

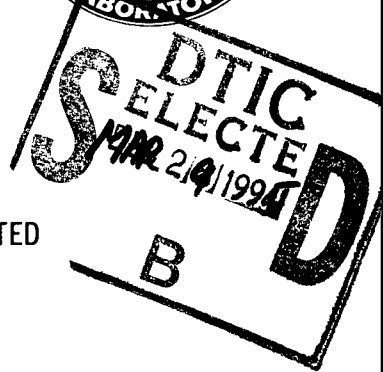
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EEDP-01-18
July 1989



Environmental Effects of Dredging Technical Notes



FACTORS INFLUENCING BIOACCUMULATION OF SEDIMENT-ASSOCIATED
CONTAMINANTS BY AQUATIC ORGANISMS; FACTORS RELATED
TO SEDIMENT AND WATER

PURPOSE: This is the second technical note in a series of four which outlines and describes the principal factors that determine uptake and retention of chemicals by aquatic organisms. The first three notes describe factors related to contaminants, sediment and water, and biota. The fourth note is a glossary and bibliography. The information contained herein is intended to assist Corps of Engineers environmental personnel in activities requiring a working knowledge of concepts and terminology in the subject of chemical uptake, retention, and elimination by aquatic organisms exposed to contaminated sediments.

BACKGROUND: Bioaccumulation is the general term used to refer to the uptake and storage of chemicals by organisms from their environment through all routes of entry. Bioaccumulation includes bioconcentration, which is the direct uptake of chemicals from water alone, and is distinguished from biomagnification, which is the increase in chemical residues taken up through two or more levels of a food chain. Assessments of the potential for bioaccumulation of toxic substances associated with dredged sediments are often required in evaluations of permit requests. Thus, familiarity with the fundamental physical, biological, and chemical factors affecting bioaccumulation is necessary for performing evaluations of the ecological impacts of dredging operations. Additionally, a basic understanding of the concepts and terminology of bioaccumulation is increasingly required of environmental personnel who are involved in dredging and disposal operations which may involve contaminated sediments and legal personnel involved with regulation and litigation.

These notes are intended to serve as a source of basic information and to provide a guide to the scientific literature for each topic discussed. The emphasis is on factors affecting bioaccumulation of sediment-associated chemicals. A brief discussion of each factor is given and a list of references is provided. The references are extensive and frequently bear on more than one topic. An effort has been made to select both historically important works and the most recent research reports in each area. Numbers in parentheses following the subject headings locate the references for each subject. Papers referenced are alphabetized for each subject for easy identification of those most pertinent to the reader's interest. The glossary of technical terminology is presented in the fourth note in the series.

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The subjects discussed in these notes reflect current research for which new findings constantly appear in the literature. Consequently, the discussions and interpretations are based on inference and best judgement regarding the interactions of factors influencing bioaccumulation and represent the best understandings of the authors. Readers are encouraged to consult the literature cited.

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Factors Relating to Sediment

Eh and pH (43-46)

Water or sediment pH (acidity/basicity) and Eh (oxidation-reduction potential) affect the concentration of metals and, to some extent, organic chemicals that are present in bioavailable form in natural systems. Natural waters are weakly to strongly oxidized and mildly acidic to mildly alkaline. Sediments, in contrast, are generally reduced and nearly neutral in pH. In sediments, both iron and manganese are in the divalent, relatively soluble state. Oxidation to the ferric and manganic forms favors formation of insoluble hydrous oxides that can coprecipitate or adsorb other soluble metallic and organic species, thus reducing their bioavailability and potential for bioaccumulation. Insoluble sulfides of many heavy metals that are formed under reduced conditions are rapidly oxidized, when conditions change to aerobic, first to elemental sulfur and then to sulfate releasing the soluble metal ion. The processes of iron and manganese oxidation produce hydrogen ions; sulfide oxidation produces sulfate, and the result of these oxidations is an increase in acidity. Acidic conditions favor the solution of free metal ions but also favor the formation of insoluble hydrous oxides that tend to reduce the concentration of metal ions in solution by adsorbing them. The interactions of these two processes are thus in opposition.

As a general rule, free ions tend to be present in greater abundance and are thus more bioavailable at low pH and under oxidizing conditions. Under reducing conditions, metals are present largely as insoluble sulfides and are not bioavailable. Trace metals associated with sediments that are not bound in the sediment crystal matrix are present either as ions, complexes, or

precipitates. Aqueous concentration of the free ions is regulated by solubility of the precipitates under prevailing conditions of Eh and pH.

Hydrous ferric and manganese oxides (45, 47-55)

Hydrous ferric and manganese oxides form amorphous aggregates that contain large amounts of water. These aggregates have surface areas many times greater than those of clay minerals. Hydrated metal ions and soluble complexes are able to diffuse through the aggregate structures in addition to being surface adsorbed. The effect is analogous to that of an ion-exchange resin in that metals can be concentrated by the aggregates. Rates of adsorption and desorption processes are variable according to conditions of external concentration, pH, Eh, temperature, and to a limited extent ionic strength of solution. Additionally, hydrous oxides which form rapidly when reduced sediments are oxidized may scavenge soluble metals and organic chemicals from the water column by coprecipitation. In low organic carbon substrates, hydrous oxides may also play a significant role in reversible sorption of organic chemicals. Hydrous oxides thus affect bioaccumulation indirectly by influencing the sorption, and thus the bioavailability, of chemicals associated with sediments.

Kinetics of adsorption/desorption (56-65)

Adsorption and desorption of hydrophobic contaminants to and from natural sediments have been described as biphasic processes having a labile (rapid) component and a nonlabile (slow or resistant) component. Sediment particle size, organic carbon content, and relative hydrophobicity of individual chemicals are major factors influencing rates of sorption. About 10-60 percent of the sorption capacity of sediment particles typically appears to be accounted for in the labile fraction; i.e., adsorption or desorption occurs in a matter of minutes. Sorption to or from the remaining sites (nonlabile fraction) takes place over a period of days to weeks in laboratory experiments. Highly hydrophobic chemicals tend to sorb slowly. It has been estimated that chemicals having sediment/water equilibrium distribution coefficients (K_p or K_d) greater than 10^5 will likely require more than a year to completely desorb from a sediment. Kinetics of desorption, then, are of particular interest in estimating the bioavailability of hydrophobic chemicals from sediments. Estimation methods that rely on equilibrium distribution of chemicals among environmental phases may overestimate the bioavailable fraction of a chemical in sediments, depending on the time frame allowed for equilibration. Rates of sorption processes

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involving metals are strongly pH and Eh dependent.

Oil and grease (66-69)

Oil and grease (O&G) is a nonspecific determination often included in sediment chemical inventories. O&G is primarily composed of nonbioaccumulating alkanes; however, in sediments O&G may affect the bioavailability of other chemicals that do bioaccumulate. If present in a sufficiently high concentration to constitute a discrete phase, O&G may concentrate organic chemicals in a manner similar to sediment organic carbon. In effect, O&G could add incrementally to the total organic carbon (TOC) pool in a sediment (see "Sediment organic carbon"), thus reducing the bioavailability of organic chemical contaminants to biota. However, the mass contributed by total O&G in sediment is usually insignificant compared with the mass represented by humic TOC, and can usually be disregarded.

Particle interactions (70-75)

The desorption of contaminants from sediment particulates is apparently affected by physical interactions among the particles. Inverse correlations between particulate concentrations in suspensions of sediments and the partition or distribution coefficients between the particulates and water have been reported for both metals and organic chemical contaminants. These observations appear contrary to equilibrium partitioning theory as partition coefficients are descriptive of absolute conditions and are subject primarily to fundamental changes in physical properties (temperature, pressure, and state), and not to secondary changes in physical conditions, such as concentration. A possible explanation of the "sliding partition coefficient" is that increasing the concentration of particulates in a suspension increases the frequency of collision between particulates. Collisions between particulates bearing organic carbon to which contaminating chemicals are "loosely sorbed" could result in an increase in the solution-phase concentration of contaminants.

In bedded sediments where the particles are at rest, partition coefficients are constant, and for hydrophobic chemicals K_{OC} (see "Sediment organic carbon") describes equilibrium distribution with the interstitial water. However, in dilute suspensions where particulates are highly organic, it is K_{OW} rather than K_{OC} that best describes partitioning. It has been suggested that only about 40 percent of the surface organic carbon of particles makes up the lining of the pores in bedded sediments and thus only 40 percent of the organic carbon by mass

is available for exchange with the interstitial water. This would account for the fact that for most neutral chemicals K_{OC} is about 40 percent of K_{OW} . The hypothesis postulates that reduced surface area within the pores and loose sorption at the surfaces of particulates account for the difference in partitioning.

The particle interaction effect is still not fully explained or accepted in the scientific community. However, the existence of such an effect could have substantial implications for contaminant bioavailability during dredging operations that produce high turbidity. The suspension of high levels of contaminated sediments during disposal operations could conceivably increase the concentration of desorbed chemicals in the water column. Such an effect would amount to an increase in bioavailability for exposed organisms because the amount of unbound chemical present would be greater than could be expected from simple desorption. The effect of particle concentration on solution-phase concentration of chemicals has been modeled, but reported research that sheds light on whether, and to what extent, such processes affect bioavailability under natural conditions is lacking.

Sediment organic carbon (62-63, 76-91)

Sediment organic carbon consists primarily of humic matter and may constitute as much as 10-20 percent of navigation channel sediments. Ranges for harbor sediments are generally on the order of 1-4 percent and may be much less than 1 percent in very sandy sediments. The organic carbon in sediments is primarily responsible for sorption of neutral organic chemicals such as PCBs or PAHs; mineral surface adsorption sites for such compounds become important only when the sediment TOC is very low, perhaps less than 0.5 percent. Organic carbon behaves as though it were an organic solvent in competition with the lipids of biota for distribution of any neutral organic chemicals that are present. For neutral organic chemicals the TOC content of the sediment is the primary determinant of bioaccumulation potential. The bioaccumulation potential of a sediment is the concentration of a chemical in an organism's tissues that would result from exposure to a contaminated sediment if an equilibrium chemical distribution could be established between the sediment and the organism. Bioaccumulation potential is a thermodynamic concept independent of rates of desorption, transport, uptake, or elimination. For a given concentration of a neutral chemical on a whole sediment basis, high TOC content reduces

bioaccumulation potential, and lower TOC proportionally increases it.

TOC provides a basis for normalizing chemical concentration data among sediments of differing origin so that comparisons can be made. This is accomplished by dividing the concentration of chemical in the sediment by the concentration of TOC in the sediment, expressed as a decimal fraction. For example, two sediments, one having 2 ppm PCB and 6 percent TOC, and the other having 1 ppm PCB and 3 percent TOC would both have 33 ppm PCB on an organic carbon-normalized basis and would have the same bioaccumulation potential.*

The concentration of PCB in the interstitial water of the two sediments would also be the same. The partition coefficient that describes equilibrium distribution of neutral organic chemicals between sediment and water, K_{OC} , is calculated using organic carbon normalization of concentration data. In the example above, if the PCB were analyzed as Aroclor 1254 ($\log K_{OC} \cong 6.05$), the organic-carbon normalized concentration of PCB in the sediment (33 ppm) would be divided by $10^{6.05}$ to get 29 ppt (parts per trillion), the expected equilibrium concentration of PCB in interstitial water. Since the solution phase concentration is the most bioavailable, these calculations lead to an estimate of bioaccumulation potential. Application of a bioconcentration factor (BCF) to the interstitial water concentration gives an estimate of chemical concentration that could be expected in an exposed organism. If the appropriate log BCF for a representative organism $\cong 5$, the bioaccumulation potential would be 2.9 ppm.

Metals also associate with the organic carbon fraction of sediments. However, the association is primarily by active bonding with functional groups rather than by passive equilibrium. In the case of metals, there is no simple relationship between TOC and bioavailability or bioaccumulation potential.

Sediment particle size (85, 92-94)

As sediment particle size decreases, the surface area of the particles per unit mass of sediment increases. Increasing the surface area increases the number of negatively charged sites for adsorption, and therefore the number of cations that can be carried on the sediment. The sediment surface also provides sorption sites for neutral organic chemicals that associate through van der

* For a discussion of calculations involving organic carbon normalization and estimates of bioaccumulation potential and bioavailability, see *Environmental Effects of Dredging Technical Note EEDP-01-8*.

Waals/London forces. Sediment particulates may have coatings of humic matter, and most of the organic carbon is associated with the finer-grained material. For these reasons chemical contaminants in sediments are associated primarily with the fine-grained fraction of sediments. Infaunal organisms that dwell in and/or ingest fine-grained material are potentially exposed to higher environmental concentrations of chemicals than are those in coarse-grained sediments, and usually reflect this in their higher bioaccumulation. The same is true of filter-feeding organisms that select small-sized particulates for ingestion.

Sediment suspension (95-104)

Dredging or disposal operations that involve the suspension of sediments can, at least transiently, increase the concentration of associated chemical contaminants in the water column. The increase is not a simple linear function of the mass of sediment suspended because the contaminant-bearing TOC of the suspended sediment fraction is typically higher than the TOC of the consolidated deposited sediment. However, particulate organic matter can act as a scavenger of metals and organic chemicals from solution, thus reducing the bioavailable fraction in the water column.

In sea water the presence of divalent cations (Mg^{++} , Ca^{++}) can cause resuspended particulate, colloidal, and soluble organic matter to flocculate and settle from the water column. Under these conditions, lower molecular weight organic acids can be precipitated as metal fulvates and humates. Trace elements may coprecipitate with flocculated material. Suspension of uncontaminated sedimentary material has been demonstrated to reduce the bioavailability of contaminants by adsorbing them from solution. Conversely, the suspension of contaminated sediments in clean water has been reported to result in bioaccumulation by exposed organisms. In such cases fugacity favors desorption from particulates to the water, and chemicals including PCBs, kepone, lead, and mercury that are bound with the particulates may be made bioavailable.

Factors Relating to Water

Dissolved organic carbon (105-119)

Dissolved organic carbon (DOC) in natural systems is composed primarily of humic substances produced by the degradation of dead plant material. Humic and

fulvic acids make up 40-80 percent of DOC and are defined according to the effects of pH on their precipitation from aqueous solution. These organic acids are structurally complex colloidal and subcolloidal compounds containing large numbers of functional groups (e.g., phenolic, hydroxylic, and carboxylic acid) and straight and branched alkyl side-chains. The functional groups make these large molecules, micelles, and aggregates water soluble and also provide cationic-exchange sites for metal ions in solution. The alkyl chains provide sites for adsorption of hydrophobic chemicals.

The concentration of DOC, or humic and fulvic acids, affects bioavailability and, thus, bioaccumulation of chemicals by aquatic biota. Reduced uptake in aquatic organisms has been demonstrated when metals or neutral organic chemicals are added to water containing uncontaminated humic acids. In the water column high DOC concentrations appear to reduce bioaccumulation by adsorbing neutral organic contaminants and making them less available to organisms. Metals such as copper and zinc may be more or less available depending on salinity and suspended particulate concentrations.

Hardness (118, 120-124)

Elevated concentrations of polyvalent cations, primarily calcium and magnesium, in water reduce the bioavailability of toxic metallic species. The interactions of hardness, alkalinity, and pH have been studied in the context of toxicity, rather than bioaccumulation. However, since bioavailability is a determinant of both toxicity and bioaccumulation of metals, it is reasonable to assume that increased water hardness may also reduce bioaccumulation of metals through a reduction in metal bioavailability. The influence of hardness on bioaccumulation of most organic compounds is negligible.

Salinity (125-137)

Salinity affects bioaccumulation both directly and indirectly. The mechanisms involve effects on physicochemical processes including desorption and solubility as well as effects on physiological processes such as osmoregulation, membrane permeability, and respiration rate and volume. In salt water there may also be competition among free ions for tissue binding sites.

For organic contaminants, especially neutral organics, increasing salinity usually decreases the water solubility of the compounds. Both particulate organic carbon, and dissolved organic carbon are inversely related to salinity. Since bioavailability of neutral organics is also inversely related to TOC, the

decrease in organic carbon with increasing salinity may under some conditions actually enhance bioavailability of neutral organics to organisms.

The relationship of salinity to metal bioaccumulation is more complex and element specific. Metals in solution have been reported to bioaccumulate to higher concentrations as salinity decreases, but the opposite may also be true. Increasing salinity decreases the binding strength of Cd, Cu, Mn, and Zn to inorganic ligands, both by the competition of other major cations for binding sites and by favoring the formation of chloride complexes. The free ion is the form of greatest bioavailability, but the variable amounts of dissolved and particulate carbon (related to salinity) confound the picture by providing sites for complexation. In general, Se solubility and bioavailability are inversely related to salinity; Zn uptake is unrelated to salinity; Cu results are erratic and are especially affected by organic complexation; Pb uptake increases with increasing salinity; Hg binds very tightly to particles and does not respond to salinity changes; and Cd uptake is inversely related to salinity.