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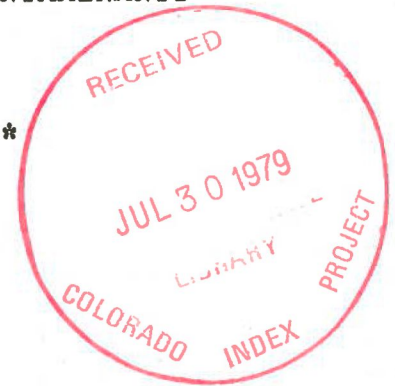


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SIGNIFICANCE OF SEDIMENT ASSOCIATED CONTAMINANTS  
IN WATER QUALITY EVALUATION\*

G. Fred Lee\*\*, Guy R. Lanza\*\*  
and George M. Mariani\*\*

Environmental Engineering  
Colorado State University  
Fort Collins, CO 80523



INTRODUCTION

The US EPA has recently released prepublication copies of Quality Criteria for Water (1). According to the US EPA this represents an update of the information that was presented in the National Academies Water Quality Criteria released in 1972 (2). Further, the Water Quality Objectives Subcommittee of the International Joint Commission for the Water Quality Treaty on the Great Lakes has released proposed water quality criteria for the Great Lakes (3) in which are listed the critical concentrations of various contaminants for Great Lakes waters. In each case, the critical concentrations of contaminants are generally presented for the total contaminant concentration present in the water. No attempt is made in these criteria to distinguish between the total concentrations present and the available forms. On the other hand, some individuals measure only the soluble forms of contaminants in evaluating the potential effects of chemicals on water quality.

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\*Occasional Paper No. 11, Environmental Engineering, Colorado State University, Fort Collins, CO 80523.

\*\*G. Fred Lee, also with EnviroQual Consultants & Laboratories, Inc., Fort Collins, CO 80525.

G. R. Lanza, University of Texas at Dallas, Richardson, TX.

G. M. Mariani, EG&G, Wareham, Mass.

Additional impetus for work on the significance of chemical contaminants associated with particulate matter will be derived from the recent passage of the Toxic Substances Act. Meaningful implementation of this act will require critical evaluation of the potential for any chemical to become associated with natural water particulate matter. As part of evaluating the potential environmental chemistry of new compounds, studies will have to be done to ascertain whether the chemical will likely become associated with natural water particulate matter and if so, what is the potential for uptake and release from these materials when the solids are suspended in the water column and when deposited on the bottom of various types of water bodies.

It is fair to state that any agency that bases its water quality standards on only the soluble form may be underestimating the pollution tendencies of the particulate input to its waters. Similarly, any agency that bases its standards or, for that matter, criteria on totals is likely to be overly restrictive and cause the expenditure of large amounts of funds for water pollution control where few improved benefits will be derived from removing a substantial part of the particulate forms of the contaminants present in or added to a natural water. Pollution control agencies throughout the world frequently face the question of what significance should be attached to particulate contaminants present in natural water. It is the purpose of this paper to review the information available in this topic area.

#### CHARACTERISTICS OF SOLIDS IN NATURAL WATERS

Contaminants may be associated with solids in a wide variety of ways. For example, some contaminants may be present in crystalline matrix of detrital mineral solids present in natural waters. For silicate minerals, the only



way in which the contaminants may be released to solution is through dissolution of the silicate matrix, which can be achieved by weathering. In the laboratory this is normally done by treatment with HF. Another group of solids in which the contaminant is intimately bound within the structure of the solid is organism remains, such as organic detritus. In general, the release of contaminants from these types of solids is dependent on mineralization processes in which the basic structure of the solid is altered, freeing the contaminant.

In addition to being present within the solid matrix, contaminants may also be present on the surface in coatings. As discussed by Lee (4), iron hydrous oxide coatings on natural water particulate matter often are implicated in playing dominant roles in the distribution of contaminants between the liquid and solid phase in natural water systems. This situation arises from the high sorption capacity of the hydrous oxides for many inorganic and organic contaminants.

A type of solid which is of limited concern in most natural waters as far as affecting water quality, is that of direct precipitation of the contaminant with some other chemical species. At the concentrations that normally occur in natural waters, however, most contaminants exist at concentrations well below those that would be allowed based on solubility equilibria. The exceptions to this are the iron and manganese hydrous oxides, various silicate minerals, and certain alkaline earth carbonates. In anoxic waters containing sulfide, there is evidence for heavy metal sulfide precipitate formation. It appears that except for these chemical forms and a few others, rarely are the majority of contaminants present in natural waters limited by their solubility considerations. Instead, sorption reactions play dominant roles in which there is adsorption and absorption by organisms and adsorption by nonliving particulate matter present in natural water systems.

In general, it can be said that in dilute solutions a substantial number of the contaminants which could potentially affect water quality at microgram or submicrogram per liter concentrations, tend to be associated with solid phases in natural water systems because of the high sorption capacity of many of the types of particles present in natural waters and a strong sorption tendency of many solutes at microgram per liter concentrations. Those who attempt to work with contaminants at these levels find that frequently under laboratory conditions, the contaminant concentration in solution decreases rapidly in laboratory solutions without any particulate phase present due to sorption on the walls of the containers.

The physical characteristics of the solids of concern range from particles typically on the order of a few microns in diameter to the lower limit of the colloidal size range, which is on the order of a millimicron in diameter. The typically used operationally defined "soluble" in the water analysis field is inappropriate in many situations to separate the contaminants associated with solids versus those in true solution. For many natural waters, 0.5 micron pore size filters will produce a clear filtrate, indicating that the amount of particulate matter passing through the filter which is readily discernible by the unaided eye, is small. However, for some waters there are large numbers of particles present with pore sizes on the order of a few tenths of a micron, which upon filtration produce a milky filtrate. An example of this type of sediment was found in the studies discussed below on the James River below Richmond, Virginia. Even with a clear filtrate, there still can be substantial amounts of particulate matter present which could influence the behavior of contaminants in natural water systems.

One of the factors that must be considered in evaluating the potential for sediment associated contaminants to influence water quality, is a change in the chemical characteristics of the water which, in turn, causes a change in the particle size or the degree of association of the contaminants with the particles. The degree of aggregation-flocculation or deflocculation of particles is frequently a function of salinity of the water. Often, it is found that finely divided and colloidal particles present in freshwater river systems tend to flocculate and settle out upon reaching the saltwater part of the estuary. There are also situations where the mixing of rivers, one with low pH, results in a neutralization of the acid waters and a precipitation of iron and aluminum oxides which in turn can scavenge large amounts of trace metal and other contaminants present in both rivers. The same type of phenomenon can be encountered in low alkalinity acid rivers entering the ocean, where the high buffer capacity of seawater may cause a several pH unit increase with the associated precipitation and flocculation of both inorganic and organic particles present in the river (4).

Organic materials present in natural waters can play an important role in influencing the degree of association of contaminants with particulate matter. A particular concern in this area is that of complexing agents interacting with suspended or deposited solids and removing heavy metals from the solid materials by solubilization reactions arising from complexation. A reverse type of reaction can also occur in which a complexing functional group can be part of a solid material which would be exposed and able to interact with metals in solution and thereby bind them and incorporate them into the solid phase. Very



little is known at this time about complexation reactions which tend to remove soluble metals from natural waters and incorporate them into the particulate form.

#### MODELS OF SORPTION REACTIONS

Increasing emphasis is being placed today on developing mathematical models that attempt to describe the distribution of contaminants in natural water systems. In general, these models are based on solution phase equilibria and consider oxidation reduction, acid base, precipitation and complexation type reactions. Rarely do they consider in a realistic way sorption reactions. It is impossible today with the current state of knowledge to properly define the fate of a contaminant in natural water systems where the contaminant tends to be associated with particulate matter through sorption reactions. It may be possible to fit a mathematical model to existing data. However, great caution should be utilized in attempting to predict conditions which may occur in the future as a result of any change in the characteristics of the system.

One of the common problems associated with trying to distinguish between particulate and dissolved contaminants is that some physical separation procedure must be employed. The routine use of membrane filters with pore sizes approaching 0.5 micron was not established based on the adequacy of separation between solid and dissolved phases. It is an outgrowth of a bacteriological technique used to screen waters for coliform organisms which are used as indicators of potential sanitary quality of water. These filters are used in limnological, oceanographic and water pollution studies because of their availability and because of the fact that they usually yield an adequate quantity of filtrate within a reasonable period of time. Smaller diameter

pore size filters have been available for many years. They are rarely used in water quality studies because they tend to plug too rapidly.

Another significant problem with many filters is the fact that they tend to have strong sorption capacity for certain types of contaminants. In some instances, the filter will remove most of the dissolved contaminant from solution through sorption on the filter surface, giving an incorrect assessment of particulate versus dissolved components in the water sample. This is an especially important problem with organic compounds. In general, if the individual conducting the study is interested in chlorinated hydrocarbon pesticides or other contaminants of this type, then filtration through membrane filters should not be used unless it is established that the particular type of filters used do not result in removal of materials in true solution. In addition to removing materials in true solution through sorption on the membrane or other media surface, the process of filtration creates a markedly different environment than has been present in the solution. Sorption reactions are often dependent on the liquid-solid ratio. Filtration of a sample containing substantial amounts of solids on a relatively small diameter filter results in a column chromatographic effect where a column of the solids is created in which all of the solution must pass through this column before it reaches the membrane filter. Such a situation, in general, would promote sorption reactions because the amount of liquid and solid in intimate contact on the surface of the filter is markedly different from that which has prevailed in the solution.

In addition to removing contaminants, filters have significant problems with respect to adding certain types of contaminants. Many membrane filters are badly contaminated with trace metals such as zinc and other constituents.

In some cases, the contaminants can be washed from the filter. In others, and this is especially true for zinc, it is virtually impossible to determine the distribution between zinc in true solution versus that associated with particulate matter because of the leaching of zinc from certain types of membrane filters.

An alternate method of separating solids from liquids is the centrifuge. High speed centrifugation can remove many particles in natural water systems with diameters smaller than that conventionally removed by 0.5 micron pore size filtration. Furthermore, centrifugation generally eliminates many of the problems discussed above associated with sorption reactions on the filter and by the chromatographic effect created on the filter by the solids accumulation thereon. It should be noted, however, that the conventional laboratory centrifuge rarely creates sufficient gravity to remove small particles. High speed centrifugation is necessary for this purpose. It is recommended in studies where it is important to distinguish between materials in true solution versus those associated with particulate matter, that filters be used once it is demonstrated that there is no loss on the filter. Some samples, however, should be subjected to high speed centrifugation after filtration in order to see if there is significant removal of the contaminants which are supposed to be in true solution based on 0.5 micron pore size diameter filtration.

#### LITERATURE ON THE SIGNIFICANCE OF PARTICULATE ASSOCIATED CONTAMINANTS

One of the questions that must be resolved in evaluating the potential significance of particulate associated contaminants is that of the availability of these contaminants to affect water quality. Included within the definition of water quality are ecological effects, such as



altering the numbers and types of desirable organisms present in natural water systems and the accumulation in aquatic organisms of excessive concentrations of contaminants, which makes their use as food hazardous to man and animals. A review of the literature will show that there is very little information available today which presents the results of studies specifically designed to evaluate this question. Presented below is a summary of some of the studies that have been published which show the potential significance or lack thereof of particulate associated contaminants in affecting water quality.

In general it can be said that particulate associated contaminants are of concern since they represent a form of the contaminant with a potentially significant different mode of transport and degree of availability. The fact that the material is particulate means that in addition to being moved with the water, its overall distribution in natural waters is influenced by gravity, which tends to cause the larger, more dense forms to become associated with the sediments. Within the sediments, the availability is altered even further because of the fact that the exchange of contaminants between water and sediments is often dependent on physical and biological processes of mixing.

Lee (5) has discussed the principal mechanisms of exchange, pointing to the importance of mixing processes in controlling exchange reactions. In general, sediments tend to act as sinks for many contaminants. However, in some instances, there is release of some fraction of the contaminant. It is these situations which are of major concern in evaluating the significance of sediment associated contaminants in affecting water quality. Particular concern in most cases focuses on conditions which promote the release of the contaminants from the solid to the overlying or surrounding waters. If

the release occurs in the sediments, then the additional step of transfer from the interstitial water to the overlying waters is of particular significance for many contaminants.

Some investigators have incorrectly interpreted their data in which they have found high concentrations of contaminants in interstitial waters compared to overlying waters as a significant water quality problem. Under most conditions, interstitial water concentrations exceed the overlying water concentrations. This is especially true for conditions where there is limited mixing of the sediments. The only thing that can be said with certainty about the situation where the interstitial waters have higher concentrations than the overlying waters is that the gradient for release is from interstitial water to the overlying water. However, water quality is not affected by gradients. It is affected by concentrations and there must be actual mass transfer in amounts to cause the concentrations in the overlying waters to be excessive before a particular gradient is of significance. In other words, the potential for release cannot be translated to the magnitude of release. This is similar to the problem of distinguishing between the thermodynamics and kinetics of a chemical reaction where the thermodynamics or the potential for the reaction indicates that such a reaction is possible. It does not say anything about the rate at which the reaction proceeds. With respect to water quality, this rate must be such as to cause an excessive concentration of contaminants in an available form before it is of significance.

As discussed by Lee (5), in addition to concern about the release of contaminants to the water and the subsequent uptake by aquatic organisms, there is also direct uptake by benthic and epibenthic organisms present in the sediments and organisms present in the water column. Of particular concern is the transfer from the solid phase to the organism that could take place within the organism's intestinal tract, where the physical, chemical and biological conditions are markedly different from those in the water. It is possible that for certain contaminants and types of organisms, there may be some transfer of particulate associated contaminants to the organism via solubilization that takes place within the organism's gut (6).

Hoss et al. (7) exposed the larvae of seven species of estuarine fish to unanalyzed seawater extracts of sediments from Charleston, S.C. Larvae were exposed to concentrations of 2, 10, 50, 75 and 100 percent extract for up to fourteen days. The authors noted variable toxicity with different species, but larval survival was generally very low to zero at high concentrations.

Doudoroff et al. (8) tested the potential toxicity to fish of taconite tailings (Reserve Mining Company) discharged into Lake Superior. The authors used 96-hour bioassays with juvenile rainbow trout (Salmo gairdneri) and low pH extracts of fresh tailings solids. No toxicity to fish was noted when the test solutions had a pH near neutral and were aged for 24 hours before use. These results demonstrated that the trace heavy metals present in taconite tailings and Lake Superior sediments may be leached from the solids under low pH conditions. However, when the pH is adjusted to near the pH of Lake Superior water, the leached metals are converted to forms which are nontoxic to juvenile rainbow trout.



Cowen and Lee (9), in a study of biologically available phosphorus in tributaries of Lake Ontario and in urban stormwater drainage from Madison, Wisconsin, have shown that only 20 percent of the particulate phosphorus present in these samples could be converted to an algal available form in a period of several months incubation under aerobic conditions. There is little doubt that, in general, the most unavailable form of contaminants to affect water quality are those forms associated with solids. Further, for many contaminants, the presence of solids will detoxify the contaminant and render it unavailable to have an adverse effect on water quality.

Mearns and Sherwood (10) studied the occurrence of fin erosion and tumors in a bottom dwelling fish, the dover sole (Microstomus pacificus), in southern California between 1969-1972. Specimens with fin erosion were concentrated in an area near a major municipal wastewater discharge site. Distribution of diseased fish and the patterns of erosion of the various fins suggested that the fin disease resulted from contact with the sediments around the wastewater outfall. Tumors were not considered to have been initiated by the wastewater discharge.

McDermott et al. (11), in another study carried out in southern California, focused on the relationships between trace metal contamination in sediments near submarine outfalls and contamination of the dover sole. They concluded that fin erosion is a prevalent problem in the fish and is associated with heavily contaminated sediments. A comparison of the seven trace metals surveyed in healthy and diseased fish, demonstrated significant differences for Cr levels in gonad, liver, kidney and heart tissues.

Fin erosion has been reported in bottom dwelling fish in other areas receiving wastewater and sludges. Mahoney et al. (12) have reported cases of fin rot disease in bottom

dwelling fish (Pseudopleuronectes americanus and Paralichthys dentatus) in New York Bight, an area receiving considerable wastewater and sludges. These observations of fin erosion are interesting in light of recent studies on fish fin repair mechanisms carried out by Weis and Weis (13, 14), which demonstrated that insecticides (DDT, malathion, Sevin) and Cd retarded the regeneration of fin tissue. Cadmium in particular retarded fin regeneration at concentrations below those toxic to fish (as low as 0.01 ppm).

Young et al. (15) studied DDT in sediments and organisms around southern California outfalls and noted that approximately 200 metric tons of DDT have accumulated in bottom sediments within a 50 sq km area of the Palos Verdes shelf. Benthic crabs and flatfish showed large contamination gradients exceeding island or coastal control DDT levels by a factor of 100. Approximately 70 percent of the dover sole collected exceeded the federal limit of 5 ppm (mg/kg wet weight) DDT. Also, dover sole from the region failed to show a significant increase between the three year interval 1971-72 and 1974-75; dover sole had median muscle concentrations of 9 and 12 mg/wet kg, respectively. The authors conclude that the sediment reservoir now may be the dominant source of DDT to benthic organisms. However, from the work completed thus far, it is impossible to rule out the potential for direct uptake from the wastewaters currently being discharged to the area.

Mowat (16) used the standard BOD test (a controlled growth microbial community) to assay the toxicity of twelve common metals (Ag, Hg, Cu, Cd, CrIII, CrVI, Al, Ni, Co, Sn, Zn, Fe) and cyanide. It is interesting to note that in spite of the variations in the quantity and composition of suspended solids and quantity and type of microorganisms in the inoculum, reasonably consistent toxicity patterns were noted in this study after five days. Low concentration toxicity was produced as follows: at 0.25 ppm, Ag and Hg; at 2.5 ppm, Cu, Cd, Co, Ni,

Cr III, Cr IV, Al and CN. However, if the test duration was extended to two weeks, all metals tested showed decreased toxicity at higher levels of suspended solids.

Broman (17) discussed the utility of using mineral slimes for the purification of industrial and municipal wastewater. He elaborated on the various phenomena involved in the adsorption of ions to mineral surfaces and suggested ways to apply mineral slimes to purify water by removing BOD, P, Hg, Fe, Cu, Zn, Pb, Cr, Mn, Cd and magnesium.

Patrick and Loutit (18) studied the passage of metals in effluents through sediment bacteria to higher organisms in a New Zealand river. They observed that bacteria were greater in number in sediments in the river area receiving effluents from various sources, and that isolates of the sediment bacteria could concentrate Cr, Cu, Mn, Fe, Pb and Zn. Tubificid worms fed cultures of the bacteria demonstrated increased concentrations of the metals. The authors suggested that sediment bacteria concentrate low levels of metals in the effluent and pass them on to other organisms in the food chain.

The transport of DDT in a river system (downstream) and into the food web is evident in a study by Fredeen et al. (19). The authors observed the adsorption of DDT on suspended solids in the Saskatchewan River in Canada and its role in black-fly control. River suspended solids levels ranged as high as 551 ppm and were composed mainly of fine silt and clay which, in the laboratory, adsorbed DDT from suspensions of 0.1 ppm DDT in distilled water. Samples of river water collected and allowed to settle out in the lab showed DDT levels of 0.24 to 2.26 ppm (ug/gm solids) a distance of 68 miles downstream from the point of pesticide application. Simulium arcticum were found to feed on suspended particles including much of the inorganic material found in the river



and demonstrated a much greater toxicity than other insect types which normally do not feed on small particles suspended in the water.

Quantitative sampling preceding and following DDT application revealed an almost complete elimination of black-fly larvae for distances ranging from 40 to 98 miles while populations of other aquatic insects were either reduced by an average of 50 percent or remained unchanged. The authors conclude that finely divided inorganic material with high DDT adsorptive properties helps to keep the insecticide in suspension and should be added with the insecticide. The results of this paper emphasize the significance of the toxicant sorb system and the variation in toxicity resulting from different organism trophic (= feeding) roles.

Reimold and Durant (20) observed the toxaphene content of estuarine organisms before, during and after the dredging of toxaphene-contaminated sediments. The authors noted that toxaphene contamination appeared to be best indicated by marsh grass (Spartina alterniflora) and fish (Endulus heteroclitus) with the highest toxaphene levels in each being 7.5 ppm and 200 ppm, respectively. The highest levels of toxaphene occurred during the dredging process.

Hargrave and Phillips (21) produced estimates of oil concentrations in sediments from Nova Scotia, Canada and found total levels ranging between 10 to 3000 ppm wet sediment, with the highest concentrations occurring in sedimenting particles. They discuss the fact that although evaporation and solubilization of oils entering natural waters occur as a result of oxidation to low molecular weight compounds, most oil remains in particulate form. Sedimentation, either directly or resulting from microbial-induced changes in specific gravity, or grazing by zooplankton which concentrates dispersed oil in fecal pellets are mentioned as being now recognized as possible major pathways for oil transport from suspension and deposition to the sediments.



Martens and Berner (28) reported that methane production in the interstitial water of anoxic sediments in Long Island Sound does not reach appreciable concentrations until about 90 percent of the seawater sulfate is removed by sulfate-reducing bacteria. The authors felt that the observed coexistence of measurable concentrations of methane and sulfate in the upper layers of anoxic sediments can be explained by the upward diffusion of methane, its production in sulfate-free microenvironments or both. Chau et al. (29) described the methylation of Se in aquatic sediments by microorganisms and emphasized that such transformations are significant in the transportation and cycling of elements in the environment.

Studies of the relationship between potential toxicant levels in the water, sediments and biota provide information on the cycling of these substances through the food web. Mathis and Cummings (30) surveyed the occurrence of Cu, Ni, Pb, Cr, Li, Zn, Co and Cd in the sediments, water and biota of the Illinois River. They noted that benthic tubificids and clams closely reflected bottom sediment metal concentrations, and a concentration gradient ranging from highest levels in the tubificids, intermediate levels in clams and lowest levels in fish existed for Cu, Pb, Ni, Cr, Li, Co and Cd. Zinc exhibited a partial reversal of this trend. Metals (except for Cu in tubificids) were at their highest concentration in the sediments and their lowest in water (except for Li).

Farrington and Quinn (31) surveyed petroleum hydrocarbons in the sediments and clams of Narragansett Bay and compared the hydrocarbon mixtures with those noted in clams from Charleston Pond, a relatively unpolluted coastal pond. They noted a very complex mixture not likely to be the result of recent biosynthesis, present in the Narragansett Bay sediments and clams, but absent in the Charleston Pond clams.

The authors surmise that hydrocarbons from small petroleum spills and/or sewage effluents become associated with particulate matter and are deposited as sediments. They further note that previous studies have established that the bulk of particulate matter from the Providence River area is deposited in the region where the survey was conducted.

Mathis and Kevern (32) studied the distribution of Hg, Cd, Pb and Ti in the sediments, water, migratory goose feces, plants, zooplankton and fish of Wintergreen Lake, a eutrophic system in Michigan. Mercury was detected in bottom sediments and in each of the five fish species examined. Mercury in the muscle of the largemouth bass (Micropterus salmoides) was highly correlated with length and weight while the other four species lacked any correlation between metals and length and weight. With regard to Hg, a pattern of increasing concentration in fish (ppm) was demonstrated as follows: lake chubsucker (Erimyzon sucetta) 0.038, yellow bullhead (Ictalurus natalis) 0.085, yellow perch (Perca flavescens) 0.124, hybrid sunfish (Lepomis cyanellus X Lepomis gibbosus) 0.255, largemouth bass (Micropterus salmoides) 0.468. Although the mean Hg concentrations in some fish species exceeded levels measured in the sediments (0.095 ppm), the authors felt that the bottom sediments function as a Hg sink composed of Hg which became bound to suspended solids and settled out. They point out that the fish built up a certain body burden of Hg in systems where Hg is undetectable in some components.

Unlike Hg, Cd and Pb were detected in all components examined while Ti was only found in in the sediments. Feces of migratory geese had high concentrations of Cd and Pb (0.529 and 14.5 ppm, respectively) and the authors suggest that migratory bird feces represent a major avenue for Cd and Pb contamination with fallout of atmospheric particulates being secondary.

Kobylinski and Livingston (33) observed the movement of mirex from sediment and uptake by a bottom dwelling fish, the hogchoker (Trinectes maculatus). The hogchoker, unlike many other benthic types, is a carnivore and the ingestion of large amounts of sediment is unlikely. The authors thus felt that the hogchoker could be used to differentiate between (a) absorption of an insecticide from a contaminated substrate and (b) consumption of insecticide-laden foods. They also studied the movement of mirex in static and constant flow soil-water systems at initial sediment concentrations of 5000, 1650, and 500 ppb and the rate of mirex absorption by the hogchoker. Sediments exposed to constant flow conditions lost about 40 percent of their initial mirex concentration while under static conditions virtually all of the mirex stayed in the sediments. Mirex in the water was directly related to sediment levels, and uptake by fish tissue showed a dose-dependent relationship (dose = initial sediment concentration).

Tissue accumulation increased over time but did not appear to reach an equilibrium. The fish gained about 0.012 mg (1650 ppb level) and 0.024 mg (5000 ppb level) during the same two week period. Although declining levels of mirex in the water indicated that mirex was being absorbed from the water by fish, considerably more was gained by fish than was lost from the water, leading the authors to conclude that a significant amount of mirex was being absorbed from the sediment by fish.

Richins and Risser (34) investigated total Hg in water, sediment and selected aquatic organisms in the Carson River, Nevada. Statistical analyses to determine the relationship between Hg levels in sediments and mean residues in fish and shellfish gave different results for different species. No correlation existed between sediments and shiners (Notemigonus crysoleucas) or carp (Cyprinus carpio). However, a significant

correlation was found between mean residue levels in suckers (Catostomus tahoensis) and crayfish (Pacifacastacus liniusculus) and Hg concentrations in bottom sediment at individual collecting stations.

#### EVALUATION OF THE TOXICITY OF US WATERWAY SEDIMENTS

The significance of contaminants associated with dredged sediments has received considerable attention during the past several years. Approximately 400 million cubic yards of sediment are dredged from US waterways each year. The cost of this dredging is approximately \$200 million. In some cases, the cost is on the order of a few tens of cents per cubic yard while in others it is many dollars per cubic yard of sediment dredged. In many cases the greatly increased costs relate to concern about the significance of chemical contaminants present in the dredged sediments. These contaminants have caused the Corps of Engineers, which is responsible for the maintenance of US waterways, to spend a considerable amount of funds for alternate methods of dredged material disposal based on the presence of chemical contaminants in these sediments. The details of this situation have been discussed previously (35-42). The basic issue is how to establish the significance of chemical contaminants associated with dredged sediment. There is considerable economic incentive to resolve this issue in such a way as to minimize the environmental impact of dredged material disposal, while at the same time minimizing the cost of dredging operations.

During the past several years, the authors have been involved in a study on the significance of chemical contaminants in dredged sediments. One phase of this study



has been concerned with the use of bioassays to estimate the reliability of chemical techniques in measuring the presence of contaminants which could be adverse to water quality at the dredged material disposal site.

The following section of this paper presents the results of some of the bioassay studies that have been conducted as part of this overall study.

#### PROCEDURES

The marine bioassays were conducted with Palaemonetes pugio obtained from Gulf Specimen Company, Panacea, Florida. The experimental procedure consisted of adding a known volume of sediment to a known volume of a standard synthetic ocean water (43), running the modified elutriate test and assaying for toxicity of the elutriate waters in the presence of the dredged sediments. All bioassays were static and the test organisms were not fed during the test period. The chemical characteristics of the bioassay elutriate waters were determined at the end of the hour settling period. Immediately following the one hour settling period, ten young adult grass shrimp were added to each test chamber. Selection of test organisms was based upon a random selection of young adults ranging from 15 to 20 mm in length. All test and control tanks were maintained at 20°C ( $\pm$  1°C) in a controlled temperature room unless field conditions warranted the use of some other temperature. The bioassays were run on a 14 hour light - 10 hour dark regime. Two replicates were run simultaneously for both the test tanks and controls.

The freshwater bioassays, using first instar Daphnia magna, were conducted in a manner similar to the marine tests, except that dredging site water was used as the test solution and the bioassays were conducted in 200 ml aliquots of the one hour settled elutriate water. This solution

was not filtered or centrifuged. It contained any solids present in the elutriate solution after the one hour settling. All other test conditions and procedures were the same as the marine tests.

The elutriate test procedure involved the use of either a five or 20 percent elutriate. The 20 percent elutriates were prepared by mixing one volume of sediment with four volumes of the test water using compressed air agitation for a 30 minute period. The five percent elutriates were prepared by mixing one volume of sediment with 19 volumes of test water. This was followed by a one hour quiescent settling.

The marine bioassay was initiated by the introduction of the grass shrimp into this solution. The freshwater bioassays were treated in an identical manner, except that at the end of the one hour settling period the supernatant was siphoned off and placed in various test vessels for the bioassay test. The Daphnia were added to the decanted supernatant.

These elutriate procedures are similar to but not the same as the elutriate test developed by the US EPA and the US Army Corps of Engineers (44-47). The principal difference between the elutriate test procedures used in this study and those used by the US EPA and US Army Corps of Engineers is that the standard elutriate test involves filtration after the one hour settling period to remove any suspended particulate matter that did not settle. It is felt that the modified elutriate test used in this study is a more severe test in that there is opportunity for release of the contaminants over the four day test period from any suspended sediment present at the time of decantation for the freshwater test and from all of the sediment used for the marine test.

Sediments tested in this study were Duwamish River-Seattle, Washington, Los Angeles Harbor, Rhode Island offshore dredged material disposal site and sediment samples collected from selected Connecticut harbors, Mississippi River near St. Paul, James River near Richmond, Virginia and Bailey's Creek near Hopewell, Virginia. The results of the bioassays conducted on these sediments are presented below. The results are part of a study evaluating the reliability of the elutriate test as a technique for estimating the release of contaminants during openwater dredged material disposal. The other parts of this study are presented in reports by Lee et al. (37, 48).

## RESULTS

### Duwamish River - Seattle, Washington

Sediments from the Duwamish River located in Seattle, Washington, were subjected to a modified elutriate test using P. pugio as the test organism. Table 1 presents the total heavy metal composition of the Duwamish River sediments collected on February 16, 1976. Some of these same sediments were used for bioassay tests. The results of the heavy metal analyses for the bioassay elutriates utilizing Duwamish River Site 3 sediments are presented in Table 2. Examination of this table compared to Table 1 shows that a relatively small amount of the heavy metals present in the sediments are released in the elutriate leaching test and the only two elements which show potentially significant release are iron and manganese.

Small releases of copper occurred in the bioassay elutriate water. There appears to be one anomalous result in the cadmium data where the test solution A under the five percent sediment of the total elutriate volume is 34 ug/l cadmium. All others showed two to six ug/l, which is in the range of the controls. The concentrations of lead decreased as a result of elutriation.

TABLE 1  
TOTAL HEAVY METAL COMPOSITION

(mg/kg)

Sampling Location	$\bar{x}$	Mn SD	$\bar{x}$	Cr SD	$\bar{x}$	Cd SD	$\bar{x}$	Ni SD	$\bar{x}$	Pb SD	$\bar{x}$	Zn SD	$\bar{x}$	Cu SD	$\bar{x}$	Fe SD	$\bar{x}$	Hg SD	$\bar{x}$	As SD	
<u>Duwamish River Sediments</u>																					
Site 1	493	57	11.2	1.8	<0.5	-	15.0	0	13.0	1.7	68.6	1.6	22.5	2.8	15,581	44	0.058	0.004	1.8	0	
Site 2	572	10	18.4	0.7	<0.5	-	15.0	3.5	17.7	8.3	73.6	1.9	42.0	2.1	16,079	88	0.085	0.007	1.7	0	
Site 3	558	54	15.3	2.0	<0.5	-	17.5	0	27.1	1.7	71.9	6.2	42.8	6.0	15,892	220	0.050	0.007	1.3	0	
<u>New England Sediments</u>																					
Newport	306	3	19.9	0.4	<0.5	-	9.5	3.2	<1	-	55.3	3.0	12.2	0.7	8847	293	0.026	0	2.8	0.3	
Stamford	451	43	86.0	6.7	2.8	0.1	37.8	9.1	122.9	13.8	339.5	52.6	217.8	23.6	9531	64	0.162	0.004	1.0	0.3	
Norwalk (North)	480	9	67.5	5.9	4.1	0.2	43.1	4.8	276.9	11.0	635.7	8.6	223.7	6.0	9414	178	0.309	0.030	3.4	0.5	
Norwalk (South)	369	68	73.9	22.2	3.5	0.6	37.8	6.7	196.9	35.9	567.3	6.6	254.5	50.2	9387	344	0.379	0.010	0.9	0.1	
<u>Los Angeles Sediments</u>																					
Los Angeles Buoy A-7	382	7	47.6	2.7	3.0	0	30.5	0	41.3	8.3	222.5	0.3	147	9.8	17,478	946	0.147	0.007	12.8	0	

$\bar{x}$  = mean

SD = standard deviation

Mean and standard deviation calculated from duplicate analyses.

Dash (-) indicates not determined.

TABLE 2  
 HEAVY METALS IN BIOASSAY ELUTRIATE WATERS  
 DUWAMISH RIVER SEDIMENTS - SEATTLE, WASHINGTON (SITE 3)

Element	Control **		Sediment Percentages **			
	A	B	5%		20%	
	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>
Cd	3.1	3.3	34	2.6	6.1	6.1
Cu	13.3	14.8	21.3	19.8	71.6	34.3
Cr	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0
Fe	11	13	8506	9772	22177	23038
Mn	49	29	2430	2177	6962	6354
Ni	11.9	13.9	15.1	14.7	21.5	13.9
Pb	47.8	49.3	12.9	12.9	33.6	14.0
Zn	76	141	94	82	188	106
Hg	0.06	0.06	0.001	< 0.001	0.096	0.13

A and B are replicates  
 Concentrations in µg/l

Table 3 presents the results of the bioassay test using five and 20 percent sediment of the total elutriate volume. Only one grass shrimp died in the 96-hour test period, indicating little or no toxicity from these sediments to this organism within this period of time. Table 4 presents the characteristics of the bioassay test used during this part of the study. Of potential concern is the four to five mg/l nitrogen present in the 20 percent elutriate test.

#### Upper Mississippi River - St. Paul

A set of sediment samples was taken from the upper Mississippi River in Pool 2, just below Minneapolis-St. Paul. This region of the river is generally considered to be one of the most polluted sections of the river. The pollution is the result of the discharge of municipal and industrial wastes from these two municipalities. The particular location where the samples were collected is the one that is most severely impacted with low dissolved oxygen arising from the BOD discharge to the river. The bioassays conducted on these sediments utilized Daphnia magna (acclimatized to 20°C) as the test organism. In addition to conducting a modified elutriate test bioassay, samples of water obtained from the discharge pipe of the hydraulic dredging operation were also utilized. The test water used in these tests was obtained upstream of the dredging site, Pool 2. The characteristics of the Mississippi River water and the dredge discharge water are presented in Table 5. Table 6 presents the characteristics of the elutriate waters.

Both these tables contain dredge discharge water characteristics. The difference between the two tables is that Table 5 describes water as it was discharged from the dredge, while Table 6 describes water which has been exposed to one hour settling with the supernatant decanted and used for the bioassay test.



TABLE 3  
MORTALITY OF P. PUGIO DURING 96 HOUR ACUTE BIOASSAY OF  
DUWAMISH RIVER (SITE 3) - SEATTLE, WASHINGTON

TIME (hr)	CONTROL		PERCENT SEDIMENT OF TOTAL ELUTRIATE VOLUME			
			5%		20%	
Number of organisms alive						
	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>
0	10	10	10	10	10	10
12	10	10	9	10	10	10
24	10	10	9	10	10	10
36	10	10	9	10	10	10
48	10	10	9	10	10	10
60	10	10	9	10	10	10
72	10	10	9	10	10	10
84	10	10	9	10	10	10
96	10	10	9	10	10	10

A and B are replicates

TABLE 4  
 PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE ELUTRIATE TEST BIOASSAY\* FOR  
 Seattle, Washington Sediments  
 Site 3

Sample	Temp (°C)	pH	D.O. (mg/l)	Salinity ‰	Total Ammonium as N (mg/l)	Turbidity (NTU)
Control A	21.0	8.1	7.0	29.0	0.14	0.4
Control B	21.0	8.1	7.0	29.0	0.12	0.5
5% A	21.0	7.3	4.3	28.5	1.65	74.0
5% B	21.0	7.0	3.8	28.7	1.42	68.0
20% A	21.0	7.0	2.0	28.2	5.29	78.0
20% B	21.0	7.2	1.1	28.3	4.41	84.0

A and B are replicates

\* Measurements taken at the end of the 1 hour settling period

TABLE 5  
CHEMICAL CHARACTERISTICS OF UPPER MISSISSIPPI  
CULTURE/DILUTION WATER AND DREDGE DISCHARGE WATER

Sample	Temp (°C)	pH	D.O. (mg/l)	Total Hardness as CaCO <sub>3</sub> (mg/l)	Total Ammonium as N (mg/l)	Turbidity (NTU)
Mississippi River	21.0	7.6	10.2	200	0.06	3
Dredge Discharge	21.0	7.0	3.4	48	5.56	1500

TABLE 6  
 CHEMICAL CHARACTERISTICS OF THE ELUTRIATE TEST AND  
 DISCHARGE WATER BIOASSAYS\* FOR  
 UPPER MISSISSIPPI RIVER NEAR ST. PAUL, MINN.

Sample	Temp (°C)	pH	D.O. (mg/l)	Total Ammonium as N (mg/l)	Turbidity (NTU)
Control	20.0	7.6	10.2	0.06	3
5%	20.0	7.8	9.3	1.19	145
20%	20.0	7.7	7.8	3.70	175
Dredge Discharge	20.0	7.1	5.0	5.97	220

\*Measurements taken after 1 hour settling period

Table 7 shows that there was no toxicity to D. magna over a 96-hour test period for either the elutriate waters or the dredge discharge water. Table 8 presents the soluble heavy metal analyses in the bioassay waters for these samples, showing release of iron and manganese in relatively large amounts and small releases of zinc, lead, nickel, copper and cadmium. However, the concentrations of toxic forms of these elements in the elutriate waters were insufficient to be adverse to D. magna during this period. It is important to emphasize that in addition to heavy metals, these solutions also contained from one to six mg/l  $\text{NH}_4^+$ -N. The sum of all of these contaminants, other unmeasured contaminants, and the synergistic effects of all contaminants present in the system was such that they did not create any toxicity to Daphnia over this test period. It is probable that no acute toxicity would be expected from dredging operations conducted in the upper Mississippi River at this location.

#### Rhode Island and Connecticut

Sediments were collected from three different areas in southern New England in November, 1975. These areas included the offshore dredged material disposal site near Narragansett Bay, Rhode Island, commonly called the Newport, Rhode Island disposal site. Also, one set of samples from Stamford Harbor, Connecticut, and two sets of samples from Norwalk River, Connecticut, were collected. All of these sediments were analyzed for the total heavy metal content, the release of heavy metals and other contaminants during the modified elutriate test and their toxicity to P. pugio. Table 1 presents the results of the heavy metal analyses for these sediments. Examination of Table 1 shows that the Newport, R.I. site generally has lower concentrations of

TABLE 7  
MORTALITY OF DAPHNIA MAGNA DURING 96 HOUR ACUTE BIOASSAY OF  
UPPER MISSISSIPPI RIVER

TIME (hr)	CONTROL		PERCENT SEDIMENT OF TOTAL ELUTRIATE VOLUME				DREDGE DISCHARGE		
			5%		20%				
	Number of organisms alive								
	A	B	A	B	A	B	A	B	
0	5	5	5	5	5	5	5	5	
12	5	5	5	5	5	5	5	5	
24	5	5	5	5	5	5	5	5	
36	5	5	5	5	5	5	5	5	
48	5	5	5	5	5	5	5	5	
60	5	5	5	5	5	5	5	5	
72	5	5	5	5	5	5	5	5	
84	5	5	5	5	5	5	5	5	
96	5	5	5	5	5	5	5	5	

A and B are replicates



TABLE 8  
 SOLUBLE HEAVY METALS IN BIOASSAY WATERS FOR  
 UPPER MISSISSIPPI RIVER SEDIMENT  
 (µg/l)

Element	Control		Sediment Percentages*				Dredge Discharge	
	A	B	5%		20%		A	B
Cd	<0.5	<0.5	11.8	12.8	21.1	21.5	6.0	6.0
Cu	4.8	4.9	66	66	87	87	39	39
Cr	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Fe	262	263	1137	1138	1175	1175	1112	1113
Mn	<10.0	<10.0	55	55	168	167	342	343
Ni	7.0	7.0	18.0	19.0	25.6	25.9	11.0	11.2
Pb	4.9	4.9	50	49	76	77	39	39
Zn	3.8	3.8	52	52	69	69	37	37

A and B are duplicate measurements.

various heavy metals than the other two sites. This is to be expected, in that the Newport, R.I. site is an offshore disposal site that was used approximately six years ago by the Corps of Engineers for disposal of dredged sediments. The Stamford Harbor and Norwalk River sites represent areas which are receiving municipal and industrial wastes and land runoff. The Norwalk North and Norwalk South sites are two different sampling locations within the Norwalk River; they are within a couple of miles of each other.

The results of the bioassay using P. pugio for the Newport, R.I. sediments are presented in Table 9. This table shows that there was no toxicity to P. pugio over the 96-hour test period from these sediments. The characteristics of this bioassay test solution are presented in Tables 10 and 11. Table 10 shows that approximately one mg/l ammonia was present in the 20 percent elutriate solution, while Table 11 shows that the cadmium content of the test water decreased as a result of the elutriate test. Similar results were found for copper, manganese, nickel, lead and zinc. The only metal which showed any release during the modified elutriate test was iron.

A similar set of data for the Stamford Harbor sediments is presented in Tables 12, 13 and 14. Table 12 shows that only one grass shrimp died in the 20 percent elutriate over the 96-hour period. Approximately two to four mg/l ammonia nitrogen were present in the elutriate tests. From Table 14 it is seen that there was a slight decrease in cadmium during the elutriation procedure. The other heavy metals showed little or no change or a slight increase, except for iron which showed up to 1000 ug/l increase for the 20 percent elutriate of these sediments.

TABLE 9  
MORTALITY OF P. PUGIO DURING 96 HOUR ACUTE BIOASSAY OF  
NEWPORT - RHODE ISLAND SEDIMENTS

TIME (hr)	CONTROL		PERCENT SEDIMENT OF TOTAL ELUTRIATE VOLUME				
			5%		20%		
Number of organisms alive							
	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>	
0	10	10	10	10	10	10	
12	10	10	10	10	10	10	
24	10	10	10	10	10	10	
36	10	10	10	10	10	10	
48	10	10	10	10	10	10	
60	10	10	10	10	10	10	
72	10	10	10	10	10	10	
84	10	10	10	10	10	10	
96	10	10	10	10	10	10	

A and B are replicates

TABLE 10  
 PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE ELUTRIATE TEST BIOASSAY\* FOR  
 NEWPORT, R.I. SEDIMENTS

Sample	Temp (°C)	pH	D.O. (mg/l)	Salinity ‰	Total Ammonium as N (mg/l)	Turbidity (NTU)
Control A	19.5	8.2	7.1	27.5	< 0.01	2.0
Control B	19.5	8.2	6.9	27.5	0.02	2.0
5% A	19.5	8.1	6.3	27.9	0.35	67.0
5% B	19.5	8.2	6.5	28.0	0.31	74.0
20% A	19.5	8.1	3.3	28.5	1.36	89.0
20% B	19.5	8.0	3.9	28.0	0.94	87.0

A and B are replicates

\*Measurements taken at the end of the 1 hour settling period

TABLE 11  
HEAVY METALS IN BIOASSAY ELUTRIATE WATERS  
NEWPORT, R.I.

Element	Control*		Sediment Percentages*			
	A	B	5% A	5% B	20% A	20% B
Cd	1.3	1.2	0.7	0.7	0.6	0.6
Cu	25.3	19.5	1.4	1.4	3.2	3.8
Cr	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0
Fe	34	65	700	900	400	500
Mn	48	48	37	27	5	37
Ni	8.0	8.6	6.1	5.8	6.1	6.1
Pb	3.8	7.6	2.5	2.5	3.8	2.5
Zn	21.7	10.4	10.3	9.5	8.4	8.0

A and B are replicates

\* Concentrations in  $\mu\text{g}/\text{l}$

TABLE 12  
MORTALITY OF P. PUGIO DURING 96 HOUR ACUTE BIOASSAY OF  
STAMFORD HARBOR, CONNECTICUT - WEST BRANCH

TIME (hr)	CONTROL		PERCENT SEDIMENT OF TOTAL ELUTRIATE VOLUME			
			5%		20%	
Number of organisms alive						
	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>
0	10	10	10	10	10	10
12	10	10	10	10	10	10
24	10	10	10	10	10	10
36	10	10	10	10	10	10
48	10	10	10	10	10	10
60	10	10	10	10	9	10
72	10	10	10	10	9	10
84	10	10	10	10	9	10
96	10	10	10	10	9	10

A and B are replicates



TABLE 13

PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE ELUTRIATE TEST BIOASSAY\* FOR  
STAMFORD HARBOR - WEST BRANCH

Sample	Temp (°C)	pH	D.O. (mg/l)	Salinity ‰	Total Ammonium as N (mg/l)	Turbidity (NTU)
Control A	19.5	8.2	7.1	27.5	< 0.01	2
Control B	19.5	8.2	6.9	27.5	0.02	2
5% A	19.5	8.0	4.2	28.0	1.54	48
5% B	19.5	8.0	3.9	28.0	1.38	53
20% A	19.5	8.0	1.1	27.9	3.84	67
20% B	19.5	8.0	1.1	27.9	3.33	30

A and B are replicates

\* Measurements taken at the end of the 1 hour settling period

TABLE 14  
HEAVY METALS IN BIOASSAY ELUTRIATE WATERS  
STAMFORD HARBOR - WEST BRANCH

Element	Control*		Sediment Percentages*			
	A	B	5%		20%	
	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>
Cd	1.3	1.2	0.9	0.9	2.3	0.7
Cu	25.3	19.5	36.5	34.9	42.5	18.3
Cr	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0
Fe	34	65	700	900	2200	1000
Mn	48	48	48	48	69	37
Ni	8.0	8.6	11.1	10.8	18.4	8.0
Pb	3.8	7.6	27.7	21.4	26.4	13.8
Zn	21.7	10.4	21.3	19.8	39.8	12.9

A and B are replicates

\* Concentrations in  $\mu\text{g}/\text{l}$

TABLE 15  
MORTALITY OF P. PUGIO DURING 96 HOUR ACUTE BIOASSAY OF  
NORWALK RIVER, CONNECTICUT - NORTH SITE

TIME (hr)	CONTROL		PERCENT SEDIMENT OF TOTAL ELUTRIATE VOLUME			
			5%		20%	
Number of organisms alive						
	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>
0	10	10	10	10	10	10
12	10	10	10	10	10	10
24	10	10	10	10	10	10
36	10	10	10	10	10	10
48	10	10	10	10	10	10
60	10	10	10	10	10	10
72	10	10	10	10	10	10
84	10	10	10	10	10	10
96	10	10	10	10	10	10

A and B are replicates

The Norwalk River North and South site bioassays and elutriate data are presented in Tables 15 through 21. No toxicity to P. pugio was found during the 96-hour test period for the North site, and one grass shrimp in the two replicate test systems applying 20 percent sediment of the total elutriate volume died after 36 hours exposure from the South site sediments. Ammonia content of the two sediment elutriates ranged from seven to slightly over 11 mg/l ammonia as N. The North site sediments showed no change in cadmium or nickel during the elutriate test while there appears to have been a slight decrease in cadmium content of the South site sediment elutriates. Copper showed a slight increase in the North site while the South site sediments showed no change to a slight decrease. There was readily measurable iron release in the South site sediments. Iron measurements were not made on the North site sediments. Manganese was released for both sediments. There was insignificant changes in the other heavy metals measured for both these sediment elutriates.

Again, with this set of data taken from a variety of harbors and disposal sites along the southern New England coast, it is found that sediments contain large amounts of heavy metals, some of which are released during the elutriate tests. However, essentially no toxicity was found to P. pugio over a 96-hour period of exposure to a 1 to 19 or 1 to 4 sediment-water mixture.

#### Los Angeles Harbor

Samples from the Los Angeles Harbor sediments were collected on July 9, 1975. The total heavy metal content of these sediments is shown in Table 1. These sediments have approximately the same general concentration of heavy metals as the other sediments that were investigated in this study. The toxicity of these sediments, however,

TABLE 16  
MORTALITY OF P. PUGIO DURING 96 HOUR ACUTE BIOASSAY OF  
NORWALK RIVER - SOUTH SITE

TIME (hr)	CONTROL		PERCENT SEDIMENT OF TOTAL ELUTRIATE VOLUME					
			5%		20%			
Number of organisms alive								
	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>
0	10	10	10	10	10	10	10	10
12	10	10	10	10	10	10	10	10
24	10	10	10	10	10	10	10	10
36	10	10	10	10	9	9		
48	10	10	10	10	9	9		
60	10	10	10	10	9	9		
72	10	10	10	10	9	9		
84	10	10	10	10	9	9		
96	10	10	10	10	9	9		

A and B are replicates

TABLE 17  
HEAVY METALS IN BIOASSAY ELUTRIATE WATERS  
NORWALK RIVER - NORTH SITE

Element	Control**		Sediment Percentages**			
	A	B	5%		20%	
	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>
Cd	2.4	2.3	2.5	2.9	2.6	3.4
Cu	29.4	26.1	41.3	50.6	34.3	31.9
Cr	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0
Mn	25	63	275	413	925	1225
Ni	10.4	8.7	13.0	13.4	12.5	12.1
Pb	2.5	2.2	26.3	23.8	20.6	20.8
Zn	25.5	16.5	75.8	70.0	59.4	58.1

A and B are replicates

\*\* Concentrations in µg/l

TABLE 18

PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE ELUTRIATE TEST BIOASSAY\* FOR  
NORWALK RIVER - NORTH SITE

Sample	Temp (°C)	pH	D.O. (mg/l)	Salinity ‰	Total Ammonium as N (mg/l)	Turbidity (NTU)
Control A	20.5	8.0	7.3	31.0	0.01	1.0
Control B	20.5	8.0	7.3	31.0	0.02	1.0
5% A	20.0	7.8	4.7	29.8	2.40	33.0
5% B	20.0	7.8	4.8	30.2	1.46	42.0
20% A	20.0	7.7	1.1	28.3	7.60	25.0
20% B	20.0	7.6	1.1	28.3	7.88	25.0

A and B are replicates

\* Measurements taken at the end of the 1 hour settling period

TABLE 19  
 PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE ELUTRIATE TEST BIOASSAY\* FOR  
 NORWALK RIVER - SOUTH SITE

Sample	Temp (°C)	pH	D.O. (mg/l)	Salinity ‰	Total Ammonium as N (mg/l)	Turbidity (NTU)
Control A	20.0	8.0	7.1	28.5	0.10	0.4
Control B	20.0	8.0	7.1	28.5	0.10	0.4
5% A	20.0	7.8	4.3	25.3	4.27	44.0
5% B	20.0	7.8	4.1	25.4	4.27	49.0
20% A	20.0	7.8	2.0	25.8	10.94	30.0
20% B	20.0	7.7	2.3	25.3	11.24	35.0

A and B are replicates

\* Measurements taken at the end of the 1 hour settling period



TABLE 20  
HEAVY METALS IN BIOASSAY ELUTRIATE WATERS  
NORWALK RIVER - SOUTH SITE

Element	Control *		Sediment Percentages *			
	A	B	5%		20%	
Cd	4.7	5.0	2.1	2.3	1.7	1.7
Cu	55.4	45.3	61.2	61.2	33.4	28.2
Cr	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0
Fe	33	49	3747	3544	3342	3139
Mn	19	10	354	380	532	582
Ni	58.9	84.6	14.7	16.7	11.1	11.5
Pb	28.1	28.8	22.2	22.9	13.3	12.2
Zn	47.1	76.5	76.5	70.6	47.1	52.9
Hg	< 0.001	< 0.001	0.200	0.200	0.15	0.096

A and B are replicates

\* Concentrations in  $\mu\text{g/l}$

TABLE 21  
MORTALITY OF P. PUGIO DURING 96 HOUR ACUTE BIOASSAY OF  
LOS ANGELES HARBOR SITE BUOY A7

TIME (hr)	CONTROL		PERCENT SEDIMENT OF TOTAL ELUTRIATE VOLUME		
			5%		20%
Number of organisms alive					
	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>	<u>A</u>
0	10	10	10	10	10
12	10	10	9	9	9
24	10	10	9	9	9
36	10	10	9	9	9
48	10	10	9	9	9
60	10	10	7	8	5
72	10	10	7	8	5
84	10	10	7	8	4
96	10	10	7	8	4

A and B are replicates

TABLE 22

PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE ELUTRIATE TEST BIOASSAY\* FOR  
LOS ANGELES HARBOR BUOY A7

Sample	Temp (°C)	pH	D.O. (mg/l)	Salinity ‰	Total Ammonium as N (mg/l)	Turbidity (NTU)
Control A	19.0	8.2	7.6	28.8	0.02	2.0
Control B	19.0	8.2	7.6	28.8	0.02	2.0
5% A	19.0	8.1	3.0	29.2	12.00	68.0
5% B	18.5	8.2	4.6	29.2	9.10	72.0
20% A	18.5	8.1	1.3	31.4	22.00	69.0

A and B are replicates

\* Measurements taken at the end of the 1 hour settling period

(Table 21) is considerably greater than any of the other sediments that have been investigated as part of this phase of the study. While only a single sample of the 20 percent elutriate was run, over half of the grass shrimp died in a 96-hour period. For the five percent elutriate, 20 to 30 percent of the grass shrimp died during the 96-hour period. These results indicate a somewhat greater toxicity of these sediments to this organism than found in the other sediments that have been tested.

Examination of the characteristics of the elutriate water (Table 22) shows that the 20 percent elutriate has approximately 22 mg/l ammonia nitrogen, while the two 5 percent elutriates have 9 and 12 mg/l ammonia nitrogen. The heavy metals released during the elutriate tests (Table 23) were copper, iron, nickel, lead and zinc. Manganese appeared to decrease for these sediments. This is an unusual pattern for this metal. It cannot be ascertained from the information available whether the increased toxicity of these sediments to P. pugio is related to the somewhat greater release of heavy metals, higher ammonia or some other unmeasured constituents.

#### James River and Bailey's Creek

A set of samples was collected in July, 1976, from Bailey's Creek and the James River. The Bailey's Creek samples were taken about one mile downstream from the Hopewell domestic wastewater treatment plant. This plant received the kepone discharged by the manufacturing firm located in Hopewell, Virginia which resulted in the widespread contamination of the James River and Chesapeake Bay with this compound. Sampling was also done of a pipeline dredge discharge water that was operating near Windmill Point on the James River. This location is several miles below the point where Bailey's Creek enters the river. The sediments in this area would

TABLE 23  
HEAVY METALS IN BIOASSAY ELUTRIATE WATERS  
LOS ANGELES HARBOR - BUOY A7

Element	Control <sup>*</sup>		Sediment Percentages <sup>**</sup>		
	A	B	5%	20%	
Cd	1.5	1.5	1.2	1.2	1.1
Cu	5.3	6.5	38.9	38.0	37.4
Cr	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0
Fe	0.29	0.16	1500	1500	1500
Mn	58.0	27.0	16.0	37.0	5.0
Ni	8.6	9.6	10.8	11.1	9.9
Pb	1.3	1.3	21.4	22.0	26.4
Zn	10.7	11.5	40.1	44.2	44.1

A and B are replicates

<sup>\*</sup>Concentrations in µg/l

be expected to be contaminated with kepone and a wide variety of other contaminants from municipal and industrial wastes of the area which include pulp and paper wastes, petrochemicals and other industries. It was impossible to sample the dredge discharge water directly because of submerged discharge. Samples were taken immediately adjacent to the discharge. There was some dilution due to the initial mixing that occurs upon the entry of the discharge water into the river.

The bioassays were conducted with Daphnia magna since this is a freshwater system. In this case, the Daphnia were acclimatized to 25°C since this was the temperature found at the disposal site. The bioassays on the elutriate on the Bailey's Creek samples were run with the James River water taken near Windmill Point. This water was not contaminated with any discharge from recent dredging operations. The characteristics of the James River water and nonsettled discharge water are presented in Table 24. Table 25 shows that the dredged discharge water showed no toxicity to Daphnia in 96 hours. The Bailey's Creek sediments, however, showed some toxicity to Daphnia for both the five and 20 percent sediment of the total elutriate volume. Slightly greater toxicity was demonstrated for the replicate number B for the five percent sediment than with either A or B for the 20 percent sediment. These results indicate some toxicity to D. magna from these sediments from Bailey's Creek. Examination of Table 26 shows that the ammonia content of the samples ranged from one to five mg/l as N, while Table 27 shows that the elutriates on the Bailey's Creek sediments showed slight releases of cadmium and readily measurable increases of copper, chromium, iron, manganese, nickel, lead and zinc. The dredge discharge water taken from the James River,

TABLE 24  
CHEMICAL CHARACTERISTICS OF BIOASSAY TEST WATERS  
FOR BAILEY'S CREEK SEDIMENT AND JAMES RIVER  
DISCHARGE WATER

Sample	Temp (°C)	pH	DO (mg/l)	Total Hardness as CaCO <sub>3</sub> (mg/l)	Total Ammonia as N (mg/l)	Turbidity (NTU)
James River	25.0	7.1	8.8	48.0	0.069	15
Dredge Discharge	25.0	7.0	8.8	232.0	0.015	85

TABLE 25.  
MORTALITY OF DAPHNIA MAGNA DURING 96 HOUR ACUTE BIOASSAY OF  
BAILEY'S CREEK, VIRGINIA SEDIMENTS

TIME (hr)	CONTROL		PERCENT SEDIMENT OF TOTAL ELUTRIATE VOLUME				DREDGE DISCHARGE		
			5%		20%				
	Number of organisms alive								
	A	B	A	B	A	B	A	B	
0	5	5	5	5	5	5	5	5	
12	5	5	5	4	4	5	5	5	
24	5	5	4	3	4	5	5	5	
36	5	5	4	3	4	5	5	5	
48	5	5	4	3	4	5	5	5	
60	5	5	4	3	4	5	5	5	
72	5	5	4	3	4	5	5	5	
84	5	5	4	3	4	5	5	5	
96	5	5	4	3	4	5	5	5	

A and B are replicates



TABLE 26  
 CHEMICAL CHARACTERISTICS OF THE ELUTRIATE TEST\* AND  
 DISCHARGE WATER BIOASSAYS FOR  
 BAILEY'S CREEK, VIRGINIA SEDIMENTS

Sample	Temp (°C)	pH	D.O. (mg/l)	Total Ammonium as N (mg/l)	Turbidity (NTU)
Control	25.0	7.1	8.8	0.06	16
5%	25.0	7.8	7.5	1.02	280
20%	25.0	7.8	6.0	5.25	340
Dredge Discharge	25.0	7.0	8.8	< 0.01	85

\*Measurements taken after 1 hour settling period

TABLE 27

## HEAVY METALS IN BIOASSAY WATERS FOR BAILEY'S CREEK, VIRGINIA SEDIMENTS

Element	Control		Sediment Percentages*				Dredge Discharge	
	A	B	5%		20%		A	B
Cd	< 0.5	< 0.5	1.9	1.7	2.8	2.5	< 0.5	< 0.5
Cu	2.7	2.6	33.7	31.0	31.8	28.2	29.1	31.6
Cr	< 2.0	< 2.0	3.5	3.6	6.1	6.5	< 2.0	< 2.0
Fe	263	252	1202	1110	1095	1024	1150	1191
Mn	8.0	8.0	192	205	305	305	92	80
Ni	2.9	2.6	17.0	17.6	22.3	23.5	8.2	9.7
Pb	3.1	1.9	44.4	43.2	43.2	40.8	26.5	27.7
Zn	2.2	2.9	102.9	102.0	100.6	117.1	32.9	40.7

A and B are replicates

\* Concentrations in  $\mu\text{g}/\text{l}$

however, showed no significant change in the cadmium content, and readily measurable release of copper, iron, manganese, lead and zinc.

One of the reasons why the dredged discharge water and the elutriates from the James River sediments showed increased concentrations of many of the heavy metals is that these sediments contained large amounts of particulate matter that would readily pass through a 0.45 micron pore size filter. The filtrate was milky in appearance, indicating that large amounts of particulate matter were present in the samples that would not readily settle in the modified elutriate test that is used for bioassay solutions. A true elutriate of these sediments, i.e., treated in such a way as to remove the particulate matter, would likely show much lower concentrations of many of these heavy metals than those found.

#### Tests on Other Sediment Samples

In addition to the sediments reported in this paper, elutriate-type bioassays on sediments from Ashtabula Harbor-Lake Erie; Bridgeport Harbor, Connecticut; Corpus Christi Harbor, Texas City Channel, Houston Ship Channel near Morgan's Point, Galveston Bay Entrance Channel, Texas; and San Francisco Bay near Mare Island and Rodeo Flats have been investigated. The results of these studies have been reported by Lee et al. (37) and Lee, Lopez and Mariani (40). Also, ongoing studies using sediments from Mobile Bay, Alabama, several sites in the New York-New Jersey area, and Apalachicola, Florida have been completed. All of these studies show that for freshwater sites using D. magna, and marine sites using P. pugio, in general, little or no toxicity was found in a 96-hour bioassay of modified elutriate test water. In some instances, as many as half of the grass shrimp would die in a 96-hour period. However, this situation was rare and in most of these

tests, from zero to 20 grass shrimp died during the test period. The lack of toxicity noted with the Ashtabula Harbor-Lake Erie sediments is supported by the fact that the Daphnia reproduced during the test period.

#### Overall Evaluation

From the results of these tests, it may be concluded that the typical openwater dredged material disposal operation involving dumping of dredged sediments should have little or no toxicity to aquatic life in the disposal site water column. This conclusion is based on the rapid dilution that occurs at the disposal site water column, coupled with the fact that relatively small amounts of contaminants present in the water sediments tested were available to be acutely toxic to aquatic life over much longer periods of time than the typical exposure that would occur in openwater disposal operations. Most openwater disposal operations will involve a dilution of many thousand-fold within a few hours of the time of disposal (37). Further, it is unlikely that any chronic toxicity would be found from openwater disposal involving dumping operations to water column organisms because of the intermittent nature of the disposal operation.

The results of these studies clearly demonstrate that chemical contaminants associated with natural water sediments taken from both fresh and marine waters from throughout the US in general are largely unavailable to be adverse to aquatic life in the water column of typical openwater disposal of dredged material.

## HAZARD EVALUATION OF SEDIMENT ASSOCIATED CONTAMINANTS

Increasing impetus will be given in the near future to evaluating the significance of sediment associated contaminants. Section 404 guidelines for Public Law 92-500 (46) governing the disposal of dredged material require that applicable water quality standards be used to judge the significance of contaminants associated with dredged sediments at the edge of a mixing zone. A similar approach has been proposed for disposal of dredged sediments in marine waters (47). While inappropriate for most dredged material disposal operations, it is likely that attempts will be made to utilize the US EPA Quality Criteria for Water (1) as a basis for judging the significance of the presence of chemical contaminants at the edge of a mixing zone for a dredged material disposal site. As discussed by Lee (49), the inappropriateness of the July, 1976, US EPA Quality Criteria for Water (1) stems from the fact that these criteria were developed for chronic exposure situations utilizing readily available forms of the chemical contaminants. The dredged material disposal operation, on the other hand, consists primarily of contaminants present in a particulate form where a substantial part of the contaminants is not available to affect water quality. Further, the time of exposure for concentrations in excess of proposed water quality criteria is generally such that it is virtually impossible to obtain an exposure similar to that used in the bioassay tests which serve as a basis for establishing the US EPA criteria.

It should be emphasized that these criteria in general represent orders of magnitude reduction in the critical levels of chemicals for various forms of aquatic life than typically in existence today for state water quality standards. Implementation of these criteria into state water quality standards will cause a significant change in the approach

used with respect to water pollution control. Many waters which in the past were judged to be safe for aquatic life, will now be judged to be harmful. Further, since the US EPA criteria are based on total concentration depending on when the samples are taken, many natural waters will fail water quality standards even though they may have good commercial and sport fisheries and no readily discernible signs of degraded water quality. In many instances, the reason that a particular water sample will likely fail the criteria is that the concentration of contaminants present is largely the result of contaminants associated with particulate forms. It is clear that the implementation of the criteria into water quality standards in which the waters would be classified for the highest quality fish and aquatic life, will result in the expenditure of large amounts of funds for pollution control efforts which may result in no improvement in overall water quality. This type of situation will likely be of particular importance in the development of dredged material disposal criteria.

Over the past few years considerable emphasis has been placed on attempting to evaluate the significance of chemical contaminants associated with dredged sediments on water quality at the dredged material disposal site. These efforts provide useful information which can serve as a basis for examining various approaches for determining the hazard of sediment associated contaminants.

#### BULK CHEMICAL CRITERIA

Occasionally pollution control agencies and others will attempt to use the bulk chemical content of natural water sediments as a measure of the potential significance of chemical contaminants present in the sediments on water quality. Sediment and water quality should be judged by the impairment of a beneficial use of water by man. Such impairment can arise from toxicity of contaminants to aquatic

organisms, birds that feed on these organisms and man, who may use the water for recreation, food resource and/or water supply. In addition to toxic effects, consideration has to be given to degradation of aesthetic quality of the water and organisms inhabiting the area.

With respect to the aquatic organisms and man, the primary concern focuses on acute lethal and chronic toxicity and bioaccumulation of the contaminants in the various trophic levels which could be of significance to higher trophic organisms and/or man who may utilize certain members of a trophic level as a food resource. The basic issue is usually one of whether the chemical contaminants present in the sediments can be released to the water column and/or taken up by the aquatic organisms present in, on, or above the sediments in sufficient quantities to be adverse to beneficial uses of water or organisms in the area. From a water quality management point of view, it is important to ascertain whether bulk chemical criteria in which a known weight of sediment is analyzed for the total contaminant content is a valid approach for assessing the potential for organism uptake or release to the water column. Lee and Plumb (35), Lee et al. (37) and Lee (38) have discussed the fact that bulk chemical criteria cannot be used to assess the significance of chemical contaminants associated with natural water sediments. The problem is that many contaminants are associated with natural water sediments in a variety of ways, many of which essentially prevent release or direct organism uptake to a sufficient extent to prevent water quality deterioration.

As noted above, however, this is not always the case. There are situations where there is sufficient release of contaminants from sediments to cause significant water quality degradation in the overlying waters. However, no relationship should be expected between the bulk content

of the sediments and the potential water quality problems that sediment associated contaminants may cause, since the character of the solid matrix present in natural waters is highly variable and the tenacity with which a particular contaminant is held by various types of solids is a function of the character of the solids. Based on this situation, it readily can be seen that the measurement of the bulk chemical content of the solid phase should bear little or no relationship to the potential significance of these contaminants to water quality.

It is important to emphasize that concentrations in solids on a mass-per-mass basis are a function not only of the flux rate of the contaminants which become incorporated into particulate matter, but also the flux rate of the solid material to be mixed into the particulate which contains the contaminants. For example, a certain amount of a pesticide could be added to a river in an industrial waste. If the pesticide is similar to many, it would tend to be sorbed by the particulates present in the river and give a certain concentration in the suspended sediment bedload and deposited sediments. If downstream, however, another river carrying large amounts of suspended sediments is mixed with this river containing pesticide-laden suspended sediments, the concentrations of pesticide per unit mass of suspended sediment will decrease because of dilution of the solid phase. However, it is important to note that the total mass of pesticide present has not changed, nor is there any well-defined relationship that would indicate that just because the contaminant has been diluted with inert solids that this in any way has changed the degree of availability of this pesticide to aquatic organisms. Many individuals mistakenly attempt to correlate concentrations in sediments with concentrations in water. This cannot generally be done because of the fact that concentrations in sediments are a function of the flux rate of the sediment material as well as the contaminants of interest.



Frequently pollution control agencies will attempt to use the ambient concentrations of contaminants in sediments which are thought to be present in the absence of any contamination from man as the basis for judging the significance of bulk chemical content of sediments. Some pollution control agencies will establish regulations which indicate that whenever the concentration of a particular contaminant exceeds the average contaminant concentration of the nation or region, then the sediments are considered to be polluted and require special handling in dredging operations or other activities. This approach has as its basic premise a bulk chemical analysis of these sediments which is to be compared to some either measured or estimated ambient levels of the contaminant and the bulk sediments which are alleged to be noncontaminated.

In some instances, such as the US EPA Region V proposed dredged material disposal criteria, the ambient levels which are used to classify sediments as polluted or non-polluted, are less than the average crustal abundance of contaminants which would be present in the absence of activities of man. It is important to emphasize that one cannot judge the significance or lack of significance of a particular contaminant present in so-called natural sediments by its bulk content and by its origin. It is relatively easy to envision a situation where a low concentration of a contaminant present in sediments derived from natural sources may be more harmful to aquatic organisms than a much higher concentration of a contaminant associated with man's activities. This would be especially true for mining wastes, where the contaminants associated with some of the waste solids (tailings) may be strongly bound in the matrix and not available to affect aquatic life, while the naturally derived contaminants may be loosely bound and much more readily available.

## ASSESSMENT OF AVAILABLE FORMS BY CHEMICAL MEANS

Various investigators have attempted to develop chemical leaching tests for the assessment of available forms of contaminants in natural water systems. In general, the procedures involve the use of a leaching solution which is designed to selectively dissolve forms of contaminants which are thought to be biologically available. In general, the procedures have followed the selective extraction procedures developed for estimating available phosphorus and subsequently, other chemicals in soils using consecutive selective leaching procedures similar to the Chang and Jackson procedures (50, 51). No attempt will be made here to review the various procedures that are used for this purpose. It is appropriate to note, however, that none of the available procedures measure a well defined biologically available fraction. One of the major problems associated with estimating the available part of contaminants in a natural water system is that a contaminant associated with one particular phase may, as a result of a selective leaching, be removed from that phase. However, there may be another solid phase present which would tend to hold or resorb the contaminant, thereby preventing release to solution.

There are situations where certain modifications of these procedures appear to measure something close to what is found to be biologically available. Cowen and Lee (9, 52) found this to be the case for the ion exchange releasable phosphorus from samples of rivers tributary to Lake Ontario from the State of New York and in urban stormwater drainage. However, even with this procedure, there is no assurance that when samples from different locations are tested, that similar results would be obtained. It is important that any investigator who utilizes any of these selective extraction procedures

not attempt to label the fraction extracted in terms of some chemical form. There is abundant evidence that none of these procedures extract well defined chemical forms. Instead, they should be labeled using the operational definition appropriate for the test such as a pH 1 acid leachable with hydrochloric acid or a sodium hydroxide leachable, etc.

The fact that well defined forms are not measured by these tests does not mean that the tests are invalid. There is need for substantial work relating the results of the selective leaching procedure to biologically available forms in which the bioassay procedures are run parallel with the chemical leaching tests. It is possible that in time reliable chemical leaching tests can be developed which would be useful to estimate the amount of available forms of selected contaminants in a natural water sample.

#### USE OF BIOASSAYS TO EVALUATE AVAILABILITY

At this time, the only way that one can judge the potential significance of contaminants associated with particulate matter is through bioassay procedures. Bioassays should check not only for toxicity effects but also bioaccumulation. The interpretation of both sediment toxicity and bioaccumulation data is difficult. About the only thing that can be said for certain is that if the sediments show a toxicity to aquatic life and the bioassay has been conducted in such a way as to properly simulate natural water conditions and an organism or organisms have been selected for testing which properly reflect the sensitivity of the organisms in the area of concern, then it is possible that a similar toxicity may be experienced in the area from which the sediments were derived.

Particular attention, however, must be given to the time-concentration relationship that exists in the area of concern. Toxicity and to some extent bioaccumulation, are

dependent on a time-concentration relationship in which high concentrations of available contaminants can be present and have little or no effect on organisms and water quality, provided that the duration of exposure is small. However, low levels of available forms over long periods of time may be significant.

The availability of many contaminants can change over long periods of time. Frequently in natural water systems, the availability of sediment associated contaminant changes toward the nonavailable form, which is part of the overall natural self purification process that occurs in almost all natural water systems. This process is related to the permanent incorporation of many contaminants into the sediments and their eventual burial with the addition of more sediment. Further, since many of the sediments of concern are derived from polluted areas with low oxygen conditions, the movement of the sediments either naturally or as a result of man's activities, i.e., in dredging, tends to result in changing the environment from an anoxic condition to those of an oxic condition, where there is the opportunity for the hydrous oxides of iron and manganese to be present and scavenge contaminants from the sediments and the overlying waters.

Also, an important part of the natural assimilative capacity of sediment associated contaminants is dilution. In natural water systems, contaminants affect water quality as a result of their concentrations of available forms. Dilution below a critical concentration in either the water column or sediments can readily render a particular contaminated sediment innocuous. There are some individuals who mistakenly indicate that dilution does not occur in sediments. This, of course, is incorrect in that dilution is readily occurring in sediments arising from the

incorporation of noncontaminated sediments into the sediment matrix or, in the case of dredged material disposal, the movement of contaminated sediments from the disposal site into the surrounding areas with the accompanying dilution that occurs arising from dispersion and mixing of the sediments.

In conducting sediment bioassays, consideration must be given to both toxicity and bioaccumulation. Generally, a 96-hour acute lethal test is used to evaluate toxicity to aquatic organisms. The National Academies of Sciences and Engineering proposed that in order to evaluate the chronic toxicity of a contaminant to a certain organism, an application factor relating the 96-hour acute lethal toxicity to the safe chronic exposure level of approximately 100 be utilized for most chemicals. In some cases, the application factor relating acute to chronic toxicity is only a factor of ten. For example, sufficient numbers of studies have been done on copper to show that there are many factors influencing the toxicity of copper to aquatic organisms. Glass (53) has recently discussed the wide variety of forms of copper and several other elements that may exist in natural water systems. He has pointed out that for some natural waters, only a small part of the soluble copper will likely be toxic to aquatic life.

Rather than attempting to establish a fixed critical concentration, the NAS(2) EPA(1) recommended acute lethal bioassay tests consisting of a 96-hour exposure. The results of this test are to be multiplied by a factor of 0.1 to assess the chronic safe level for copper to these aquatic organisms under the conditions of the test. It is important to emphasize that the NAS-NAE recommended (2) application factors have been determined for soluble species and may have limited applicability to contaminants associated with natural water particulate matter. There is an urgent

need for chronic studies which would involve the addition of the contaminant in a form similar to what the organism would be exposed to in various types of natural waters in order to determine what, if any, application factor should be used as a guide to relate acute to chronic exposure.

An appropriate model for most natural water systems is one in which the contaminant is partitioned between the organisms, the solution and the solids present in the system. This type of partitioning makes bioassay studies conducted in the laboratory, in which there is only a two phase system involving organisms and dissolved solids, have limited applicability to determining the toxicity of bioaccumulation of many contaminants in natural water systems. This can be readily demonstrated by a number of previous studies. Dickson (54) showed that both taconite tailings (crushed iron ore) and the red clay sediments from the shores of the western arm of Lake Superior would detoxify copper to trout fingerlings. The experiment involved the establishment of three test aquaria to which was added sufficient copper as a chloride to produce a final copper concentration of 200 ug/l in Lake Superior water. One of the test aquaria received taconite tailings and the other received the red clay sediments. The amount of solids added to each aquarium was approximately 5 g of solids dry weight per liter. To each aquarium was added ten 1.5 inch rainbow trout fingerlings. All trout fingerlings died during the 96-hour exposure in the aquarium to which no solids had been added. No trout fingerlings died in the two aquaria which received the red clay or the taconite tailings.

Measurements of the copper content of the water after the 96-hour period showed that 125 ug/l of copper was still present in the aquarium which had received no solids, while the aquarium that received the taconite tailings had only

20 ug/l soluble copper. These results clearly demonstrate the ability of both natural water sediments and taconite tailings which are iron silicate minerals with large amounts of quartz, to sorb copper and detoxify a copper solution.

#### DREDGED MATERIAL DISPOSAL CRITERIA

The development of meaningful dredged material disposal criteria provides considerable impetus for development of a reasonable approach for interpretation of the significance of sediment bioassay test results. As noted in other sections of this paper, some sediments will show toxicity to aquatic organisms. For example, two to three grass shrimp will die in a four day exposure period when the sediments and water are mixed in a one to four volumetric ratio. The important question that must be resolved is, what is the significance of these results? Should results of this type be of concern in a dredged material disposal-dredging operation? First, it is obvious that the toxicity encountered is not in any way related to the bulk chemical content of these sediments. If it were, all organisms would die in a very short period of time based on the presence of relatively large amounts of many different contaminants which are acutely toxic to aquatic life at the bulk concentrations present in the test system. These bioassays clearly demonstrate the lack of validity of bulk chemical criteria for judging the significance of contaminants associated with dredged sediments.

With respect to openwater dredged material disposal, the toxicity associated with the deposition of contaminated sediments at the designated disposal site is of limited concern. Studies currently underway on behalf of the Corps of Engineers as part of the dredged material disposal research program are showing that there are changes in the

numbers and types of benthic and epibenthic organisms present in the dredged material disposal site. Further, the disposal operations, even though conducted with sediments derived from waters which are classically considered grossly polluted, do not create a biological desert at the disposal site. What is generally observed is a change in the numbers and types of organisms. Even the deposition of clean sand causes a change in the numbers and types of organisms present at a disposal site because of the physical effects of the matrix on the organisms and their habitat.

The toxicity effects should focus on the conditions that prevail at the edge of the deposition area, not on the dredged material disposal mound. Since the disposal mound represents an area which has been set aside for disposal operations, it is analogous to a landfill site in terrestrial disposal of contaminants in that one would expect to find toxicity at the disposal site. However, the concern is whether the materials that are transported from the disposal site have a significant adverse effect on water quality. This should be measured outside the designated disposal area. Such an approach requires some understanding of the rate of conditions of transport that prevail at the edge of the designated disposal area. It would be rare if the conditions that prevail there are not significantly different from those present in the disposal mound immediately after disposal. For example, the concentrations of sediment associated contaminants should, in general, be considerably less than that present in the sediments that were originally dredged, due to dilution. Further, for many contaminants, the characteristic of the environment at the edge of the disposal site should generally be one in which the contaminant would be likely to be less available to affect water quality.



Another factor that must be considered in interpretation of bioassay results designed to evaluate the significance of disposal of contaminated sediments in natural water systems is that the sediments at the edge of the designated deposition zone are probably moving with the currents of the area. Therefore, long term chronic exposure at the specific site by benthic organisms that inhabit that area may be difficult to achieve. In the case of water column effects, it is virtually impossible in typical dredging operations for organisms in the water column associated with the dredged material disposal site, to receive chronic exposure of contaminants arising from the dumping of dredged sediments in open waters. The intermittent nature of most dredged material disposal operations makes it unlikely that most contaminants will be present in the water column in sufficient concentrations and in a sufficient area to cause chronic exposure to planktonic and nektonic organisms. The planktonic organisms encounter the same rapid dispersion as the suspended sediment that is not immediately settled upon disposal and any solutes released from the disposal operation. The nektonic (free swimming) organisms in addition to dilution and dispersion, have the ability to swim in and out of the area. The interpretation of bioassays directed toward water column effects must focus on the proper time concentration relationships that would exist at a particular disposal site and type of operation.

The federal regulations for disposal of dredged sediments (45, 46) currently call for an evaluation of the concentrations of contaminants at the edge of a mixing zone using appropriate water quality criteria. As discussed above, Quality Criteria for Water (1) developed by the US EPA are in general inappropriate for judging the significance of contaminants associated with dredged material disposal at the edge of the mixing zone. The basis for their inappropriateness is that

these criteria are, in general, based on chronic exposure to the most readily available forms of the contaminants in laboratory situations. As noted above, it is virtually impossible to achieve a chronic exposure situation in normal dredged material disposal in open waters. Second, many of the contaminants present at the edge of the mixing zone will be in a particulate form and will probably be in what might be considered the most unavailable form that would normally be encountered. Therefore, finding a concentration of contaminants at the edge of a mixing zone which exceeds the US EPA Quality Criteria for Water released in July, 1976, should not be interpreted as being representative of an adverse environmental impact. Further, any acute bioassays conducted to assess the significance of the contaminants at the edge of the mixing zone should be interpreted in terms of the time-concentration relationship that will be encountered in a particular disposal operation.

The effects of the bioaccumulation of contaminants for dredged sediments are different from toxicity effects. For bioaccumulation, where the concern is the impact on higher trophic level organisms or man, emphasis should be placed on accumulation in organisms at or near the dredged material disposal site which results in excessive concentrations in higher forms of aquatic life. The interest should not be restricted to just measurement of some transfer from the sediment or sediment associated water to a form of aquatic life. There are many situations in which you can readily detect some transfer. However, as with toxicity problems, bioaccumulation problems are related to concentrations.

Almost all aquatic and terrestrial organisms have some readily measurable concentration of chlorinated hydrocarbon pesticides present within them. The mere presence is not the reason for concern. It is presence in sufficient con-

centrations to make the use of fish and other aquatic life unsuitable for food either to man or fish-eating birds that is of concern.

Interpretation of bioaccumulation bioassays must consider the fact that it is rare that fish, shrimp, crab, lobster or many other normally used food species accumulate sufficient concentrations of contaminants to render the food unsuitable for human use or a hazard to other forms of aquatic life, even though many of these organisms live in sediments with elevated concentrations of chlorinated hydrocarbon pesticides, PCB's and heavy metals.

With respect to dredged material disposal, one of the best ways to screen for potential bioaccumulation problems is to collect organisms from the disposal site and examine their tissue content for the contaminants of concern. If the tissue content is less than the known critical levels then bioaccumulation problems can be generally ruled out from all other sources of contaminants. If, however, the concentrations in organisms in the region of the dredged material disposal site exceed the critical levels, then further studies are necessary to ascertain whether these excessive concentrations are derived from dredged material disposal or from other sources. It is important to emphasize that the study of the concentrations of contaminants present in the organisms should take place over about a one year period in which particular attention is given to reproductive cycles, molting of crustaceans, and sex of the organisms, since these have all been shown to be of some significance in determining the significance of bioaccumulation within aquatic organisms.

One of the methods that is sometimes utilized to assess bioaccumulation in solids is the activation of the elements present in the solid phase by nuclear bombardment. Such an approach greatly increases the sensitivity of detecting

transfer from the solids to the organism for certain of the elements that are readily activated. However, rarely is this approach appropriate for real world situations in that if the bioaccumulation cannot be measured with normally used analytical procedures, then the potential for it to be of any major significance in affecting water quality or food quality is small.

A factor that should be considered in any bioaccumulation studies is that of the ability of many organisms to deplete the excessive concentrations of contaminants once the source of the elevated concentrations has been removed. Several studies have shown that the concentrations of contaminants in aquatic organisms will increase in association with dredging. However, within a few weeks or a month or more after the dredging has ceased, the levels within the organisms are back to predredging concentrations. It may be necessary to control the taking of certain organisms at or near dredged material disposal sites during certain times of the year in order to allow the organisms to adjust to normal body burden for contaminants of concern to man when the organism is utilized as food.

The time-concentration relationships of importance in properly evaluating the hazards associated with dredged material disposal should also be considered with natural phenomena such as the conditions that are considered with storms or high currents arising from tides which cause suspension of sediment materials. It is possible that the magnitude of release of sediment associated contaminants accompanying a storm could be significant in terms of a readily measurable amount, yet since the duration of the storm is relatively short, the overall significance to water quality could be small. It is important in considering dredged material disposal operations to examine the relative magnitude of releases from dredging operations compared to other events of man (such as shipping, where the

boat propellers stir up the sediments), storms, high tides, high river discharges, etc. In many situations, if there is release of contaminants as a result of sediment suspension, the relative amount of release from natural or other man-derived activities, would completely overshadow any release associated with the highly localized, relatively short term effects accompanying the dredging.

Evaluation of the environmental hazards associated with dredged material disposal in natural waters should include an evaluation of the environmental hazards associated with alternate methods of disposal. As discussed by Lee (37, 38), many of the alternate methods of disposal that have been adopted as a more "environmentally safe" method of disposal arising from the use of bulk chemical criteria, may actually be more environmentally harmful than the previously used, often less expensive, openwater disposal. A much better mechanism must be developed than exists today for evaluating the related environmental hazards of alternate methods of dredged material disposal where the primary concern is the presence of potentially significant amounts of chemical contaminants in the dredged sediments.

#### CONCLUSIONS

The sediments of natural water systems generally act as sinks for many contaminants which are of concern in affecting water quality. There are conditions, however, where for certain types of solids in a particular environment, sediment associated contaminants can be released to the overlying or surrounding water. Further, some aquatic organisms may sorb certain contaminants from sediments through the organism's intestinal tract, gills and other exterior surfaces, and possibly fins. There is considerable evidence today which indicates that natural water particulate matter may render contaminants nontoxic or otherwise unavailable to affect water quality.

The availability of sediment associated contaminants has been found to be dependent not only on the chemical and biological characteristics of the system, but also on the degree of mixing of the solids and associated interstitial waters with the overlying waters. This mixing, in addition to promoting release, also may render any releases that occur insignificant because of the associated dilution.

No general relationship exists between the bulk contaminant content of sediment associated contaminants and the content in the overlying waters. The bulk contaminant content is dependent not only on the flux of the contaminant to the sediments, but also on the mixing of uncontaminated sediments with the sediments of concern. Numerous attempts have been made to try to develop chemical leaching tests which can selectively extract biologically available forms. With few exceptions, these tests do not extract well defined forms of contaminants with known degrees of biological availability. The only potentially reliable procedures available today for assessment of biological forms are those involving bioassays in which consideration is given to both acute and chronic toxicity and bioaccumulation.

In addition to bioassays of this type, information must be available on the aqueous environmental chemistry of the contaminant in the particular system of concern in order to determine the potential for changes in the degree of availability that may occur at some time in the future. The interpretation of bioassays of availability must be done with caution, with particular attention being given to the time-concentration relationships that will prevail for sediment associated contamination in the area of concern.

Greater impetus will likely soon be found for properly evaluating the significance of sediment associated contaminants arising from the adoption of recently released water quality criteria as state water quality standards. In general, these criteria are much more restrictive than existing standards. The recent passage of the Toxic Substances Act will also require a much better understanding of the significance of sediment associated contaminants than is generally available today. However, the greatest impetus for work in this area will arise from the development of dredged material disposal criteria which are designed to both minimize significant adverse environmental impact and at the same time minimize the cost of dredging and dredged material disposal for maintenance of US waterways.

Recent changes in the criteria governing dredged material disposal provide the opportunity for a more realistic assessment of the significance of sediment associated contaminants than has generally been possible in the past. However, a number of problem areas still remain, the most important of which is the development of the appropriate water quality criteria for use at the edge of a mixing zone associated with openwater dredged material disposal. Further, any meaningful hazard evaluation for dredged sediment associated contaminants must include an evaluation of the potential environmental impact of alternate methods of disposal.

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