest at that location. This information, in turn, must be used to determine the number of samples that must be taken at one location in order to evaluate the characteristics for the parameters of concern at that location within a desired statistical degree of confidence. Not only must the areal heterogeneity be evaluated, but also vertical heterogeneity must be considered. Often, there are significant differences in the concentrations and impacts of contaminants in sediments over small vertical distances. Rarely do sediment regulatory programs take proper consideration of this heterogeneity.

The availability of a sediment-associated contaminant to aquatic life is controlled by the bonding affinity of the contaminant for the various solid phases present in the sediments. In general, the reason that contaminants are present in sediments is that they are particulate or tend to bind to some component of the sediment that has a density greater than water, causing it to settle under quiescent conditions. The solid-phase components of sediments that tend to bind contaminants include sulfides and polysulfides; carbonates; clay minerals and clay-sized particles; hydrous oxides of iron, manganese, and aluminum; natural terrestrial and aquatic detrital organics, and organic carbon introduced from the activities of man; and coatings on inorganic particles, detrital minerals, etc. **A low concentration of a contaminant in a sediment with low binding capacity for the contaminant can be much more damaging to the beneficial uses of a waterbody than a high concentration of the same contaminant in a different sediment.** It is clear from the aqueous environmental chemistry of sediment-associated contaminants, and is borne out by practical experience, there is no relationship between concentrations of contaminants in sediment and the potential impact of those contaminants on water quality. Therefore, approaches for evaluation and regulation of sediment-associated contaminants that are based on bulk concentrations of contaminants in sediment are unreliable (see also Wright, 1992; Wright *et al.* 1992).

Since the primary points of concern with contaminated sediment are the effects that their associated contaminants have on aquatic life and on organisms' suitability for use as food, and because of the complex chemistry of sediment-associated contaminants, the most reliable way to assess whether contaminants in a sediment potentially adversely affect water quality is to use a number of sensitive aquatic organisms in toxicity tests of the sediments, and to determine the body burdens of chemicals in ambient edible organisms. That information forms the foundation

for technically valid, cost-effective evaluation of sediments and management of those that are excessively contaminated, as discussed further subsequently.

Regulators have claimed the need for simple, numeric concentration values that can be readily measured on sediment for the regulation of sediment-associated contaminants because of their ease of implementation. It is understandable for regulators to try to adopt what initially appear to be the most bureaucratically simple requirements and approaches. However, while ease of implementation is a legitimate factor to be considered in deciding among equally valid approaches, such a consideration provides no justification for the promotion and imposition of technically unreliable evaluation and regulatory approaches.

## CURRENT APPROACHES

Most current approaches to developing sediment quality criteria and standards have abandoned bulk sediment composition as the sole basis for criteria development. However, the approaches are in fact based on the concentrations of selected contaminants in sediments. While much is known about the general reactions and mechanisms that render chemical contaminants associated with sediments less-available or non-toxic to aquatic life, the details of the chemical and biological processes that occur in sediments to regulate the toxicity of a particular contaminant to aquatic life are not able to be measured or quantified reliably. The understanding and quantification capabilities are inadequate to allow the meaningful "normalization" of bulk constituent concentrations in sediment in the development of sediment quality criteria for the evaluation and regulation of sediment-associated contaminants. Ignoring the complexity of those systems can readily result in an inappropriate assessment of the true hazards that chemical contaminants in sediments represent to aquatic life-related beneficial uses of a waterbody.

### Equilibrium Partitioning as a Basis for Developing Sediment Quality Criteria

The US EPA (1991) has proposed the development of sediment quality criteria for non-polar organic chemicals such as chlorinated hydrocarbon pesticides and PAH's, based on estimates of their equilibrium partitioning between the solid phase organics and the liquid phase (interstitial water) of a sediment. The total concentration of the non-polar organic is "normalized" based on the total organic carbon (TOC) concentration of the sediment; the octanol/water partition coefficient for the chemical is assumed to reliably describe the partitioning of that chemical that will occur between the organic carbon in the sediment and the sediment's interstitial water. If the estimated interstitial water concentration of the non-polar organic chemical exceeds the US EPA's water quality criterion, then the chemical is judged to be present in the sediment in an excessive amount that can cause toxicity to aquatic life.

There is some technical basis for using the TOC content of sediments to estimate one component of the detoxification potential of sediments for some non-polar organic chemicals. However, review of the US EPA's approach for developing sediment quality criteria using equilibrium partitioning shows a variety of potentially significant technical problems with its TOC-normalization (Lee and Jones, 1992a; Mancini and Plummer, 1993; WEF, 1992). For example, it assumes that all partitioning of non-polar organic chemicals (for which the approach is proposed) between the sediment and interstitial water is properly described by the octanol/water partition

coefficient. It is well-known that the various types of organic matter that can be present in sediments can have significantly different binding capacities (partitioning) for organic contaminants; the affinity depends in large part on the source and nature of the carbon. Boyd and Sun (1990), for example, found that the sorption of several organics onto petroleum hydrocarbons was a factor of about 20 greater than their sorption onto natural TOC. Therefore, organics associated with sediments contaminated with petroleum hydrocarbons would tend to be much less toxic than those associated with sediments whose organic carbon is natural TOC.

Wang *et al.* (1972) found that other organics dissolved in the water that sorb on the surface of the sediment particles can significantly affect the uptake of pesticides by aquatic sediments. They reported that some dissolved organics enhanced sorption while others inhibited sorption of pesticides onto the lake sediments. It has also been known for many years that certain organics such as natural "humics" tend to bind to solid surfaces more strongly than other principally low molecular weight organics. Binding by natural dissolved organic carbon can preclude the sorption of lower molecular weight organics onto solids. It is also well-known that many pesticides that are sorbed onto soils and sediments are in the form of "bound" pesticide residues that do not readily participate in equilibrium reactions with water. Lee *et al.* (1982) reviewed the environmental significance of pesticide residues associated with soils and aquatic sediments and concluded that it is highly likely that those bound residues would be measured in analysis of those sediments, since they would be extracted with organic solvents, yet they would not participate in equilibrium reactions with the associated interstitial waters. It can therefore be very misleading to assume that uptake of contaminants on aquatic sediments is a simple equilibrium partitioning described by the octanol/water partition coefficient that can lead to both under- and over-regulation of contaminants in sediments.

Use of EqP-based sediment quality criteria for water quality protection does not address some realities of the systems to which they are applied. Equilibrium partitioning is supposed to be between the organic carbon present as particles in the sediment or as coatings on other particles, and the water associated with those particles. In the case of sediments, the water associated with those particles is the interstitial water. However, in many sediments, that water is devoid of oxygen, and in many cases contains high levels of sulfide and ammonia, both of which can be toxic to aquatic life. It is apparent that many of the organisms cannot be obtaining their non-polar organics, or for that matter other contaminants, from the interstitial water, because that is a hostile environment to the organisms (Lee and Jones, 1992a; O'Connor, 1993).

Another factor that has not been adequately addressed in the use of the EqP approach, is that several of the types of organisms used for aquatic sediment toxicity testing are tube-dwelling amphipods. The tubes tend to isolate them from the interstitial water, causing some to speculate that their exposure is at the sediment/water interface. The sediment/water interface has some special characteristics that can cause it to have significantly different properties than the bulk of the sediments in which the equilibrium partitioning is said to take place; of particular importance is hydrous iron oxide (Lee, 1970). Further, amphipod tubes are matrices of organics and inorganics; the tube walls could sorb appreciable amounts of organic contaminants which could alter the availability of sediment-associated contaminants to those organisms.

The TOC-normalization approach proposed by the US EPA is known to not work for at least some of the common non-polar organics of concern in aquatic sediments. Nebeker *et al.* (1989) reported, "*While the toxicity in the DDT-spiked sediment decreased with TOC content, the TOC content of the endrin-spiked sediment had little apparent effect on toxicity.*"

An area that is beginning to be recognized as of importance in sediment chemistry and its associated impacts on water quality is the role of colloidal particles in interstitial waters. Increasing evidence is showing that colloidal particles play important roles in the distribution of contaminants between the bulk solid phase (large particles) and the interstitial water (see Valsaraj *et al.*, 1993). The partitioning of solutes in interstitial water between the water and colloidal particles present in the water can lead to a highly unreliable assessment of the "dissolved" phase solutes, since colloidal-associated contaminants are typically measured as dissolved contaminants by the filtration techniques normally used. High-speed centrifugation should be used to determine whether constituents in interstitial waters are in fact dissolved or are associated with finely divided particulates that are measured as dissolved.

From the information available today, it is certainly premature, at best, for the US EPA to promulgate equilibrium partitioning-based sediment quality criteria for non-polar organic chemicals to predict the toxicity of those types of chemicals in sediments to aquatic life.

#### Acid Volatile Sulfide-Normalization as a Basis for Development of Sediment Quality Criteria for Heavy Metals

The US EPA has suggested that the sulfide precipitation reaction with heavy metals be used as a basis for estimating the capacity of sediments to detoxify heavy metals. The US EPA proposed that if the molar sum of the concentrations of non-iron heavy metals (e.g., Cu, Cd, Zn, Pb, Ni) in a sediment exceeds the molar sum of the sulfides in the sediment as measured by acidification and gas-stripping of H<sub>2</sub>S (acid-volatile sulfides or AVS), the heavy metals in the sediment in excess of the sulfides would be toxic to aquatic life. The assumption is that the heavy metals not rendered unavailable by sulfides would be available and toxic to aquatic life. This approach, however, does not take into account other important detoxification processes that occur in sediments, does not address artifacts of the analytical approaches used, and does not sufficiently take into account realities of organism exposure to sediment-associated heavy metals.

It has been known for many years that particulate forms of many contaminants such as heavy metals and organics are generally not toxic to aquatic life. Sulfides in aquatic sediments exist in a variety of reduced sulfur forms which precipitate with many of the heavy metals to form highly insoluble compounds. Some heavy metals, however, also precipitate with other constituents such as hydroxide and carbonate. Many of the heavy metals tend to be complexed by complexing functional groups such as hydroxyl and amine groups and organic acids that can exist on particulate matter in sediments. Such complexes would also be expected to detoxify the heavy metals in much the same way as strong, soluble complexes detoxify soluble heavy metals. Further, many heavy metals participate in a variety of sorption reactions with various solid phases in sediments reducing the availability of the heavy metals to aquatic organisms and to the overlying waters. A variety of heavy metals form insoluble species through ligand exchange reactions with particles in aquatic systems. In summary, as would be expected based on

chemistry and geochemistry, heavy metals in sediments tend to be highly unavailable to aquatic life and, therefore, non-toxic to aquatic life.

Some support for the sulfide-normalization of heavy metal concentrations in sediment to estimate potential toxicity of sediment-associated heavy metals is derived from the work of DiToro *et al.* (1990). Basically, that approach, when used as a basis for sediment quality criteria, over-simplifies the sediment system to consider the non-mineral (amorphous) sulfide content of aquatic sediments as the only significant detoxification mechanism for heavy metals in sediments. While for some sediments it is possible that the relative role of other detoxification mechanisms is small compared to the sulfide detoxification, there are sediments in which the other detoxification mechanisms mentioned above can play major roles in rendering heavy metals in sediments non-toxic (see also Ankley *et al.*, 1993). Unpublished data presented at recent US EPA workshops by US EPA-supported sponsors of that approach have shown that for some sediments, the sulfide-detoxification (normalization) approach for heavy metals in sediments overestimates heavy metal toxicity by a factor of about 10. Therefore, using sediment quality criteria for heavy metals based on an AVS normalization could result in significant errors in estimates of the toxicity of heavy metals in sediments; large amounts of public and/or private funds could be spent in remediation of heavy metal-contaminated sediments with little or no improvement in the beneficial uses of a waterbody, since the heavy metals remediated were in non-toxic forms and therefore had not been adversely affecting the beneficial uses of the waterbody.

While sulfide precipitation of heavy metals is an important detoxification mechanism for heavy metals in aquatic sediments, it is clear that the US EPA's proposed approach for developing sediment quality criteria for heavy metals based on AVS-normalization of sediment heavy metal concentrations for equilibrium partitioning of heavy metals between the solid phase and the sediment's pore waters can lead to highly inappropriate classification of heavy metals in sediments as toxic when, in fact, the heavy metals are having no adverse impact on the beneficial uses of a waterbody.

The primary utility of the AVS-normalization approach will be in the investigation of the cause of measured toxicity of a sediment. If the molar concentration of AVS exceeds that of non-iron heavy metals, the heavy metals would not likely be the cause of the toxicity. If, however, the molar concentration of non-iron heavy metals exceeds that of acid volatile sulfides, it must be determined whether the sulfides that could precipitate heavy metals in the sediments were measured properly and whether any of the variety of other heavy metal detoxification mechanisms that occur in aquatic sediments are important in the sediments of concern (see also Ankley *et al.*, 1993).

#### AET and Triad

Recognition of the technical inappropriateness of using bulk chemical composition for assessing the water quality significance of contaminants in sediments has led to a number of attempts to modify that approach to give the impression of accounting for "effects" of sediment-associated contaminants. The Apparent Effects Threshold (AET) and the Triad numeric index are two approaches that have received considerable attention in this regard. As discussed below, both of

those approaches have significant technical deficiencies that render them unreliable for use in assessing the potential water quality significance of sediment-associated contaminants (see also Lee and Jones, 1992a; NRC, 1989).

The AET is supposed to be the concentration of a contaminant in sediment above which there is some statistical probability that the contaminant would have an adverse impact. The entire foundation for developing an AET, however, is technically invalid (see discussion by Lee and Jones, 1992a; US ACE, 1989). The AET values are developed by listing concentrations of a particular chemical in each sediment in the group considered and an associated assessment of the "effect" of that sediment measured in any number of ways (e.g., benthic faunal analysis, toxicity tests), without consideration of causality. The sediments are ranked based on concentration and an AET value for that chemical is selected statistically. If a sediment contains a chemical above its AET value, the sediment is judged to be polluted, and to require special consideration such as "remediation" or alternate methods of dredged sediment disposal. One of the most significant deficiencies of the AET approach is that it relies on the "co-occurrence" of conditions as though it represented a cause-and-effect relationship. It makes the presumption that there is a causal relationship between the concentration of each contaminant considered in a sediment and the water quality impact of that sediment, and that the "effect" reported in the AET development was caused by each of the measured chemical contaminants in that sediment. Many of the bases upon which "effects" are determined, are unreliable. Further, as being developed, AET gives consideration to a limited number of chemical contaminants and does not consider some that are known to be of water quality concern. The co-occurrence data bases presented by Long and Morgan (1990) and MacDonald (1992) suffer the same fundamental deficiencies in reliability as discussed above for the AET approach (see comments of Lee and Jones-Lee, 1992b).

The fact is that each of the factors upon which the AET is based can vary significantly without reflecting in any way on the impacts that the contaminants present in a sediment have on the beneficial uses of the waterbody in which the sediments are located. It is well-known from aqueous environmental chemistry and toxicology and practical experience that there is no relationship between the bulk concentration of a contaminant or a group of contaminants in sediments and the impact that the contaminant(s) has on the beneficial uses of the waterbody in which the sediments are located. While appropriate toxicity testing of sediments can be a reliable basis upon which to evaluate the potential impact of sediment-associated contaminants, incorporation of chemical composition data with toxicity test results distorts, and can render unreliable, the useful information obtained from appropriate toxicity tests. Further, it is well-known that the numbers and types of organisms present in a sediment depend on a variety of often ill-defined physical factors, such as sediment grain-size, organic content, energy of the area, and meteorological events, not related to the chemical contaminant characteristics of the sediment.

In their review of technical aspects of approaches for developing sediment quality criteria, Giesy and Hoke (1990) reported "*...AET approach does not have much predictive power or potential to adequately protect local populations.*" They concluded, "*We do not feel that the AET approach is a particularly useful method for establishing sediment quality criteria. There are too many uncertainties. Criteria established by using this method would also need to be validated for each contaminant by the use of either the field bioassay or spiked bioassay approach.*" Technical



deficiencies with spiked bioassay approaches are discussed below. Giesy and Hoke (1990) recognized that spiked bioassays are not useful for sediment toxicity screening tests but suggested that they may be useful in identifying effects of suspected toxicants. From an overall point of view, the AET and other co-occurrence-based procedures, even when used for screening purposes to indicate the need for additional studies on the sediments, are not technically valid and can readily lead to inappropriate classification of the hazards of contaminants present in sediments.

The Triad approach for assessing sediment quality characteristics is similar to the AET approach, in that it is based on determining the chemical characteristics of the sediments, conducting sediment bioassays, and assessing benthic organism community structure (the "Triad"). Power (1991), Chapman *et al.* (1992), and Lee and Jones (1992a) reviewed the use of the Triad approach for assessing sediment quality. With the exception of the inclusion of bulk chemical composition, the Triad approach provides the opportunity for inclusion of a wider range of pertinent information in the evaluation process, and the possibility of making an appropriate assessment of potential impacts of sediment-associated contaminants on water quality. However, in practice, the users of the Triad approach typically reduce the technical information to an inappropriate numeric index, and incorporate concentrations of contaminants in sediments not causally related to impacts.

Power (1991) indicated that, in using the Triad approach, she and her colleagues have not found any situations in which there was indication of altered numbers and types of organisms but no toxicity in sediment toxicity tests. Since toxicity tests are generally far less expensive than benthic organism population census studies, it appears that for the purposes of sediment quality evaluation for protection of beneficial uses, as much useful information can be gained from appropriately conducted and interpreted toxicity tests as can be gained by detailed field studies on the numbers and types of organisms present within or upon the sediments. That is an especially attractive proposition, since such toxicity tests would have to be conducted in any reliable assessment of toxicological impacts of contaminants on aquatic life.

### Spiked Bioassays

Some regulatory agencies promote the use of "spiked" bioassays as a tool for evaluating the water quality significance of a sediment-associated contaminant. The concept is to add known amounts of a particular chemical ("spike") to the sediment to determine if proportionately greater toxicity response is obtained in laboratory toxicity tests. Lee and Jones (1991; 1992a) and Ankley *et al.* (1991) have discussed some of the problems with using spiked sediment bioassays as a tool for evaluating the water quality significance of a contaminant in sediment. In order to render a meaningful, interpretable spiked bioassay result, the chemical forms of the contaminant of focus in the "spiked" sediment must be the same and have the same distribution among forms as that chemical in the unspiked sediment. This cannot be assured, and in fact is highly unlikely to be achieved. Aquatic sediments are complex mixtures of forms of chemicals and chemical contaminants; a chemical of focus may be expected to exist in sediments in a variety of forms of independent availabilities to aquatic organisms. For many chemicals such as heavy metals and many organics, the various forms of a particular chemical in aquatic sediments are not in equilibrium with each other or with other constituents of the sediment. The rate of equilibration

of a chemical in a sediment can be very slow and is highly dependent on the matrix with which it is associated.

In general, a chemical "spike" added to a sediment cannot be expected to be present in the sediment in the same forms and same proportions as the chemical in the unspiked sediment; the spike may well not come to equilibrium with the chemical of focus or other constituents in the sediment prior to the bioassay. Thus it cannot be assumed without a major research effort that a chemical "spike" will behave in a manner in any way related to that of that chemical in the unspiked sample. Since the reliability of that assumption is key to the spiked sediment bioassay methodology, that approach cannot, in general, be used to reliably assess the water quality significance of a contaminant or group of contaminants in a sediment.

#### SUGGESTED APPROACH FOR EVALUATING WATER QUALITY SIGNIFICANCE OF SEDIMENT-ASSOCIATED CONTAMINANTS

The US EPA and states should abandon efforts to develop numeric, chemical composition-based criteria and standards for assessing sediment quality in favor of more direct, technically valid, effects-based assessments of the toxicity and bioaccumulation of sediment-associated contaminants. Since even the US EPA (1991) recognized that its sediment quality criteria cannot be used alone, but need to be augmented by biological (effects-based) test methods, and since effects-based test methods offer the opportunity to make proper evaluations of the significance of sediment-associated contaminants, there is little point in pursuing unreliable, chemical composition-based criteria. While some claim that co-occurrence-based approaches such as Long and Morgan and MacDonald indices and AET and numeric Triad approaches are "effects-based" and/or represent "weight of evidence," an understanding the foundation of those approaches shows that they are not effects-based or weight of evidence, but rather incorporate unreliable information into the decision-making process.

The situation today in regulating chemically contaminated sediments is very similar to that faced by the Corps of Engineers in the early 1970's in regulating contaminated sediments that were to be dredged as part of US waterway navigation depth maintenance. The predecessor organization to the US EPA (the FWQA) developed some highly arbitrary dredged sediment disposal criteria (Jensen criteria) that were based on bulk sediment chemical analysis. The implementation of those criteria caused massive expenditures of public funds for additional dredged sediment disposal costs because of exceedances of the criteria values. It was obvious then that the FWQA's approach was technically invalid. This stimulated the US Congress to appropriate more than \$30 million over a five-year period for the Corps of Engineers to conduct the Dredged Materials Research Program (DMRP). Ultimately, through additional funding from various Corps districts, on the order of \$50 million were spent in the mid-1970's to develop approaches for evaluating and managing contaminated dredged sediments. Based on the DMRP results, the US EPA and the Corps of Engineers developed a biological effects-based regulatory approach for determining the appropriate method of disposal for contaminated dredged sediments. The key to that approach was the use of dredged sediment bioassays (toxicity tests). It became clear through the DMRP studies at various locations in the US that there were no reliable methods for using the chemical concentrations of contaminants in dredged sediments as a basis for dredged sediment management. The current biological effects-based approaches for managing toxicity in

dredged sediments are published in the US EPA and US ACE (1991) "Green Book." The Green Book is an updated version of an earlier manual that was developed by these agencies for this purpose. Lee and Jones-Lee (1992d) reviewed the development of dredged sediment disposal criteria and recommended approaches that will protect designated beneficial use of waterbodies without significant expenditure of funds for unnecessary dredged sediment management.

The situation with respect to managing contaminated dredged sediments is no different from that of managing contaminated sediments for which another group within the US EPA is attempting to develop sediment quality criteria. While, since the 1970's, a number of new approaches have evolved which attempt to use chemical concentrations for regulation of sediments, such as those discussed herein, it is clear that a review of the reliability of these approaches shows that they would not be expected to be, and are not, reliable. Instead, biological effects-based approaches should be used.

The first step that should be taken in sediment quality assessment is to determine if there is a potentially significant source of contaminants for sediments in the region of concern, such as municipal and industrial point source discharges and non-point source runoff, agricultural and rural runoff, and atmospheric sources. If there is reason to believe that there may be contamination of the sediments, screening toxicity tests with reasonably sensitive organisms should be conducted. In addition, a determination should be made of whether the edible flesh of fish and shellfish of the area have chemical residues in excess of FDA action levels or other appropriate standards for concentrations of contaminants in lower-trophic-level organisms that could be adverse to higher trophic-level organisms through their use as food. If no toxicity and no excessive tissue residues are found, no further evaluations should be immediately required, but these characteristics should be monitored for changes. If toxicity is found in laboratory tests, the cause and water quality significance of that toxicity should be further evaluated.

The US EPA and US Army Corps of Engineers' guidance manual (US EPA and US ACE, 1991) for evaluating the significance of chemical contaminants in dredged sediments that are of concern because they tend to bioaccumulate in aquatic organism tissue, prescribes a laboratory-based bioaccumulation test to estimate the bioaccumulation that will occur in organisms in the waterbody where the dredged sediments will be deposited. This test involves the placement of test organisms in an aquarium that contains the sediments and the measurement of the concentrations of the contaminants that accumulate in the organisms' tissue at a prescribed time, relative to a sediment from a "reference" site. However, as discussed by Lee and Jones (1992d), such approaches are not reliable for predicting the amount of bioaccumulation that will occur in ambient organisms that are in waters in contact with the sediments. There is obviously a wide variety of factors that govern the transport and uptake of sediment-associated contaminants by organisms, such as fish and other aquatic life, in ambient water systems that cannot be properly simulated in the laboratory test conditions. At best, the laboratory tests for bioaccumulation can show that, under the test conditions, the organisms can acquire a certain chemical from the sediments. Such information, however, has no predictive capability for what will occur under real-world conditions.

The US EPA and US ACE (1991) also presented a Tier II: Theoretical Bioaccumulation Potential (TBP) of Nonpolar Organic Chemicals approach, which is purported to enable

estimates to be made of the ". . . *magnitude of bioaccumulation of nonpolar organic compounds that may be encountered in Tiers III and/or IV testing.*" This approach utilizes the concentration of nonpolar organic chemicals and total organic carbon content of the sediments and the percent lipid content of aquatic organisms. It suffers from many of the same problems as the US EPA's proposed EqP approach for developing sediment quality criteria. The TBP approach is not reliable for predicting the extent of bioaccumulation that will occur in aquatic organisms in contact with sediments containing certain concentrations of nonpolar organics. There is no reliable way to calculate the extent of bioaccumulation that will occur in ambient water organisms based on measured characteristics of sediments.

The toxicity, bioaccumulation, and organism assemblage information should be evaluated in a non-numeric "weight of evidence" framework in which best professional judgement involving aqueous environmental chemistry and toxicology is used to establish the need for, and extent of, sediment and discharge remediation. Chapman *et al.* (1992) discussed the use of a weight-of-evidence approach for evaluation and management of sediment-associated contaminants. This approach, if properly conducted, should prove useful in directing sediment remediation projects and in preventing future sediment quality problems.

The economic consequences of failing to develop reliable approaches for evaluating and managing contaminated sediments can be very large. Many aquatic sediments near urban and industrial areas contain elevated concentrations of a wide variety of potentially significant chemical contaminants. The studies of the authors in the 1970's, as well as others subsequently (Lee and Jones-Lee, 1992d), have shown that aquatic sediments from industrial and urban areas frequently have some aquatic life toxicity. While it is clear that most of the contaminants in the sediments are detoxified, there are contaminants in sediments that are toxic to aquatic life. It is very important that reliable sediment quality evaluation procedures be developed that enable the determination of those situations where there is justification to spend the very large amount of money that will be needed to dredge and treat the sediments.

It is important that the sediment evaluation procedures not result in unreliable estimates of the potential water quality significance of sediment-associated potential toxicants or measured toxicity. The regulatory system that is utilized today for water pollution control has evolved to one that is based, to a considerable extent, on a litigious approach, in which environmental groups, municipalities and others take an adversarial approach toward developing water/sediment pollution control programs, such as for establishing site-specific sediment cleanup objectives. The authors have frequently observed that those who wish to provide the ultimate in environmental protection, irrespective of cost, or to use a bureaucratically simple approach, will grasp for any "findings" that give the appearance of support for their position, whether or not the "findings" are technically reliable. This leads to the development of sediment cleanup objectives for particular waterbodies that are obviously technically invalid and unreliable sediment. It is also very important that obviously grossly overprotective sediment quality criteria/standards not be advanced for a particular situation, since the current regulatory approach cannot back-track to what is superficially a less protective approach that evolves from further study of the situation. In the adversarial system, there are few advocates who will and can use a true weight of evidence approach and consent to adoption of a less stringent standard for clean-up than one that they have previously proposed. Rather than following a true weight of

evidence approach, in which knowledgeable professionals review the information available for a particular pollution control matter and determine its sufficiency, the environmental groups, municipalities and industry threaten and/or pursue litigation in an effort to force their will on the public. It has been typically found by the authors, however, that the positions adopted in preparation for litigation do not properly collect and evaluate the technical information pertinent to the issues of concern. This results in the litigation's being based to a considerable extent on inadequate and/or unreliable information on the water quality significance of contaminants in sediments. The courts and regulatory boards, however, do not have or avail themselves of the independent technical expertise in a proper peer review arena that is available and that should be used in formulating public policy in water pollution control programs. The incorporation of a true non-numeric-index weight of evidence and best professional judgment approach by qualified experts into the decision-making process could eliminate a significant amount of unreliable information that is now being used to formulate public policy in sediment remediation programs.

## CONCLUSIONS

Some US sediments are contaminated with a variety of chemicals that could be adverse to the beneficial uses of a waterbody. Most of those contaminants are detoxified-immobilized, and therefore cause little or no water quality impairment. Ammonia, low dissolved oxygen and hydrogen sulfide appear to be common constituents of many sediments that could cause toxicity to some forms of aquatic life (see Jones-Lee and Lee, 1993), but are not included in most of the current sediment quality criteria evaluation approaches.

The sorption of contaminants on organic matter in sediments measured as TOC can prevent manifestation of toxicity of non-polar organics such as chlorinated hydrocarbon pesticides, PCB's, dioxins, and PAH's. Precipitation as sulfides and carbonates and the uptake by complexing groups on solid surfaces causes many heavy metals in sediments to be non-toxic. Equilibrium partitioning using TOC-normalization, and acid volatile sulfide-normalization is not technically valid for establishment of sediment quality criteria; its use could lead to unnecessary sediment "remediation."

In light of technical deficiencies of current sediment quality criteria approaches, some suggest that such criteria be relegated to "screening" sediments. As discussed by Lee and Jones-Lee (1993b), however, 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.

Rather than trying to develop numeric chemical composition-based sediment quality criteria, the US EPA and state regulatory agencies should focus their efforts on developing effects-based regulatory approaches using sediment toxicity tests and proper assessment of bioaccumulation potential of sediment-associated contaminants. Particular attention should be given to how to

translate the laboratory toxicity test results to impairment of the designated beneficial uses of waterbodies. The approach that some regulatory agencies have adopted of equating statistically significant laboratory-based toxicity with ecologically significant toxicity in receiving waters is highly inappropriate. It is well-known that many lakes have toxic sediments due to low dissolved oxygen, ammonia and hydrogen sulfide that have excellent fisheries. It is certainly inappropriate to claim that any toxicity found in sediments in the laboratory-based tests used must be controlled. There is an urgent need for large-scale research efforts to be conducted on the significance of natural toxicity in aquatic sediments to aquatic life-related beneficial uses of waterbodies. Such studies would ultimately enable the development of the needed information on how to translate laboratory toxicity test results to whole-waterbody use impairment. In addition, there is need to understand if there is any significant difference between the "natural" toxicity due to ammonia, hydrogen sulfide and low dissolved oxygen and the toxicity associated with organics or heavy metals to the impairment of the designated beneficial uses of waterbodies. Without this information, large amounts of public and private funds could be used to "remediate" contaminated sediments that have little or no impact on the designated beneficial uses of the waterbody.

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