From the desk of

9/24/75

W. B. PAPAGEORGE

H. S. Bergen
W. R. Richard
R. E. Keller
D. Wood

The attached report is a chapter from a study by Dr. Fred Lee and his group for the Corps of Engineers. Please treat as confidential. For PCBs it concludes that organic content of a soil is the determining factor in the adsorption of PCBs. The higher the organic content, the more tenacious the PCBs.

DEPOSITION EXHIBIT
Papageorge
90
PENGAD-Bayonne, N. J.

0010415

WATER_PCB-SD0000040432

Draft

PART V: ENVIRONMENTAL IMPACT OF DREDGING ON CHLORINATED HYDROCARBON PESTICIDES AND OTHER ORGANIC CONTAMINANTS

INTRODUCTION

Two of the groups of compounds present in dredged sediments which are of concern because of their potential environmental impact on water quality are the chlorinated hydrocarbon pesticides and chlorinated biphenyl compounds (PCB's). Because of the potential significance of these compounds it was felt that some studies should be conducted in order to determine whether there is any release of these compounds to the water column at dredged material disposal sites. This section of the report presents the results of the studies that have been conducted on the release of chlorinated hydrocarbon pesticides and PCB's from dredged sediments.

The purpose of this phase of the project is to evaluate the validity of the Elutriate Test (now required by the US EPA and the Corps of Engineers) as a method of estimating the release of organic contaminants from dredged material to the water column. Specifically, it attempts to determine whether there is significant release of the chlorinated hydrocarbon pesticides and PCB's listed in Volume I of the 1973 US EPA Proposed Criteria[49] and, if so, to identify the factors which could affect the release of these compounds from the sediments.

The release of chlorinated hydrocarbons was not investigated until the latter phase of this study period. Therefore, this aspect of the project did not progress to the same extent as the study of the release of other contaminants during the Elutriate Test. It should also be noted that analyses of organic compounds in sediments require much longer periods of time per sample than analyses of nutrients and

WATER_PCB-SD0000040433

heavy metals. Therefore, the number of samples that could be processed for pesticides during this test was greatly reduced.

LITERATURE REVIEW*

The presence of potentially toxic organic compounds, notably chlorinated hydrocarbon pesticides and PCB's, in many sediments has led to some concern that these materials may be released when dredged sediments are disposed of in open water. The US EPA and Army Corps of Engineers developed the Elutriate Test (Keeley and Engler[5]) to determine if a dredged sediment would have an adverse effect on water quality upon disposal in open water. A description of the Elutriate Test and modifications required for determination of organic compound release, is given in Appendix I. The purpose of this phase of the study is to evaluate the validity and practicality of the Elutriate Test for determining organic contaminant release, and to identify factors which significantly affect the test.

Bulk Analysis Criteria

Bulk analysis had been used by the US EPA to determine if a dredged sediment could be dumped in open water. The US EPA dredged material disposal criteria which are related to the organic content of a sediment are chemical oxygen demand, total volatile solids, and hexane-extractable oil and grease. The problems with these criteria have been discussed by Lee and Plumb.[2] The oil and grease criterion has also been discussed by Lee et al.[62] In brief, the attempt to use sanitary wastewater parameters to evaluate natural waters and sediments, for which they are not

---

*This literature review has been designed to supplement the literature review on this topic by Lee and Plumb.[2]

0110447

WATER_PCB-SD0000040434

necessarily valid, has led to the problems discussed in the above papers.

Because bulk analysis of a sediment does not truly evaluate the potential for release of a compound into solution, the Elutriate Test was developed. A number of studies lend support to this belief. Boucher and Lee[91] found that 70 percent of lindane sorbed on natural aquifer sands was leached by three washes with distilled water, but less than 20 percent of sorbed dieldrin was released. Huang and Liao [92] found that about 25 percent of dieldrin sorbed on pure montmorillonite could be leached into distilled water, but that very little DDT or heptachlor could be leached. Nissenbaum et al.[93] found no correlation between the organic matter in a sediment and that in the interstitial water.

Significance of Organic Materials in Water

Both natural and synthetic organic compounds may be significant in natural water for a number of reasons. The classical reason for concern about organics is that they can increase biological oxygen demand, resulting in oxygen depletion and possible resultant damage to aquatic life. Another possible effect of organics release is the chelation of heavy metals, which would lead to higher metal concentrations in the water than would be expected from the solubility of the metal. Certain metals have been associated with organic material in natural water (Duce et al.[94]). There is evidence that some chelated metals are less toxic to organisms (Steeman-Nielsen and Wium-Andersen [95]), and that chelated micronutrients such as iron are more available to algae for growth (Siegel [96]).

Natural organic matter may promote biological activity in ways other than chelation of trace metals. Some algae require organic micronutrients such as B_{12} for growth, and some invertebrate larvae develop better in one water type

WATER_PCB-SD0000040435

than another, a phenomenon which has been attributed to the organic content of the water (Raymont [97]). Humic material has been found to stimulate growth of marine dinoflagellates in synthetic culture mediums (Prakash and Rashid [98]). This effect seems to have been due to more than chelation of metals, since the chelator EDTA was already present in the culture media.

Perhaps the greatest reason for concern about organic compounds in natural waters is that some of them are toxic to aquatic and marine organisms. For example, some steroids are toxic to minnows (Miller and Mumma [99]). Petroleum deposited in sediments can be taken up by benthic organisms, although there does not appear to be any concentration in the food chain (Scarratt and Zitko [100]). However, some petroleum fractions are more toxic than others. Aromatic and light hydrocarbons are the most toxic, while weathered petroleum is relatively harmless (Nelson-Smith [101]). Another possible effect of oil is the concentration of pesticides, either in surface slicks (Duce et al.[94]) or in sediments (Hartung and Klinger [102]). Pthalate esters, commonly used as plasticizers, can interfere with reproduction of fish. They have been identified in a number of species of fish from North American waters (Mayer et al.[103]).

The group of compounds that has received perhaps the greatest attention recently is the chlorinated hydrocarbons, which include polychlorinated biphenyls (PCB's) and the pesticides DDT, aldrin, endrin, and lindane. These compounds are significant not only because of their toxicities in water, but also because they accumulate in organisms at concentrations much higher than those in the surrounding water (Hannon et al. [104]). It has long been thought that this concentration was due to magnification within a food web; however, it has recently been suggested that the concentration is due to partitions between lipids in an organism and the

0010449

WATER_PCB-SD0000040436

surrounding water (Hamelink et al.[105]). Algae (Hamelink et al.[105]), crustaceans (Hamelink et al.[105]; Johnson et al.[106]), and oysters (Westlake and Gunther[107]) are all capable of accumulating DDT directly from water. While accumulation from water may be important for invertebrates at lower trophic levels, there is evidence that food web magnification is the more important mechanism for some fish in higher trophic levels (Macek and Korn[108]).

The reports on the occurrence of chlorinated hydrocarbons and other compounds in organisms are too numerous to be covered here; however, mention of a few of these demonstrates the range of their occurrence. PCB's have been found in fish from the Milwaukee River in Wisconsin (Veith and Lee[109]) and in zooplankton from the Atlantic Ocean off North America (Risebrough et al.[110]). Dieldrin and endrin have been detected in oysters from estuaries of the Gulf of Mexico (Rowe et al[111]). DDT and its metabolites, DDD and DDE, have been found in oysters (Rowe et al.[111]), crayfish, aquatic insects (Hannon et al.[104]), freshwater algae, zooplankton, and fish (Hamelink et al.[105]). Bacteria (Leshniowsky et al.[112]) and several species of algae (Hill and McCarty[113]; King et al.[114]) sorb chlorinated hydrocarbons from solution very efficiently.

Factors Affecting Exchange Between Sediment and Water

A number of factors may affect the exchange of an organic compound between sediment and water. These include: the pH, salinity, temperature, and organic composition of the receiving water; the composition and organic content of the sediment; redox conditions of the water and sediment; the concentration of the compound in the water and sediment; and the chemical nature of the compound. The time of contact and the solid-liquid ratio of the sediment and water are also factors which could affect exchange. Some of these factors are discussed in subsequent sections.

0010450

WATER_PCB-SD0000040437

pH of Water

Luh and Baker[115] found that m-aminophenol and 2,4-diaminophenol were sorbed at acidic, not basic, pH values by montmorillonite and kaolinite. Phenol, m-cresol, 2,4-dichlorophenol, valeric acid, and n-hexanoic acid were not sorbed at any pH. The same investigators[116] found that maximum desorption of pyridine occurred at pH's of 1 and 11; minimum desorption occurred at pH 4.0-5.5. Schnitzer[117] found that sorption of a soil fulvic acid fraction on montmorillonite decreased with decreasing pH. The decrease was greatest between pH 4 and 5, which corresponds to the pH of the fulvic acid carboxylic groups.

In general, it appears that greatest desorption of organic compounds from clay minerals occurs at basic pH values at which organic acids are ionized and, thus, electrostatically repelled from the negatively charged clays. This effect may be more noticeable for acids than for bases, since increasing pH generally increases solubility of organic acids but decreases solubility of organic bases. In natural sediments, electrostatic interactions with clay minerals may be largely overshadowed by other factors, such as organic-organic interactions and organic-iron oxide interactions.

The effect of pH on sorption and desorption of neutral organic molecules is not clear. Boucher and Lee[91] report that the pH range normally found in an aquifer had no significant effect on the sorption of lindane and dieldrin by unconsolidated aquifer sands. Huang[118] found that within the pH range of 6 to 10, the sorption of dieldrin by montmorillonite decreased slightly with increased pH.

Rowe et al.[111] studied the sorption and release of dieldrin by estuarine sediments. They found that after one hour only 2 percent of the dieldrin in solution had been sorbed at pH 7.8 to 9.0, while 25 percent had been sorbed at pH 3.8 to 4.2, and 23 percent at pH 6.7 to 7.1.

0010451

WATER_PCB-SD0000040438

After three days, about 60 percent had been sorbed at all three pH values. A difference was again observed after seven days, however, with 2 percent sorbed at pH 7.8 to 9.0, 10 percent at pH 3.8 to 4.2, and 23 percent at pH 6.7 to 7.1. Although the effect of pH on sorption and release of neutral organic compounds is probably slight within the pH range usually found in natural water, the study by Rowe et al.[111] indicates that it should be further investigated.

Salinity

Salinity and changes in salinity may have an effect on sorption-desorption because of ion exchange, alteration of clay crystal structure, or flocculation of organic matter and clay particles. Wang et al.[119] found no difference between sodium and calcium montmorillonite for the adsorption of parathion, which indicated that the ionic form of a clay does not influence its sorption characteristics. Huang[118] determined the sorption of dieldrin by montmorillonite at sodium chloride concentrations of 3.0, 0.3, and 0.03 percent (representing approximate salinities of marine, estuarine, and freshwater environments, respectively). Variations in sorption and retention were slight. Greatest sorption and desorption occurred at 3.0 percent sodium chloride, followed by 0.03 percent, and 0.3 percent; thus, it appears that the tendency for sorption of dieldrin by montmorillonite is slightly stronger at marine and freshwater salt concentrations than at estuarine concentrations.

Rowe et al.[111] studied the effects of salinity (ranging from 9 to 25 parts per thousand) on the sorption and release of dieldrin and aldrin by estuarine sediments. They found that maximum sorption after one day occurred in the salinity range of 13 to 17 parts per thousand for both dieldrin and aldrin. After seven days, however, there was no variations in sorption of aldrin with salinity; minimum

0010452

WATER_PCB-SD0000040439

sorption of dieldrin occurred in the 13 to 17 parts per thousand salinity range.

All of these studies show some variations with salinity, but the results are contradictory. Further work should be done to establish the effects of salinity and salinity changes on leaching and sorption of organics.

Temperature

Baker and Luh[120] found that sorption of pyridine on montmorillonite and kaolinite was twice as great at 1°C as at 24°C. Boucher and Lee[91] determined that within the temperature range normally found in a Wisconsin aquifer, there was no significant temperature effect on the uptake of lindane and dieldrin by aquifer sands. Huang[118] found that in the range of 10°C to 30°C, sorption and desorption of dieldrin by montmorillonite was not significantly affected by water temperature. These studies indicate that in the temperature range normally found in natural waters, temperature does not have a very significant effect on sorption and desorption of organics.

Organic Content of Water

Organic material in the receiving water may have an effect on sorption and desorption of a compound, either by competing for sorption sites or by affecting the solubility of the compounds. Huang[118] found that the presence of glucose, alanine, stearic acid, and soluble organic matter from domestic sewage had no effect on the uptake of dieldrin, heptachlor, and DDT by montmorillonite and illite. The presence of rhodamine B increased the sorption of parathion by kaolinite and montmorillonite and illite, but methylene blue, phenol, and organics from natural water had no effect (Wang et al.[119]). Boucher and Lee[91] found that naturally occurring organic material in water decreased the sorption of dieldrin on an aquifer sand but had no effect on the

WATER_PCB-SD0000040440

sorption of lindane. Pthalate esters have been found associated with fulvic acid extracted from soil. The pthalates were strongly bound and could be separated from the fulvic acid only after methylation and adsorption of the fulvic acid on aluminum oxide (Ogner and Schnitzer [121]). Wershaw et al.[122] showed that sodium humate increased the solubility of DDT by a factor of 20 to 40, and that humic acid strongly sorbed 2, 4,5- T from solution. Poirrier et al.[123] found that DDT tended to associate with colored iron-organic colloids (<10 nm diameter), and that DDT was concentrated by the colloids by a factor of at least 16,000. The association of compounds such as DDT with naturally occurring soluble or colloidal organic material could be a mechanism for their solubilization and mobilization; however, it could also lead to their deposition if the organic matter were to become sorbed or be flocculated by changes in salinity or redox conditions.

From these studies, it is apparent that organics in water can affect the sorption, desorption, and solubility of an organic compound. The effect depends on the type of compound being sorbed, the nature of the organic material in the water, and the characteristics of the sediment.

Organisms

Organisms in natural water can also affect the uptake and release of organic material. Bacterial floc is able to sorb aldrin from solution with about the same efficiency as natural sediments (Lechniowsky et al.[112]). Algae are able to sorb chlorinated hydrocarbon pesticides from solution 10 to 100 times more effectively than either bentonite clay (Hill and McCarty [113]) or natural lake sediment (King et al.[114]). Thus, water disposal of dredged sediments containing pesticides could result in sorption of the pesticides by algae. These pesticides might then either be passed on to organisms feeding on the algae or deposited in the sedi-

0010454

WATER_PCB-SD0000040441

ment upon death of the algae.

Composition of Sediment

Both the organic and inorganic composition of a sediment could affect its ability to sorb and release organic material. Different pesticides may be associated with different types of particles. For example, Pfister et al.[124] fractionated particulate matter isolated from natural water and found that lindane was associated with the heavier inorganic material, while aldrin and endrin tended to be associated with the less dense organic fractions. DDT, DDD, and DDE were associated with all fractions.

The clay mineral content is likely to be one of the most significant inorganic characteristics of a sediment. Routh[125] found that the concentration of DDT in river sediments was strongly correlated to the amount of fine material in the sediment, and Lotse et al.[126] found a positive correlation between clay content and lindane sorption by lake sediments. King et al.[114] showed that soil with a high clay content sorbed about twice as much lindane and parathion as sandy soil.

The type of clay mineral present may also be important. Bader[127] found that the effectiveness of clays for sorbing alanine, sucrose, fructose, succinic acid, and oxalic acid decreased from montmorillonite to illite to kaolinite. Baker and Luh[120] showed that more pyridine was sorbed by montmorillonite than by kaolinite. For DDT sorption, the relative capacities decrease in the following order: montmorillonite > kaolinite ≈ illite. For heptachlor, the order is montmorillonite ≈ kaolinite > illite; for dieldrin, the order is illite > montmorillonite > kaolinite (Huang and Liao[92]). Sorption capacity for the PCB Aroclor 1254 decreased in the order illite > montmorillonite > kaolinite (Haque et al.[128]). For no. 2 fuel oil, consisting of a mixture of hydrocarbons, sorption capacity decreased in the

0010455

WATER_PCB-SD0000040442

order bentonite > kaolinite > illite > montmorillonite (Meyers and Quinn [129]). In general, for the more polar compounds, sorption capacity decreases with decreasing cation exchange capacity. For clay minerals, cation exchange capacity decreases in the order montmorillonite (0.8 to 0.4 meq/g), illite (0.1 to 0.4 meq/g), kaolinite (0.01 to 0.1 meq/g) (Berner [130]). There is no apparent correlation of sorption with cation exchange capacity for chlorinated hydrocarbons; for the fuel oil hydrocarbons there is an inverse correlation.

The organic content of a sediment also affects its sorption-desorption characteristics. In sediments containing petroleum hydrocarbons, Hartung and Klinger [102] calculated that the partition coefficient between sedimented oil and the overlying water was one to eight million for DDT in the hydrocarbon phase. Lotse et al.[126] found a positive correlation between organic content of lake sediments and lindane sorption capacity. Wang et al.,[119] however, found that partially removing organic matter from a lake sediment by hexane extraction increased the sorption capacity of the sediment for parathion. Rowe et al.[111] reported that the initial uptake of dieldrin and endrin was higher in sediments containing organics, but that after seven days there was little difference between the amounts sorbed by organic and inorganic sediments. A PCB mixture was sorbed more by a soil containing 3.1 percent organic matter than by pure clay minerals (Haque et al.[128]). Although organic matter in sediment enhances sorption of chlorinated hydrocarbons, the opposite may be true for petroleum hydrocarbons. Meyers and Quinn[129] found that oxidizing the organic matter of a marine sediment with hydrogen peroxide approximately doubled the sediment's sorption capacity for hydrocarbons. This result may have been due to other effects of the oxidation process, however.

0010156

WATER_PCB-SD0000040443

Results could be attributed to the solubility of hydrocarbons, fats, and humic acids.

In 1972, a US Government interdepartmental task force reported that there were few data on the removal, disappearance, and sequestering of PCB's in soils or bottom sediments of rivers, lakes, estuaries, or the ocean. Available data at that time suggested that sediments may be a major reservoir of PCB residues. Experimental data also indicated transfer of PCB residues from the sediment to the overlying waters.

Veith and Lee [131] reported the occurrence of PCB's in water from the Milwaukee River at concentration levels of 0.1 µg/l. Their study also showed that many of the PCB's in the water were associated with suspended solids in the water and were removed during the water treatment and filtration process. Haile and Lee[132] reported the presence of PCB's in Lake Ontario water and sediment at concentrations of 55 µg/l and 120 µg/kg, respectively. Their water analysis results did not discriminate between dissolved and particulate fractions.

Haque et al.[128] investigated the water solubility, adsorption from aqueous solution, and vapor phase behavior of Aroclor 1254. (The Aroclors represent a series of commercial formulations of PCB's manufactured by Monsanto Company.) Aqueous solubility at room temperature was reported as ≈56 µg/l. Adsorption experiments showed that the amount sorbed depends upon the nature of the sorbing surface. Soil with high clay and organic content was found to sorb much larger amounts than sand. The study did not identify the nature of the organic content in the soil.

0010457

WATER_PCB-SD0000040444

Redox Conditions

Conditions in sediments are often reducing; thus, metals such as iron can occur in the soluble, reduced form. When these sediments are brought into contact with oxygenated water, however, the metals are oxidized and precipitated from solution. This precipitation can cause flocculation and coprecipitation of other materials, including organics. Sridharan and Lee[133] found that flocculation with ferric chloride removed 100 percent of the color from a highly colored lake water. They also found that flocculation by iron would at least partially coprecipitate phenol, citric acid, and cycline from both natural fresh water and distilled water. However, it did not remove dextrose, alkylbenzene sulfonate, or formaldehyde. There was a positive correlation between the organic content of the water and the amount of phenol precipitated, a negative correlation for citric acid, and no correlation for glycine. Flocculation with ferric sulfate removed about 10 percent of the soluble COD from Mississippi River water above St. Louis (Dornbush and Ryckman[134]).

Other lab studies on coagulation showed that iron was not effective in removing 2,4-D organic esters of 2,4-D, and 2,4-DCP from solution (Faust and Aly[135]). In studies with a model sewage plant, Robeck et al.[136] found that coagulation with alum removed almost all DDT, 50 percent of the dieldrin, 35 percent of the aldrin, but none of the lindane or parathion. The lime-soda process followed by flocculation with iron was less efficient; about 50 percent of the DDT and less than 10 percent of the dieldrin were removed. As noted previously, pesticides associated with naturally occurring organic matter, such as that responsible for color, may be removed if the organic matter is precipitated.

0010458

WATER_PCB-SD0000040445

Another effect of redox conditions is observed in the degradation of organic compounds. Many naturally occurring lipids, such as sterols, are more readily degraded in aerobic conditions than in anaerobic conditions (Turfitt[137]). The opposite appears to be true for some pesticides, however. Hill and McCarty[113] demonstrated that DDT, lindane, and aldrin degrade more rapidly under anaerobic conditions than aerobic, and that heptachlor epoxide and dieldrin were equally persistent in both environments. Thus, if a sediment containing DDT were removed from an anaerobic environment and placed in an aerobic one, the persistence of the DDT might be increased.

Liquid-Solid Ratio

Lotse et al.[126] report that the liquid-solid ratio is the most significant variable in the degree of sorption of lindane by lake sediments. Luh and Baker[116] found that for a fixed amount of clay, the amount of pyridine desorbed was directly related to the volume of water. Huang and Liao[92] showed that the higher the clay concentration in water, the greater the amount of pesticide sorbed or released. The relationship was not linear, however. For every order of magnitude increase in solids concentration, the amount of material sorbed or released approximately doubled. Thus, although higher solids concentration will result in a greater change in the aqueous concentration of the compound in question, lower solids concentration will result in higher uptake or release of a compound per gram of sediment.

Time of Contact

Most investigators report that sorption and desorption of pesticides occur rapidly and that there is little change

0010459

WATER_PCB-SD0000040446