

# Sediment Quality Criteria Development: Technical Difficulties with Current Approaches (Condensed Version)

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Published In: Proc. HMCRI R&D 92 Conference on the Control of Hazardous Materials, HMCRI, Greenbelt, MD, pp 204-211 (1992)

Expanded version:

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

## ABSTRACT

Some aquatic sediments, especially those near urban and industrial areas, are contaminated with a variety of potentially toxic or otherwise deleterious chemicals. The U.S. EPA and water quality regulatory agencies in several states are developing sediment quality criteria and standards to be used to survey sediments and judge whether the concentrations of contaminants in them are "excessive" and therefore in need of "remediation." The U.S. EPA has proposed using equilibrium partitioning of contaminants with total organic carbon (TOC) as a basis for regulating some nonpolar organic chemicals (such as chlorinated hydrocarbon pesticides and polynuclear aromatic hydrocarbons) and acid volatile sulfide-normalization of noniron heavy metal concentrations to determine whether heavy metals are present in excessive amounts. A review of the technical bases for these chemical composition-based approaches shows that neither reliably establishes the critical concentrations of contaminants for cost-effective protection of beneficial uses of waterbodies.

Aquatic sediments contain a variety of other constituents that detoxify contaminants but are not accounted for in the proposed approaches. In its sediment quality criteria development efforts, the U.S. EPA has not considered one of the most significant sediment-associated contaminants that represents a real threat of toxicity to aquatic organisms; ammonia. U.S. EPA representatives have acknowledged that deficiency, although as of the summer of 1991, the agency had not begun to adequately address it. Based on our work, ammonia is likely to be a common pollutant of sediments that can be derived from natural sources.

A review is presented of technical problems with current approaches for chemical composition-based sediment quality criteria and standards. Alternative, biological effects-based approaches incorporating toxicity tests and assessments of contaminant bioaccumulation in aquatic organism tissue are discussed. These effects-based approaches effectively evaluate and manage the disposal of dredged sediments.

## BACKGROUND

Some aquatic sediments, especially those near urban and industrial areas, are highly contaminated with a variety of potentially toxic or otherwise deleterious chemicals such as heavy metals, chlorinated hydrocarbons and other pesticides, PCBs, aquatic plant nutrients (N and P), polynuclear aromatic compounds and petroleum hydrocarbons. While such contamination has generally been known since the late 1960s and measures have been taken to identify potentially hazardous situations associated with dredging for waterway channel depth-maintenance, some environmental activist groups have recently stimulated federal and some state legislative bodies to develop additional

legislation to regulate contaminated sediments.

The U.S. EPA and water quality regulatory agencies in several states are developing sediment quality criteria and standards (called "objectives" in California). Those criteria are to be used to survey sediments and judge whether the concentrations of contaminants in them are "excessive" and thus in need of "remediation." They would also be used to regulate the amounts of chemical contaminants discharged in (1) municipal and industrial point-source wastewater effluents and in (2) nonpoint source run-off from urban, agricultural and rural areas to avoid "excessive" accumulations of contaminants in downstream aquatic sediments.

There is justifiably considerable concern in the regulated community, including all point and nonpoint source dischargers as well as the Corps of Engineers who must maintain the navigational depths of waterways by dredging, that the sediment quality criteria that are adopted and implemented be technically valid and remediate only those sediments that do, or could through dredging, adversely affect beneficial uses of waters. From the work that has been done to develop sediment quality criteria,<sup>1</sup> however, it is becoming increasingly evident that the criteria and standards being developed at the federal and state levels have serious technical deficiencies that could unnecessarily and greatly increase the costs of (1) municipal and industrial wastewater treatment and (2) management of contaminants in urban and rural land run-off and in dredged sediments. These deficiencies are recognized and discussed by other groups within the U.S. EPA.<sup>2</sup>

Since there are few in situ treatment methodologies for contaminated sediments, the typical remediation approach will likely involve (1) excavation of the sediments that have "excessive" concentrations of one or more contaminants and (2) treatment of the excavated sediments using one of the many types of procedures being used to treat contaminated soils from federal and state Superfund sites. Such remediation approaches can easily cost \$100 to \$1000 per cubic meter (ton) of sediment. It is sometimes said that there is going to be a need for an "Aquatic Superfund" ("Aquafund") program which may in the long-term be more expensive than the current terrestrial program. Considering the funds that will be required to remediate "excessive" contaminants in aquatic sediments, it is very important to use reliable methods to classify their degree of contamination; methods that do not result in unnecessary expenditures for treating nonproblems.

After spending several million dollars in research, the U.S. EPA and the Corps of Engineers in the 1970s determined that it was not possible to use chemical analytical methods to reliably assess whether contaminants present in sediments could have a significant adverse impact on the beneficial uses of a waterbody. The U.S. EPA and Corps of Engineers developed a biological effects-based approach for making such assessments; aquatic organism toxicity tests and aquatic organ-

ism bioaccumulation evaluations were the foundation of the assessments. Based on the results of those tests, site-specific evaluations were made regarding how and where polluted dredged sediments could be deposited. That approach has worked well since it was adopted in the mid-1970s and it has recently been reaffirmed as the basis for regulating the ocean disposal of polluted sediments. Since the primary point of concern with contaminated sediments is the effect of their associated contaminants on aquatic life, and because the chemistry of sediment-associated contaminants is complex, the most reliable way to assess whether contaminants in a sediment potentially adversely affect aquatic life is to use a number of sensitive aquatic organisms in toxicity tests of the sediments. That information forms the foundation for a technically valid, cost-effective evaluation of the sediments and management of those sediments that are excessively contaminated.

The U.S. EPA has announced that it plans to promulgate a number of chemical composition-based sediment quality criteria each year for the next several years, beginning in the fall of 1991. It has announced that those sediment quality criteria will be based on equilibrium partitioning (EP) and total organic carbon-normalization for nonpolar organic chemicals and on acid volatile sulfide (AVS)-normalization of sediment-associated heavy metals. Those approaches, based on the chemical composition of sediments, will be used to judge what constitutes an excessive concentration of selected contaminants in aquatic sediments and, therefore, which sediments require "remediation" and contaminant input controls. There is concern that the U.S. EPA's sediment quality criteria, as well as standards being developed by states, could cause unnecessary expenditures of public and private funds to "manage" aquatic sediments that do not need to be remediated. This could result because of the unreliability of those criteria for classification of the hazard that contaminants in a particular sediment represent to aquatic life and other beneficial uses of the waterbody in which they are located.

This paper discusses key technical aspects of the approaches being used for, and potential problems associated with, developing chemical composition-based sediment quality criteria such as those being promulgated by the U.S. EPA. Also presented is an overview of approaches that have reliably identified and regulated impacts of sediment-associated contaminants, namely biological effects-based approaches based on results of toxicity tests and tests of bioaccumulation of contaminants in aquatic organism tissue. This paper is a condensation of a more comprehensive discussion of this topic prepared by the authors. The longer report is available upon request.

## OBJECTIVES OF DEVELOPING SEDIMENT QUALITY CRITERIA

### Protection of Water Quality

In accord with the law (PL 92-500 and its amendments), water quality regulatory programs should be designed to protect the designated beneficial uses of a waterbody. All waters of the United States have had their designated uses delineated in public processes in which federal and state regulatory agencies and the public have determined the uses that are to be protected for each particular waterbody. Those uses typically include fish and aquatic life, domestic water supply, recreation, wildlife habitat, navigation, agricultural water supply, industrial water supply, waste-heat dissipation and wastewater dilution. The U.S. EPA and the states must develop water quality criteria and standards that will protect the designated beneficial uses. Typical standards are numeric concentration limits for the designated beneficial use(s) of the given waterbody that are not to be exceeded beyond the edge of a mixing zone for wastewater discharges to the waterbody. The states, with approval of the U.S. EPA, can designate the size of the mixing zone.

Typically, the general phrase "protection of water quality" means the protection of all designated beneficial uses which usually include fish and aquatic life, recreation and, for freshwater, the domestic water supply as well. With few exceptions, the water quality criteria that will protect those uses will also protect other uses.

## The Water Quality Criteria Model for Sediment Quality Criteria

The U.S. EPA<sup>1</sup> repeatedly referred to the numeric water quality criteria's serving as a model for the development of sediment quality criteria. DiToro et al.<sup>3</sup> stated in their discussion of the technical basis for developing sediment quality criteria, "They are intended to be predictive of biological effects. As a consequence they could be used in much the same way as the chronic water quality criteria—as the concentration of a chemical which is protective of benthic aquatic life." The issue is not simply developing an approach that is protective of aquatic life. The issue is the development of an approach to provide protection or enhancement of aquatic life-related beneficial uses without unwarranted expenditures for unnecessary "remediation."

That notwithstanding, it must be recognized that significant difficulties have arisen with the use of water quality criteria and state standards equivalent to them for attempting to control potential subtle and chronic impacts of chemical contaminants in water. The U.S. EPA water quality criteria were developed to be chronic exposure, safe concentrations of available forms of certain potentially harmful contaminants. However, when those values are used as numeric standards in a particular waterway, they are typically applied to the total concentrations of the contaminants, irrespective of the ability of the forms of the contaminants present to impair beneficial uses of the waterbody. That approach toward criteria and standards implementation does not recognize that (1) for many, chemicals exist in aquatic systems in a variety of forms only some of which are toxic-available or that (2) there are many situations in which organisms do not or cannot receive a chronic exposure to the contaminants. That approach also does not properly consider the wide range of physical, chemical and biological factors that affect the impact of a contaminant on aquatic life.

State water quality standards equivalent to chronic exposure, safe concentration criteria tend to be unnecessarily overly conservative; that is, they can result in the regulation of chemicals that are not adversely affecting water quality. Unjustifiably overly restrictive standards can lead to the construction of unnecessary treatment works and/or the development of unnecessarily expensive contaminant control programs in the name of protecting water quality (designated beneficial uses) of a waterbody without effecting benefits to water quality beyond those which could be attained using a more technically valid approach. This problem will be even more pronounced for sediment quality criteria and standards being developed today because of the wide variety of detoxification mechanisms well-known to be associated with sediments that convert potentially toxic forms of chemicals to non-toxic forms but are not being considered by the U.S. EPA and because of the implementation approach the U.S. EPA has indicated.<sup>4</sup>

### Implementation of Criteria and Standards

Inadequate attention has been given to the implementation of criteria and standards developed by federal and state agencies into technically valid, cost-effective regulations. The authors have repeatedly heard individuals responsible for developing criteria and standards state that they do not have to consider whether the criteria and standards can be implemented into contaminant control programs; they indicate that that is "someone else's responsibility."

That apparent dichotomy of responsibility has given rise to some of the problems encountered in the development of technically valid, cost-effective approaches for managing the potential chronic toxicity from heavy metals in point and nonpoint source discharges and runoff from urban and rural sources. For example, it has been well-known since the late 1960s that many heavy metals occur in aquatic systems in forms that are not toxic; the toxic and nontoxic forms cannot be separately quantified using chemical analytical techniques. However, the U.S. EPA has been unable to develop contaminant control programs for heavy metals in wastewater discharges that are based on those forms of heavy metals that are, in fact, toxic in the receiving waters. Until recently, that situation was not a significant problem since neither federal nor state regulatory agencies were attempting to enforce criteria or standards equivalent to chronic exposure, safe concentrations of available forms of heavy metals in ambient waters. Today, however, it is becoming a pivotal issue in many parts of the country in the

regulation of heavy metals in aquatic systems.

Since the U.S. EPA has been unable to develop technically valid water quality criteria for heavy metals that focus on available forms of contaminants using chemical analytical procedures, it is highly unlikely that federal and state agencies will be able to develop sediment quality criteria and standards based on chemical analyses that will properly assess those parts of the contaminants present in aquatic sediments that can impair beneficial uses of the waters in which the sediments are located. The development of that type of approach for sediments will be even more difficult to achieve than for the water column. The U.S. EPA<sup>4</sup> has indicated that the sediment quality criteria that are being developed supposedly to meet chronic safe water quality criteria in interstitial water, will be "not-to-exceed" values, a step that further disregards realities of contaminant transport and organism exposure discussed elsewhere herein.

It is essential that those developing sediment quality criteria designed to protect and, where appropriate, enhance the designated beneficial uses of a waterbody, properly and appropriately consider how those criteria and standards are going to be implemented into pollutant control programs that will protect beneficial uses without unnecessary expenditures. Sediment quality criteria and standards are being developed in the "abstract" by the U.S. EPA and the agencies of some states such as California; the ability to implement the criteria and standards is not being properly considered. This program can readily result in the same kinds of problems that resulted from the "Jensen" bulk sediment composition criteria used to regulate dredged sediment disposal in the early 1970s; such problems caused massive waste of public and private funds for control of contaminants that had no adverse impact on water quality.

#### Contaminants versus Pollutants

Because chemicals exist in aquatic systems in a variety of forms and only some of those forms are available to affect water quality, making the distinction between "contaminants" and "pollutants" is critical to appropriate regulation of chemicals for water quality protection. A "contaminant" is any material added to an environmental medium; in the context of this discussion, to a sediment. A "pollutant" is a contaminant that is present in sufficient concentrations of available forms and to which exposure is sufficient to result in an adverse impact on beneficial uses of the waterbody. This distinction reflects the fact that the mere presence of a particular chemical does not demonstrate that there is an adverse impact on water quality. Only if the concentrations of available forms of that chemical contaminant are present in sufficient concentrations in relation to the duration of exposure of sensitive organisms is there a potential for adverse impacts to occur. That distinction is also recognized in the federal water pollution control legislation; pollutants, not contaminants, are the focus of water quality control requirements.

Sediment quality criteria that are based on the chemical composition of sediments do not discriminate between control of pollutants and the unnecessary control of contaminants. A water quality control program that focuses on contaminants will likely be protective of beneficial uses of water. However, such a program does not make use of the technical information available regarding the behavior and impact of chemical contaminants. Such a program will cause unwarranted expenditures to control chemicals that are not adversely affecting water quality; the program will not achieve greater protection of beneficial uses than could be afforded with an appropriate pollutant control program.

### AQUATIC SEDIMENTS—COMPLEX CHEMICAL SYSTEMS

#### Chemical Aspects

If a sediment-associated contaminant is going 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 water column above the sediments. It is generally found that dissolved, uncomplexed contaminants are available to aquatic life and, therefore, could be toxic to them if the organisms are in contact with the dissolved chemical species for a sufficient period of time. Particulate forms of

many contaminants, on the other hand, generally are not available and therefore are not toxic to aquatic life. While that fact has been known for many years, recent work by the U.S. EPA laboratories associated with the development of sediment quality criteria has provided additional demonstration that particulate forms of many contaminants such as nonpolar organics and heavy metals are nontoxic.

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 ( $H_2O$ ) 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. Furthermore, sediments are often highly heterogeneous; their nature, composition and contaminant characteristics can vary greatly within small areas.

The importance of understanding that many forms of heavy metals and other contaminants in aquatic systems are unavailable to affect aquatic life is echoed throughout the technical literature. For example, Tessier and Campbell<sup>5</sup> concluded from their study of the partitioning of trace heavy metals in sediments, "... the total concentrations of a metal in sediments provides little indication of the potential interactions of the sediments with the abiotic [non-living] and biotic [living] components..." They noted the complexity of heavy metal/sediment associations, pointing out that heavy metals in sediments can be associated with clay surfaces, clay structural matrices, fuming acids, iron and manganese hydrous oxide surfaces, detrital as well as freshly precipitated carbonates, nodules, detrital organic matter of terrestrial and aquatic origin, and crystalline and amorphous sulfides. The complexity of the chemistry of heavy metals and other chemical contaminants in sediments makes their significance to aquatic life difficult to ascertain by chemical means. This complexity is recognized by groups within the U.S. EPA who are developing toxicity identification evaluation procedures for sediments.<sup>2</sup>

Particulate (insoluble) forms of heavy metals, such as those which result from precipitation reactions and sorption (attachment of dissolved species onto sediment particle surfaces), are essentially unavailable to be toxic to or accumulate within aquatic organisms. Further, while the ionic aquo-species of many heavy metals are generally considered available, not all other soluble forms of contaminants are available to be toxic to aquatic life. For example, soluble heavy metals can react with organics and inorganics to form soluble chemical complexes that are not toxic to aquatic life. Both the insoluble and the nontoxic soluble forms of heavy metals reduce the impact that the total concentration of any has on aquatic organisms.

The availability of a sediment-associated contaminant is controlled by the bonding affinity of the contaminant for the various solid phases present in the sediments. In general, contaminants are present in sediments because 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.

The affinity that a contaminant has for any of those particles depends on a variety of factors, many of which are poorly characterized and understood. Since the solid-phase matrix differs from one sediment to another, the potential water quality impact that a particular concentration of a contaminant in sediments may have on beneficial uses of a water is different. 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. The U.S. EPA's attempt to relate all of the detoxification ability of sediments for groups of chemicals to analytically-defined parameters is unjustifiably simplistic and inadequate.

### Trying to Make the System Simple

While much is known about the general reactions and mechanisms that render chemical contaminants associated with sediments less-available or nontoxic 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 cannot be reliably measured or quantified. 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.

As discussed above, the affinity that a contaminant has for solids depends on a variety of factors, many of which are poorly understood and characterized. It is well-known, however, that attempting to relate all of the detoxification ability of sediments for groups of chemicals to analytically-defined parameters is unjustifiably simplistic and inadequate (i.e., the U.S. EPA attempts based on the natural organic carbon content of the sediments for nonpolar organics and the acid volatile sulfide content for non-iron heavy metals.)

Since the primary impact that contaminants in sediments could have on aquatic life is toxicity, it is far more technically valid to assess toxicity directly with toxicity tests rather than trying to infer it from some overly simplistic relationships and some chemical characterization of the sediments. There are many detoxification mechanisms of aquatic sediments other than natural TOC and acid volatile sulfides. As discussed below, equilibrium partitioning-TOC and acid volatile sulfide-normalization of contaminant concentrations in aquatic sediments do not properly consider the wide variety of factors that control the toxicity of contaminants to aquatic life in aquatic sediments. Chemical analysis may not include all potentially toxic parameters and the toxicity of many chemicals is not known.

### EQUILIBRIUM PARTITIONING AS A BASIS FOR DEVELOPING SEDIMENT QUALITY CRITERIA

The U.S. EPA<sup>1</sup> has proposed the development of sediment quality criteria for nonpolar organic chemicals such as chlorinated hydrocarbon pesticides, PCBs and PAHs, based on estimates of their equilibrium partitioning between the solid phase organics and the liquid phase of a sediment. By this approach, the concentration of those chemicals beyond that which is predicted based on a partitioning with the organic carbon in sediments is assumed to be toxic to aquatic life. The octanol/water partition coefficient for a 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 nonpolar organic chemical exceeds the U.S. 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. Therefore, if a chemical such as DDT is found in a sediment at a concentration that, based on the organic carbon content and the octanol/water partition coefficient, would result in an estimated concentration of DDT in the interstitial water above the U.S. EPA criterion value for chronic toxicity of DDT to aquatic life, then the DDT in the sediment would require remediation. Further, if there was an identifiable source of DDT, the source(s) would have to reduce the load of DDT discharged to the waterbody because of the accumulation of DDT in the sediments above the sediment quality criterion value.

There is some technical basis for using the TOC content of sediments to estimate one component of the detoxification potential of sediments for some nonpolar organic chemicals. However, review of the U.S. EPA's approach for developing sediment quality criteria using equilibrium partitioning shows a variety of potentially significant tech-

nical problems with its TOC-normalization. For example, it assumes that all partitioning of nonpolar 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, however, 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 is largely dependant on the source and nature of the carbon. The U.S. EPA approach assumes that the particulate TOC present in sediments derived primarily from terrestrial plant detritus is representative of all the TOC present in all sediments. For sediments in rural areas, that may be an appropriate assumption; for sediments from industrial areas that assumption could cause one to significantly underestimate the binding capacity of the sediments for nonpolar organics and, therefore, overestimate the hazards that some nonpolar organics represent to aquatic life.

While that topic has not been investigated extensively, Boyd and Sun<sup>6</sup> found that the sorption of several organics onto petroleum hydrocarbons was a factor of approximately 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.

Work of Wang et al.<sup>7</sup> on the sorption of pesticides onto aquatic sediments showed that other organics dissolved in the water can significantly affect the uptake of pesticides by aquatic sediments. Wang et al.<sup>7</sup> found that some dissolved organics enhanced sorption while others inhibited sorption of pesticides onto the lake sediments. It has also been known for many years (from the work on the removal of specific contaminants from water on activated carbon as part of water treatment processes) that certain organics such as natural "humics" tend to bind to the 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 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.

A basic assumption of equilibrium partitioning is that contaminants in aquatic sediments exist in equilibrium with the water that is in contact with the sediments. However, it has been known for many years and discussed in the soils-pesticides literature that many pesticides that are sorbed onto soils and sediments are not in equilibrium with the waters with which they have contact. Both sediments and soils tend to form "bound" pesticide residues that do not participate in equilibrium reactions with water.

Lee et al.<sup>8</sup> reviewed the environmental significance of pesticide residues associated with soils and aquatic sediments. Based on that review, it is highly likely that those bound residues would be measured in an 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. Thus that assumption of equilibrium would lead to an overestimation of the hazard that the contaminants present in the sediments would represent to aquatic life in the vicinity of the sediments.

Use of equilibrium partitioning as part of 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. Aquatic sediments can be from approximately 30 to 80% water. However, in many sediments, that water is devoid of oxygen, and in many cases, it 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 nonpolar organics, or for that matter other contaminants, from the interstitial water because that is a hostile environment to the organisms.

Another factor that has not been adequately addressed in the use of the equilibrium partitioning approach is that several of the types

of test organisms used for aquatic sediment toxicity testing are tube-dwelling amphipods. The tubes of those amphipods tend to isolate them from the interstitial water. Further, those 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.

Because of the protection from exposure to sediment-associated contaminants that could be provided by tubes of tube-dwelling benthic organisms, some speculate that the source for uptake of the nonpolar organics from the water is the water at the sediment/water interface. However, as discussed by Lee,<sup>9</sup> the aquatic sediment/water interface has some special characteristics that 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 the presence of hydrous iron oxide at the sediment/water interface. It is well-known that iron hydroxide is a scavenger of organic and inorganic chemicals, removing them from solution. Lee<sup>10</sup> reviewed the role of hydrous metal oxides in the transport of heavy metals and other contaminants in aquatic systems. Sridharan and Lee<sup>11</sup> found that many organic chemicals are strongly sorbed on freshly precipitated ferric hydroxide. Jones and Lee<sup>12</sup> and Lee and Jones<sup>13</sup> discussed the potential roles of hydrous oxides of iron in affecting the availability of sediment-associated chemical contaminants to aquatic life. It would therefore be expected that, at the sediment/water interface, another solid phase (hydrous iron oxide) would be available for partitioning organics and thus could influence the availability of nonpolar organics to aquatic organisms present in that area.

Nonpolar organics that are not bound by the sediment TOC but that come in contact with the overlying water would be expected to be rapidly diluted with the overlying waters. That would tend to reduce potential toxicity associated with nonsorbed chemicals in equilibrium with the sediments.

It is known that the TOC-normalization approach proposed by the U.S. EPA does not work for at least some of the common nonpolar organics of concern in aquatic sediments. Nebeker et al.<sup>14</sup> 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." Based on the information available today, it is certainly premature, at best, for the U.S. EPA to promulgate equilibrium partitioning-based sediment quality criteria for nonpolar organic chemicals to predict the toxicity of those types of chemicals in sediments to aquatic life.

From the discussions presented by the U.S. EPA personnel at sediment quality criteria development workshops in Galilee, Rhode Island, and New Orleans, Louisiana, in the summer of 1991, it was clear to the authors that the development efforts have not included careful consideration of how the equilibrium partitioning approach could be implemented into a water quality management program to protect designated beneficial uses of a waterbody without unnecessary expenditures for contaminant control. A review of the applicable chemistry, geochemistry and toxicology of aquatic systems shows that a variety of factors and situations could cause concentrations predicted by the equilibrium partitioning approach to significantly overestimate the amount of nonpolar organics in equilibrium with the sediments that would be available to aquatic life and cause toxicity to them. The U.S. EPA's<sup>4</sup> recommended approach of establishing "not-to-exceed" concentration criteria to avoid exceeding a chronic exposure safe water quality criterion in the interstitial water reflects the inadequacy of consideration given to implementation of sediment quality criteria.

#### ACID VOLATILE SULFIDE-NORMALIZATION AS A BASIS FOR DEVELOPMENT OF SEDIMENT QUALITY CRITERIA

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. Since many heavy metals form precipitates in aquatic systems, precipitation is an important mechanism by which those heavy metals are detoxified. The organic content of many aquatic sediments is sufficient to cause the sediment oxygen demand to exceed the rate of dissolved oxygen transport into the sediment through diffusion and

mass transport resulting in sediments that become anoxic except at the surface. Once anoxic, anaerobic conditions are established that lead to bacterial reduction of sulfate to sulfide. Sulfides in aquatic sediments exist in a variety of reduced sulfur forms [S(-II), S(-I) and S(0)] some of which are polymeric. These sulfides precipitate with many of the heavy metals to form highly insoluble compounds. Morse et al.<sup>15</sup> reviewed the chemistry of sulfide species in aquatic sediments. There is also substantial soils chemistry literature devoted to heavy metal-sulfide interactions in aqueous soils such as those found in rice paddies and wetlands. W. Patrick and co-workers at the Center for Wetlands Research at Louisiana State University have published extensively on the chemistry of sulfides and heavy metal-sulfides in sediments and wetland soils.<sup>16</sup>

Some heavy metals 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 be expected to detoxify the heavy metals in much the same way that strong, soluble complexes detoxify soluble heavy metals. Further, many heavy metals participate in a variety of sorption reactions with various solid phases in sediments, thus 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. Some of those reactions, such as those that take place on MnO<sub>2</sub>, are highly pH-dependent; the sorption of the metals on the solids increases by an order of magnitude for each unit of pH increase in the neutral pH range. While it is possible that those pH-dependent reactions play important roles in influencing the toxicity of heavy metals in aquatic systems, their importance has not been demonstrated. As discussed by Lee and Jones,<sup>17</sup> the significance of dependence of sorption on pH in aquatic systems is unknown. In summary, it has been known for many years (as would be expected based on chemistry and geochemistry) that heavy metals in sediments tend to be highly unavailable to, and therefore nontoxic to, aquatic life.

The U.S. EPA has recently proposed to use the sulfide precipitation reaction with heavy metals as a basis for estimating the capacity of sediments to detoxify heavy metals. The U.S. EPA proposed that if the molar sum of the concentrations of noniron heavy metals (i.e., Cu, Cd, Zn, Pb, Ni, etc.) 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), then the heavy metals in the sediments 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.

The use of the noniron heavy metals as an assessment of the potentially toxic heavy metals stems from the fact that those heavy metals tend to form more insoluble amorphous sulfides than the iron sulfides. Further, it is well known that except under acid conditions iron does not tend to be toxic to aquatic life as a result of the precipitation reactions between ferric iron and hydroxide. In the presence of dissolved oxygen in mildly acidic and alkaline systems, ferrous iron, which would be the form present in reducing sediments containing sulfides, is rapidly oxidized to ferric iron which precipitates as ferric hydroxide.<sup>18,19</sup>

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.<sup>20</sup> Basically, that approach when used as a basis for sediment quality criteria, simplifies the sediment system to consider the nonmineral (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 with the sulfide detoxification, there are sediments in which the other detoxification mechanisms mentioned above can play major roles in rendering heavy metals in sediments nontoxic. Unpublished data presented at recent U.S. EPA workshops by U.S. EPA-supported sponsors of that approach have shown that for some sediments, the sulfide-detoxification (nor-



malization) 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 acid volatile sulfide 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 remediating heavy metal-contaminated sediments with little or no improvement in the beneficial uses of a waterbody since the heavy metals remediated were in nontoxic forms and therefore had not been adversely affecting the beneficial uses of the waterbody.

The U.S. EPA has developed a standardized acid volatile sulfide test procedure<sup>21</sup> that involves acidification of the sediment sample with hydrochloric acid followed by gas-stripping of the  $H_2S$ . Based on the senior author's experience working on acid volatile sulfide systems in sediments, he believes the U.S. EPA's standardized approach has a number of potentially significant problems. In the early 1960s, the senior author and his graduate students found that an acid volatile sulfide test developed by Tomiyama and Kanzaki<sup>22</sup> involving steam distillation instead of gas stripping produced a more reproducible assessment of the amorphous sulfides present in aquatic sediments. Lee and his graduate students modified the Tomiyama and Kanzaki procedure by using an AMINCO Kjeldahl steam distillation apparatus to steam-strip the  $H_2S$  from sediment samples after acidification.<sup>23,24</sup> That method was found to be rapid, highly reproducible and easily performed.

While sulfide precipitation of heavy metals is an important detoxification mechanism for heavy metals in aquatic sediments, it is clear that the U.S. EPA's proposed approach for developing sediment quality criteria for heavy metals based on acid volatile sulfide-normalization of sediment heavy metal concentrations and/or 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.

In the opinion of the authors, the primary utility of the acid volatile sulfide-normalization approach will be in toxicity identification evaluations (TIEs) to investigate the cause of measured toxicity of a sediment. If the molar concentration of acid volatile sulfides exceeds that of noniron heavy metals, it is clear that the heavy metals would not likely be the cause of the toxicity. If, however, the molar concentration of noniron 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/or whether any of the variety of other heavy metal detoxification mechanisms that occur in aquatic sediments are important in the sediments of concern.

#### SEDIMENT-ASSOCIATED AMMONIA

A significant deficiency in the approaches being proposed by the U.S. EPA for the development of sediment quality criteria is that they have not considered one of the most significant sediment-associated contaminants that in fact represents a real threat of toxicity to aquatic organisms; that contaminant is ammonia. U.S. EPA representatives have acknowledged that deficiency, although as of the summer of 1991, the agency had not begun to adequately address it even though the agency has been working for a number of years in the development of sediment quality criteria.

The neglect of ammonia has apparently resulted from the focus of the agency's work on sediment toxicity testing with amphipods that are typically insensitive to ammonia. As discussed below, there are many other types of organisms that are sensitive to ammonia.

Lee and Jones<sup>25</sup> reviewed the potential significance of ammonia in aquatic sediments as a cause of toxicity to aquatic life. Jones and Lee<sup>12</sup> and Lee et al.<sup>26</sup> had found that sediments from many waterways in the United States contain potentially significant amounts of ammonia that could be readily released upon elutriation of the sediments. Those and other studies demonstrated that the interstitial waters of many aquatic sediments contain sufficient concentrations of ammonia to be of concern as a potential toxicant in any evaluation of sediment quality criteria.

It has been well-established that the primary toxic form of ammonia is the un-ionized form ( $NH_3$ ). The distribution between the ammonium ion and un-ionized ammonia depends on pH, temperature and ionic strength. Acute toxicity of ammonia (96-hr LC50) is on the order of 0.1 mg/L  $NH_3$ ; the chronic safe concentration (criterion value) is on the order of 0.02 to 0.03 mg/L  $NH_3$  in freshwater and marine systems.

Jones and Lee<sup>27</sup> were the first to identify ammonia as a potential major cause of toxicity in U.S. waterway sediments. From the data of Lee et al.<sup>26</sup> it is evident that many U.S. waterway sediments contain sufficient amounts of free, un-ionized ammonia to be toxic to some forms of aquatic life. Recently, Ankley et al.<sup>28</sup> found that ammonia was the constituent responsible for sediment toxicity to aquatic life in the upper Fox River (Wisconsin) sediments (freshwater). It is now widely recognized that sediment toxicity studies must include evaluation of the potential for ammonia toxicity as one of the first tests in sediment toxicity screening.

In the 1970s, the authors conducted an extensive set of studies of aquatic sediments principally from estuarine and marine United States waterways in which the total ammonia and a variety of other contaminants were determined.<sup>12,26</sup> The mean total ammonia content of those sediments was 194 mg N/kg dry weight; the concentration range was 19 to 628 mg/kg with a standard deviation of 172. Following the U.S. EPA's equilibrium partitioning approach and its assumptions and based on the chronic toxicity of ammonia, a sediment quality criterion for ammonia would be 1.5 mg N/kg dry weight for sediments that are 40% solids (such as those evaluated by Lee et al.). It is therefore clear that at least for that set of sediments, which are thought to be representative of many of the sediments of coastal waters throughout the United States, the ammonia content of the interstitial waters greatly exceeds the U.S. EPA water quality criterion for un-ionized ammonia. Therefore, if equilibrium partitioning is a valid basis for regulating contaminants in sediments, there appear to be few sediments in U.S. coastal waters that would not be toxic to some forms of aquatic life because of the presence of ammonia in interstitial waters.

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

##### Abandon Chemical Composition-Based Approach

The U.S. EPA should abandon its efforts to develop numeric, chemical composition-based criteria for assessing sediment quality in favor of more direct, technically valid, effects-based assessments of the toxicity and bioaccumulation of sediment-associated contaminants. If the U.S. EPA wishes to develop numeric values for chemical composition of sediments, it should do so only with proper qualification and after it accomplishes the following:

- Develops a technically valid, cost-effective approach for assessing the availability of chemical contaminants in the water column, including those contaminants associated with particulates; and develops appropriate chemical composition-based water quality criteria that are applicable to particulate forms of contaminants in urban stormwater drainage, other nonpoint source run-off and point source discharges.
- Develops water quality criteria of the type outlined above for at least 10 chemical contaminants and properly field verifies each of them; exposes those criteria, the approach and basis for their development, the results of the field verification and the proposed implementation approach to a proper peer review and publication.
- Develops, evaluates and reviews water quality criteria as outlined in the second item above; proceeds to develop chemical composition-based sediment quality criteria for specific chemicals; properly field verifies each criterion; develops a management strategy for contaminated sediments that is compatible with the proposed sediment quality criteria; subjects the strategy to extensive review by the potentially regulated community, by federal, state and local regulatory agency personnel and by the technical community; exposes those criteria, the approach and basis for their

development, the results of the field verification and proposed implementation approach to a proper peer review and publication. If the U.S. EPA can accomplish the above, then it would be in a position to effectively promulgate sediment quality criteria that would protect beneficial uses of U.S. waters from those chemicals without unnecessary expenditures for remediation of chemically contaminated sediments.

However, it is not the recommendation of the authors that the U.S. EPA expend its resources developing chemical composition-based water quality criteria. Rather, it is recommended that the U.S. EPA focus its research efforts on the development of effects-based sediment quality criteria that make use of the foundation provided by the work of the U.S. EPA and Corps of Engineers on dredged sediment disposal criteria. The primary basis for those criteria should be sediment toxicity tests and proper assessment of the potential for bioaccumulation. Such tests directly measure whether the myriad contaminants in their many and varied forms in sediments are available and potentially harmful to aquatic life-related beneficial uses of water.

As stated by the U.S. EPA<sup>1</sup> with reference to some of the disadvantages of its methods for developing sediment quality criteria, "Most of these shortcomings can be overcome by using EqP-based sediment quality criteria in conjunction with biological test methods." Since even the U.S. EPA recognizes 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.

There can be little doubt that sediment toxicity tests will always have to be used as the ultimate determiner of whether the sediment water quality criteria that the U.S. EPA plans to adopt are reliable. It is the authors' view that instead of wasting public funds on developing and using unreliable sediment quality criteria that have to be evaluated each time with toxicity tests, toxicity tests should be used as the basis for evaluating the potential water quality significance of contaminants in sediments. The U.S. EPA should also focus its attention on developing approaches for assessing excessive bioaccumulation of persistent chemicals that could be adverse to human health.

A high priority for laboratory and especially for field research should be to develop guidance on how to determine, for a particular sediment, what constitutes an excessive amount of organism toxicity that should result in the removal of existing sediments. It is clear from the work that has been done that the finding of some amount of toxicity in laboratory sediment toxicity tests does not necessarily reflect adverse effects of the sediment on the beneficial uses of a waterbody. While much is understood about problems in translating laboratory results to field situations, research is needed to ameliorate those problems. Work is also needed to understand the water quality significance of results of toxicity tests with benthic organisms, especially tube-dwelling amphipods, and how they compare with results of standard, commonly used tests on larvae of fish and other aquatic organisms.

### Develop Effects-Based Criteria

Presented below is an overall approach that the authors feel should be used to evaluate the water quality significance of contaminants in aquatic sediments.

1. The first step should be 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 nonpoint source run-off, agricultural and rural run-off and atmospheric sources.
- 2A. If there is reason to believe that the sediments may be contaminated, conduct screening toxicity tests with reasonably sensitive organisms. Determine if the fish and shellfish of the area have chemical residues in edible tissue above FDA action levels.
  - If no toxicity and no excessive tissue residues are found, do no further evaluation and monitor for changes.
  - If toxicity is found, evaluate the cause and water

quality significance. Conduct tests in Part 2B.

- 2B. If the potential for contamination exists and substantial funds are available, determine: pH, temperature, salinity-conductivity; ammonia, organic N; D.O. just above the sediment/water interface; acid volatile sulfides; total Fe; carbonate; total organic carbon (do not use loss on ignition); oil and grease; concentrations of heavy metals (Cd, Zn, Cu, Pb, Ni, Cr, As, Se and Hg); particle size (not deflocculated); chlorinated hydrocarbon pesticides and PCBs; PAHs; dioxins if there is a potential source; general numbers and types of sediment organisms; sediment bioassay-toxicity test using reasonably sensitive organism(s); and whether organism tissue residues are above FDA action limits for edible area organisms. Also make those measurements if there is interest in understanding the cause of toxicity-availability.

This approach should help direct sediment remediation projects and prevent future sediment quality problems.

### CONCLUSIONS

Some 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 appears to be a common constituent of many sediments that could cause toxicity to some forms of aquatic life.

The sorption of contaminants on organic matter in sediments measured as TOC can prevent manifestation of toxicity of nonpolar organics such as chlorinated hydrocarbon pesticides, PCBs, dioxins and PAHs. Precipitation as sulfides and carbonates and the uptake by hydroxyl and other groups on solid surfaces causes many heavy metals in sediments to be nontoxic. Equilibrium partitioning using TOC-normalization and acid volatile sulfide-normalization are not technically valid, cost-effective approaches for establishing sediment quality criteria and could lead to unnecessary sediment "remediation."

Rather than trying to develop numeric chemical composition-based sediment quality criteria, the U.S. 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 determining the amount of toxicity that can occur under laboratory toxicity test conditions before there would be an indication that the sediment should be remediated in order to remedy impairment of the beneficial uses of a waterbody. The adoption of this approach will lead to sediment quality assessment programs that will be technically valid, cost-effective and protective of beneficial uses of waters without significant unnecessary expenditures for sediment remediation.

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#### NOTE

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