DREDGED MATERIAL
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LITERATURE REVIEW ON RESEARCH STUDY FOR THE DEVELOPMENT OF DREDGED MATERIAL DISPOSAL CRITERIA

by

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FOREWORD

The work described in this report was performed under Contract No. DACW-39-74-C-0024, titled "Reasearch Study for the Development of Dredged Material Disposal Criteria" dated August 21, 1973, between the U.S. Army Engineer Waterways Experiment Station (WES), Vicksburg, Mississippi, and Texas A & M Research Foundation - Texas A&M University. The research was sponsored by the Office, Chief of Engineers (DAEN-CWO-M) under the civil works research program, "Dredged Material Research Program."

This report is a literature review and discussion of the factors influencing the release of chemical contaminants from natural water sediment with emphasis on review of the Elutriate Test.

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SUMMARY

Some of the sediments that are dredged for waterways im-
provement are contaminated with municipal, industrial and
agricultural wastes and runoff. This contamination consists
of potentially significant amounts of chemical toxicants and
growth stimulants. It is conceivable that under certain conditions
the contaminants present in these sediments could have an adverse
effect on environmental quality at both the dredging and disposal
sites. One area of concern is the release of these contaminants
from the solids. Such a release could be adverse to water quality
in the water columns and adjacent areas at both sites. In order
to protect and where possible enhance environmental quality, a
test or tests need to be developed that can be used on samples of
sediment that is scheduled to be dredged in order to determine
whether or not release of potentially significant amounts of
the contaminants present could occur under the various methods
used for dredging and disposal of dredged material. This report
discusses the literature pertinent to this topic area with emphasis
on the development of a standard Elutriate Test that could be used
to detect potential water-column quality problems at the dredging
and disposal sites.

A review of the literature on the release of chemical contami-
nants from dredged material and natural water sediment has shown
that the bulk chemical composition is not a useful index of
potential environmental quality problems for waters that come
in contact with the sediment. Chemical constituents exist in
sediment in a wide variety of forms, many of which are not avail-
able to aquatic organisms. In addition, for deposited sediment,
the primary factor often controlling contaminant release is the
mixing or degree of agitation of the sediment with the overlying
waters.

It has been generally found that natural water sediment
tend to be sinks of chemical toxicants where toxicants present
in the water column become associated with particulate matter
and become incorporated in the sediment. Eventually, a con-
taminated sediment particle will become buried in the sediment
so that it becomes part of the historical sediment and thereby
be removed from interaction with the overlying waters. A key
part of the sediment chemical contaminant holding capacity is
the hydrous metal oxides of iron, manganese and aluminum. It
has been found that these species tend to prevent the release
of chemical contaminants during dredging operations and dis-
posal.

The Corps of Engineers and the U.S. Environmental Protection
Agency (EPA) have developed an Elutriate Test which is designed
to detect any significant release of chemical contaminants in
dredged material. This test involves the mixing of one volume
of the sediment which is to be dredged with four volumes of
the disposal site water for a 30-minute shaking period. A
one-hour settling period followed by appropriate filtration or
centrifugation is used to determine the release of potentially
significant chemical constituents from the sediment. A review
of the literature on the leaching of contaminants from
dredged material and sediment shows that a wide variety of
factors could affect the results of the Elutriate Test. These
factors include: solid-liquid ratio, time of contact, pH,
dissolved oxygen concentration, agitation, particle size, han-
dling of solids, characteristics of water and sediment, and
solid-liquid separation. It is apparent that a considerable
amount of research is needed on the significance of these
factors in influencing the Elutriate Test results for a wide
variety of sediments that are likely to be dredged. From these
studies it should be possible to develop a modified Elutriate
Test which would be relatively insensitive to minor modifications
in test procedures yet simulate to a reasonable degree the

release of chemical contaminants in the sediment that may take place at the dredging and disposal sites during normal dredging operations.

The standard Elutriate Test requires that if at any time the soluble chemical constituents of selected contaminants in the elutriate exceed 1.5 times the ambient concentration in the disposal site water, special conditions will govern the disposal of this dredged material. The 1.5 factor is not intended to be a critical concentration increase which would signify significant environmental damage in the disposal site water column. It should be used to indicate that release does occur and this release deserves further consideration in order to ascertain its potential significance with respect to environmental quality. The proper interpretation of the amount of release that occurs requires consideration of the contaminant assimilative capacity in the disposal site water column relative to the critical concentration for this contaminant to selected organisms in the water column. Because of the intermittent nature of normal dredged material disposal and the high dilution available in almost any open-water disposal operation, it is improper to apply water-quality criteria based on chronic continuous exposure of the organism to the contaminant. Also, the 96-hour LC_{50} commonly used in the water pollution control field to detect acute lethal toxicity should not be used. The proper approach for bioassays is to estimate the concentration-time relationship that will exist in the water column at the disposal site for soluble contaminants released from the dredged material. From this relationship a bioassay should be conducted in which selected organisms would be exposed to a similar concentration-time relationship. It should be emphasized that lesser importance should be attached to toxicity to planktonic organisms because of their high reproductive capacity. Some toxicity or inhibition of phytoplankton growth at the disposal site may be of no significance in the water body as a whole due

to the fact that nutrient-limited populations which did not grow at the site may compensate for this lack of growth by increased growth in nearby waters.

One of the areas of potential concern in the disposal of chemically contaminated dredged material is the possibility of toxicity of the chemical contaminants to benthic organisms at the disposal site. The Elutriate Test is not designed to detect potential problems of this type. This test is designed to detect water column problems. Since the physical and chemical environments that occur at the disposal site water column and sediment are likely to be markedly different, another type of test may be necessary in order to detect potential toxicity problems to benthic organisms. A laboratory test based on the chemical characteristics of the interstitial waters that would be formed at the disposal site is suggested.

It is important to emphasize that the conventionally developed water-quality criteria such as those recently proposed by the U.S. EPA (October, 1973) are not suitable to judge the toxicity of chemical contaminants present in solid form. Further, there is little or no basis to use an application factor of 0.01 that is commonly used for soluble solutes to relate acute lethal to chronic sublethal toxicity where the acute lethal toxicity is caused by contaminants present in solid form. Further research is needed in this area in order to define the proper application factor that should be used under these conditions.

The key to the successful development of an Elutriate Test will be a number of intensive studies in which the results of the tests are compared to the actual environmental impact of the chemical contaminants present in the dredged material. It is recommended that as soon as some of the key factors influencing the response of the Elutriate Test are evaluated, detailed large scale field studies be initiated in order to develop an empirical correlation between the results of the Elutriate Test and actual environmental impact.

EXECUTIVE SUMMARY

Chemical contaminants present in natural water sediment that is to be dredged represent a potential hazard to terrestrial and aquatic ecosystems that receive the dredged material. There is need to develop criteria that can be used to evaluate the potential environmental impact of dredging and dredged material disposal.

DREDGED MATERIAL DISPOSAL CRITERIA

There is little or no evidence to support the premise that there is a relationship between bulk-sediment composition and the pollutional tendencies of the sediment. To base dredged material disposal criteria on a bulk analysis of sediments is technically unsound because it assumes that all forms of each chemical have an equal impact on the environment. Also, the use of existing arbitrary dredged material disposal criteria based on bulk sediment analysis has required the expenditure of large amounts of additional funds.

The parameters on which bulk dredged material disposal criteria have been established are parameters normally used in evaluating the environmental impact of domestic and industrial wastewaters, and it is unlikely that a relationship exists between environmental impact of a particular dredged sediment and a particular numerical value for any of these parameters in sediment. The chemical oxygen demand (COD) test is nonspecific and measures a variable undefined fraction of the organic and inorganic compounds present in sediment. It is recommended that the COD test not be used to develop criteria or to characterize pollutional characteristics of sediment. Also, total Kjeldahl nitrogen should not be used as a dredged material disposal criteria because it is not the total Kjeldahl nitrogen concentration in the sediment that is important, but rather it is the amount of ammonia or oxidized

forms of nitrogen arising from the Kjeldahl nitrogen that is potentially significant. Volatile solids contents have sometimes been advocated as a measurement of the pollutional characteristic of dredged material. However, this procedure measures an undefined mixture of organic and inorganic compounds in sediment and, as such, provides little or no information on the pollutional tendencies of dredged material.

One of the potential problems associated with chemical contaminants in sediment is the release of chemicals to the water column at both dredging and disposal sites. There is a need to develop one or more simple, relatively inexpensive testing procedures that can be used to evaluate the potential significance on water quality of chemical contaminants in sediment that is to be dredged. The Elutriate Test devised by the U. S. Environmental Protection Agency and the U. S. Army Corps of Engineers offers some potential to evaluate water quality problems associated with chemical release from dredged material.

FACTORS AFFECTING THE ELUTRIATE TEST RESULTS

The use of the Elutriate Test to regulate dredged material disposal is superior to bulk-analysis criteria since it recognizes that all chemicals in sediment are not equally available to aquatic organisms. However, the 1.5 factor specified in the Elutriate Test should be used only as an indicator of contaminant release and not as a standard that can be used to determine environmental impact.

The release of dissolved solids during laboratory leaching studies will be influenced by the liquid-to-solid ratio used in the test. Because of the rapidly changing liquid-to-solid ratio that occurs at an actual dredged material disposal site, this parameter should be extensively studied in order to evaluate the significance of the liquid-to-solid ratio on Elutriate Test results.

Since the amount of chemical contaminant that may be leached

from dredged sediment will be influenced by the contact time between sediment and water, the chemical contaminant of interest, and the chemical form of the contaminant, studies should be initiated to evaluate the appropriateness of the 30-minute shaking period and 1-hour settling specified in the Elutriate Test. These studies should be based on the period of time that dredged sediment is likely to remain in suspension as a result of dredging and dredged material disposal operations.

Changes in pH during the Elutriate Test could have a pronounced effect on the release of chemical contaminants from dredged sediment. However, the magnitude of the effect will not be the same for each chemical parameter. It is suggested that pH be measured during the Elutriate Test, but no attempt should be made to control the pH unless test conditions are markedly different from prevailing pH conditions at the dredging and disposal sites.

The presence or absence of dissolved oxygen will influence the chemical form, solubility, and mobility of several elements. Since dredged sediment could have a direct effect on dissolved oxygen concentrations during the Elutriate Test, this could have an indirect effect on the release of chemical contaminants from the sediment during the Elutriate Test. It is suggested that an attempt be made to ensure that the oxygen concentration during Elutriate Test is representative of the oxygen status at the dredging and disposal sites during dredging operations.

Under proper conditions, the process of agitation will control the rate of release of dissolved solids from particulate matter. The degree of agitation in the Elutriate Test should be sufficient so that the release of any chemical contaminant from dredged material is controlled by chemical availability and not diffusion.

A delay between collection of dredged material and running of the Elutriate Test can result in chemical and physical changes in the sediment. This could have a significant effect on Elutriate Test results. For example, an oxidation of the sediment would

inhibit or reduce the release of reduced forms of iron and manganese. This could also have an indirect effect on other chemical contaminants since hydrous oxides of these metals influence the mobility and release of other contaminants.

Another factor that could affect the results of the Elutriate Test is the characteristics of the water used in the test. This could be important during dredging operations in complex hydrologic areas of rapidly changing water compositions such as river mouths and estuaries. Consequently, it may be desirable to explore the possibility of developing a standard Elutriate Test water or to utilize extraction procedures presently in use in the soil fertility field.

Filtration and centrifugation steps should be properly evaluated to ensure that Elutriate Test results reflect release from dredged sediment and not contamination due to sample handling or processing. In addition, it may be necessary to distinguish between colloidal and dissolved forms of chemical contaminants released from dredged material in order to properly evaluate the Elutriate Test results in terms of environmental impact.

PRACTICABILITY OF THE ELUTRIATE TEST

The Elutriate Test can be performed in a reasonable period of time at a reasonable cost and provides a better estimate of chemical availability in sediment than the bulk-analysis approach formerly used to evaluate dredging activities. Any modifications of the Elutriate Test must consider economic and technical aspects of the test.

INTERPRETATION OF THE ELUTRIATE TEST RESULTS

The Elutriate Test is designed to detect the release of chemical contaminants from dredged sediment suspended in a water column. It will not detect biological problems due to the physical presence of dredged material in the water column, effects of

solids deposition on aquatic organisms, or the effect of chemical contaminants on dredged sediment on benthic fauna. Proper interpretation of Elutriate Test results requires consideration of existing concentrations of the contaminants of interest at the disposal site, potential concentration increases at the disposal site, and the critical concentrations of each parameter for aquatic life rather than a concentration increase percentage under laboratory conditions.

Exceeding the 50 percent concentration increase presently specified in the Elutriate Test does not mean that water-quality changes or deteriorations will occur. As an example, manganese increased by 1800 percent in Lake Superior water when taconite tailings were subjected to the Elutriate Test, and yet the daily discharge of tailings into Lake Superior for 18 years has not produced a measurable change in the manganese concentration of the lake.

In attempting to interpret Elutriate Test results, it would be improper to apply water-quality criteria recently recommended by the EPA to regulate dredged material disposal. The criteria are based on a 96-hour bioassay in which the organisms are exposed continuously to a soluble chemical species. However, although concentrations at some disposal sites may exceed the water-quality criteria, this condition does not exist for 96 hours. Also, the disposal site concentrations will be composed of soluble plus particulate which will not have the same biological effect as an equal concentration entirely in the soluble form. It is recommended that dredged material disposal criteria should be based on a time-concentration-toxicity relationship for each chemical constituent, which is developed from short-term bioassays with selected organisms.

WATER-QUALITY CRITERIA FOR PARTICULATE SPECIES

Some of the recommended EPA-proposed water-quality criteria were obtained from acute bioassay results based on the use of an

empirical application factor. It is unlikely that the same factor used to relate the acute and chronic toxicity of a specific soluble chemical can be validly applied to acute toxicity levels of particulate species in order to determine chronic toxicity levels of the particulate species. Particulate matter will often increase the assimilative capacity of a natural water for soluble toxic contaminants by sorption.

It is suggested that the mixing-zone concept be used to evaluate the significance of dissolved chemicals solubilized during the disposal of dredged material. An equation is presented that incorporates initial concentrations at the disposal site, amount of dredged material being discharged, availability of chemical constituents in dredged material, and the volume of a proposed mixing zone.

Although chemical contaminants in dredged material could create toxic conditions in disposal site sediment, existing water-quality criteria do not apply to sediment because of the different conditions that exist in the sediment. In order to estimate toxic conditions, it will be necessary to conduct bioassays using representative benthic organisms.

PREVIOUS STUDIES WITH DREDGED MATERIAL

Past dredged material studies concentrated on biological and physical problems associated with disposal activities. The principal potential physical problems related to dredged material disposal are turbidity increases and sediment accumulation. Turbidity increases are usually of short-term duration and tend to be more severe in flowing systems such as rivers and streams. Biological studies with organisms, including fish, algae, and bottom fauna, indicate that a wide variety of species can tolerate some changes due to dredged material disposal. The most significant biological changes resulted from the burial of bottom fauna, but the populations usually became reestablished within six months to two years, suggesting that the changes are reversible.

Additional concern has been expressed over the potential effect of dredged material disposal on chemical water quality. However, early studies in which only total concentration values were reported are of little value because the significance of a specific chemical in water depends on the form of the chemical. Other studies, in which soluble and total concentrations were measured, demonstrated that little or no change occurred in the soluble concentrations although large total concentration increases were measured. Such studies demonstrate that there is no correlation between bulk composition of dredged material and resultant chemical effects of open-water disposal.

Several authors have concluded that transfer of chemical contaminants from dredged sediment to water is regulated by the effect of dredged material on disposal site conditions rather than the concentration of chemical contaminants in dredged material. The condition most susceptible to change by dredged material disposal would be the oxygen concentration (redox potential), which could be lowered or depleted by sediment under reducing conditions. A lower redox potential would tend to favor the reduced state of several chemical species, and these are generally more soluble.

Another mechanism that has been proposed as a factor controlling the release of chemical contaminants from dredged material is the iron cycle. The highly soluble ferrous species is favored under reducing conditions. However, ferrous iron is rapidly converted to ferric iron and precipitated under oxidizing conditions. In addition, the iron hydroxide precipitate, as well as other hydrous metal oxides, will concentrate other trace metals relative to the concentrations in surrounding water and carry them to the bottom where they will be incorporated into the sediment. Thus, the net transfer of chemicals from sediment to overlying water is influenced by the physicochemical state of chemicals in the sediment and the prevailing conditions of dissolved oxygen and pH in the overlying water.

Dredged material disposal can create changes in the interstitial water composition of disposal site sediment. These changes may exist for a relatively long period of time depending on the volume of dredged sediment being discharged, but such changes are not indicative of changes in overlying water because sediments are influenced by different conditions of pH, dissolved oxygen, and redox potential. It should be pointed out that the altered interstitial water composition may be toxic to bottom fauna and this factor may be potentially more important than the toxicity of chemical contaminants leached from dredged sediment and diluted in disposal site water.

It has been suggested that dredged material can be categorized based on the results of bioassays. Although there is no direct correlation between bioassay results using single species and any single chemical or physical analysis of the sediment, one classification system was presented based on the use of benthic fauna, phytoplankton, and Cladophora as test organisims. However, this system may be subject to revision because of uncertainties in the algae data and uncontrolled factors in the benthic fauna bioassays. Observed mortalities may have been caused by toxic components or an oxygen reduction due to a high oxygen demand in the dredged material. Thus, the classification system may be related to experimental conditions rather than characteristics of the dredged material studied.

Field studies at the time of dredging only indicate the presence or absence of extreme ecosystem damage. Year-round studies are required to assess the biological impact of dredged material disposal. Because the magnitude of biological changes will be influenced by concentration of suspended solids, the type of suspended solids, the length of exposure, the presence of other toxic materials, the condition of the exposed organism, and the phase of the life cycle of the organism, it has been suggested that rigid turbidity standards not be set.

Changes in bottom fauna populations resulting from the addition of suspended solids will be influenced by the type of solid

being discharged. However, it is difficult to predict the effect
of suspended solids on benthic communities at the time because no
information is available on the sensitivity of organisms to in-
creased rates of siltation. It has been observed that normal
activity resumes when turbidity and siltation return to background
levels.

Studies on Bulk Properties of Dredged Material and Sediment

The general direction of material transport in natural
water systems is from the water phase to the sediment phase.
The resultant bulk composition of sediment is determined by
the relative flux of chemical contaminants to the sediment
and the flux of noncontaminant solids. Changes in the bulk
composition of sediment have been used successfully to lo-
cate industrial and municipal discharge sources. This pro-
cedure requires extensive sampling to determine background
levels and variations in order to verify any changes that
might occur. However, no attempt has been made to correlate
sediment composition with chemical quality of the overlying
water.

The first attempt at developing criteria to regulate dredged
material disposal was based on a bulk analysis of dried solids,
but this approach suffered from several weaknesses. First, the
parameters selected were more representative of domestic sewage
rather than lake, river, and harbor sediments. Also, there was
no technical support given for the arbitrary numbers selected as
standards. Another major weakness of the bulk-property approach
to regulate dredged material disposal is that no universally ap-
plicable criteria are possible. This was shown by the fact that
sediment collected from several unpolluted areas have exceeded the
initial criteria. Finally, sediment-leaching studies have failed
to establish a correlation between chemical contaminants leached
from solids and the bulk composition of the solids.

Interstitial Water Composition

Dissolved constituents are generally enriched in interstitial
water compared to overlying bulk water. Changes in interstitial

water composition at a dredged material disposal site are generally related to increased concentrations of reduced species, which reflects the lower redox potential, pH, and oxygen concentration in a sediment phase compared to a water phase. Concentration profiles vary from top to bottom in the sediment column and with the chemistry of the individual chemicals.

Concentration gradients between sediment interstitial water and overlying water cannot be used to predict the transfer of chemicals across the sediment-water interface. Also, chemical migration is dependent upon specific chemical forms and existing chemical conditions and not the total concentration in the sediment. The depth of sediment available for exchange with overlying water may be as great as 30 cm. The exact depth of the transfer zone will be influenced by the fluidity of the sediment, biological effects, and turbulence.

Release of Materials from Sediment

Although the net transport of phosphate is generally to the sediment, dissolved phosphate is often transported out of sediment into the water. It has been observed that an appreciable release of phosphate occurs in a well-mixed system of lake sediment and water. The release increases under anaerobic conditions. The pattern is closely related to the iron cycle.

Nitrogen is another potential nutrient that may be released from lake sediment. The form of any released nitrogen is dependent upon the presence or absence of oxygen in overlying water. The reduced species is favored in the first case, and the oxidized species is favored in the second case.

Sediment serves as a sink for metals introduced into natural water systems. For example, the addition of soluble zinc to experimental ponds resulted in 94 to 99.8 percent of the labeled zinc being incorporated into the sediment within 100 days. Also, sorption of copper, chromium, cesium, and lead on particulate matter has resulted in these metals being carried to the sediment. Other metals such as iron and manganese reach the sediment due to low solubility of their hydrous oxide forms.

The addition of particulate solids can, under proper circumstances, increase the concentration of dissolved metals in lake water. This was demonstrated by a study of the effect of copper mine tailings on water quality in Michigan's Upper Peninsula. However, this effect is not universal, as the discharge of taconite tailings did not alter metal concentrations in Lake Superior, although interstitial-water metal concentrations did increase. Potential metal concentration increases are not related to the total analysis of the solids being discharged but are controlled by the characteristics and composition of the receiving water and the solids. The most favorable conditions for the transfer of metals from sedimentary material to the water are reducing conditions in the sediment and anoxic conditions in the overlying water. The single most important factor determining the magnitude and significance of metal concentrations resulting from the leaching of metals from sediment is the volume of water available for dilution. The fate of leached metals is determined by sorption, complexation, and redox reactions.

Sediment has been shown to be a sink for a wide variety of natural and man-made compounds, including pesticides, oil and grease, and natural-colored organics. An important pathway contributing to the accumulation of organics in sediments is sorption on particulate matter with subsequent settling of the particulate matter. The organic matter-particulate matter association will be influenced by the type of functional groups present, the molecular weight of the organic material, salinity, pH, temperature, and surface area and organic content of the particulate matter. The significance of these compounds in the sediment has not been determined, but there is very little evidence indicating that these chemical contaminants become mobile once they reach the sediment. One exception to this is oil and grease, which can form surface films that selectively concentrate pesticides and other nonpolar compounds.

CONCLUSIONS

The Elutriate Test is superior to a bulk-analysis approach for regulating dredged material disposal because it recognizes that chemicals are not equally available. As such, the Elutriate Test is a potentially valuable tool that can provide information needed to assess the environmental impact of dredging activities. However, the Elutriate Test is empirical, and a factor is needed to relate results of the laboratory test with actual environmental impacts. Studies are needed on the factors that may influence the Elutriate Test results.

INTRODUCTION

Dredging is a process of removing solids from the bottom of a waterway. This process may also be conducted for mining bottom sediments such as shell dredging. The process is usually used to develop or maintain navigable waterways. In this case the solids are regarded as having little economic value and must be deposited in some other part of the waterway or on land. The disposal of dredged material in waterways can create several potential water-quality problems as a result of the fact that the dredged sediments contain potentially significant amounts of chemical contaminants. The purpose of this report is to summarize information regarding water-quality problems resulting from the release of chemical contaminants to the water at the dredging or dredged material disposal site. Particular emphasis is given to evaluate the use of the Elutriate Test for assessing potential water-quality problems associated with chemically contaminated sediments.

Dredging is of major importance to maritime commerce. Boyd et al.[1] estimated that approximately 380 million cubic yards of sediment are dredged annually in the United States. Maintenance projects account for 300 million cubic yards of this figure with 80 million cubic yards for new construction projects. Because of the variability in dredging operations, these figures are five year averages. It should also be noted that these figures are low since they do not include all the dredging done by private companies.

Dredging activities influence maritime trade economics. Trimble[2] presented a demonstration of the potential significance on shipping as is provided in a report on the Port of Saginaw, Michigan. Due to indecision about method of dredged material disposal, there has been no dredging in the Saginaw River navigation channel for four years. As a result, an estimated 2.4 million cubic yards of silt has accumulated in the channel reducing

the usable navigation depth by four to six feet. The effect on shipping companies is a reduction in vessel capacity by 60 to 90 tons per vessel per inch of lost draft. This amounts to approximately 4500 tons per trip at Saginaw, Michigan (90 ton/inch) (50 inches lost draft). Since the total commercial traffic at Saginaw in 1971 was 388 vessels and the average carrying rate was $1.50/ton, the lost revenue due to shoaling was 2.6 million dollars. This value is expected to increase due to lead time necessary for construction of dredged material disposal facilities, continued siltation in the channel and an expected decrease in water levels in the future.

The dredging process consists of moving accumulated sediment from navigation channels and harbors and disposing of the sedimentary material at designated open-water sites or selected on-land disposal sites. The environmental significance of dredging has to be evaluated at each dredging and disposal site. An exception to this would be shell dredging in which overburden and washings are discharged in the fresh dredge cut.[3]

The water-quality problems associated with dredging operations may be conveniently divided into two broad categories: those problems that are generated at the dredging site and those at the disposal site. The problems at the dredging site include the mixing of the sediments and sediment interstitial water with the overlying waters. In addition to causing physical problems, such as increasing turbidity, this mixing process could result in the release of potentially significant amounts of chemical contaminants to the aquatic ecosystem.

In general the water-quality problems associated with in-water dredged material disposal may be further subdivided into problems that develop in the water column at the disposal site and those which arise from the presence of dredged material on the bottom. On-land disposal of dredged material also has many

potential problems arising primarily from the contamination of surface or groundwaters by water that has contacted the dredged material. A summary of the literature that exists on each of these types of potential problems associated with dredging and dredged material disposal is discussed in this report.

DREDGED MATERIAL DISPOSAL CRITERIA

The first attempt at regulating dredged material disposal
was based on bulk chemical analysis. The Environmental Protection
Agency (EPA) proposed criteria for volatile solids, chemical oxygen
demand, oil and grease, Kjeldahl nitrogen and several metals on
a dry weight basis.[1,4,5] These criteria are presented in Table 9,
page 84. While the basis for these criteria are not discussed in
the literature, it must be presumed that the authors of these
criteria assumed that there is some relationship between the bulk-
sediment composition and the pollutional tendencies of the sedi-
ment. It is apparent from the following literature review, that
there is little or no evidence to support this premise. Unfor-
tunately, these criteria have been used to determine whether
or not a particular sediment that is scheduled to be dredged
may be discharged in open waters, as has been the common practice
for many years, or must be disposed of in diked areas or on land.
The latter methods of disposal are generally much more expensive.
It appears that very large amounts of funds have been spent in
the name of water pollution control as a result of the utilization
of arbitrarily developed criteria for dredged material disposal.
In fact, little or no improvement in water quality is expected
and, in some instances, the alternate methods of disposal could
possibly cause a greater degree of water quality deterioration than
would have occurred if the open-water disposal methods of the
past had been used.

In many areas land is not readily available for dredged material
disposal. Under these circumstances disposal practices involved
utilization of a diked area where the supernatant water would have
a retention time of one hour to several days before being returned
to the lake, river or estuary.[6] During this period the large

particles settle out, and the dissolved solids and fine materials are returned to the water course. Some on-land disposal methods of dredged sediment follow a similar approach. The primary problem with this approach is that the short settling period will not remove the bulk of the potentially significant contaminants in the dredged material. Generally, the potentially significant fraction is of the fine-colloidal size. From several points of view the discharge of colloidal-size fraction into nearshore water represents a potentially much worse situation than having this size of fraction dispersed in the open waters. In open waters, materials could be rapidly dispersed and thereby reduced below any critical concentrations. The nearshore waters, on the other hand, are the primary nursery grounds for lakes and estuaries. These waters would tend to have less rapid dispersion of the contaminants and, therefore, some of the most sensitive forms of aquatic life are exposed to the highest and possibly the most adverse concentrations of chemical contaminants as a result of on-land or nearshore dike disposal of dredged material. Disposal in these areas may require extensive pretreatment in order to ensure that any supernatant or other water that has been in contact with the dredged material does not cause a significant adverse effect on surface and/or groundwaters in the region.

Dredged material disposal criteria based on bulk analysis is technically unsound because it is assumed that all forms of chemicals would have an equal impact on the environment. For example, it assumes that a copper bar would create the same problems as an equal amount of copper present in solution. This assumption is not defendable except from the point of administrative ease of application of the disposal criteria. Also, the expression of dredged material composition on a dry weight basis is not an indication of potential environmental effects. Water present

in the sediment will influence the distribution of solids between total, soluble, and exchangeable forms;[7] porosity; and the depth of sediments available for mixing with overlying water.

The EPA and its predecessor agencies have proposed dredged material disposal criteria based on bulk analysis of the sediment for certain parameters normally used in evaluating the environmental impact of domestic and industrial wastewaters. Parameters of this type include Kjeldahl nitrogen, volatile solids, chemical oxygen demand (COD), and oil and grease, etc. While, in some instances, parameters of this type may be useful in municipal and industrial wastewater treatment, their application to dredged material disposal criteria should be done with great caution. In general, it is likely there will be little or no relationship between environmental impact of a particular dredged sediment and a particular numerical value for any of these parameters. It is indeed unfortunate that these parameters have been propagated as criteria for dredged material disposal in that extremely arbitrary numbers have been selected as a maximum value for one or more of these parameters used to determine whether or not the sediment in a particular region scheduled for dredging is judged to be polluted and requires special disposal means.

Chemical Oxygen Demand

One of the best examples of a parameter which should not be used as a dredged material disposal criteria is the chemical oxygen demand (COD) test. This test was devised as an alternate biochemical oxygen demand test (BOD) for domestic wastewaters. It has been known for many years that an empirical correlation can be developed between the BOD and the COD of a domestic wastewater. It is also known that this correlation did not work well in many instances where large amounts of industrial wastes are present

in the municipal wastewater. Also, it does not work well for
natural water organic matter. It is known that even the
modified version of this test currently in use, where a mercury
salt is added in attempt to eliminate the effective chloride, is
not satisfactory in the estuarine environment where markedly
different chloride levels are encountered. The COD test, in
addition to measuring a somewhat variable undefined fraction of
the organic matter present in sediments, also measures a variable
undefined fraction of the inorganic compounds present. Because
of the lack of specificity of this test in measuring any pollu-
tional characteristics of sediment, no further use of it should
be made in developing criteria for the disposal of dredged
sediment.

Total Kjeldahl Nitrogen

     Total Kjeldahl nitrogen is one of the parameters proposed by
the Federal Water Quality Administration (FWQA) which has been
used to determine whether or not sediment to be dredged is pol-
luted. Total Kjeldahl nitrogen represents the majority of the or-
ganic nitrogen and ammonia present in the sample. The ammonia
content of the sediment is of potential importance in fertilizing
the overlying waters and as a toxicant. Normally, ammonia is
present in relatively low levels in sediment. Organic nitrogen,
on the other hand, is normally present at high levels in sediment
with the amounts present being highly dependent on the clastics
(nonorganic and carbonate materials) and other inorganic minerals.
Organic nitrogen, per se, is not adverse to water quality. It is
of potential significance in that it may be converted to ammonia
by biochemical processes. However, the rates of this conversion
are sufficiently slow so that it would be rare that the receiving
waters would either become toxic to aquatic life or aquatic plant
growth would be stimulated by the ammonia release. There is no
rational basis upon which a total Kjeldahl nitrogen level can be
established that can be used to determine whether or not the
disposal of dredged material in the particular location would be
adverse to aquatic life.

Volatile Solids

The FWQA proposed a limit of six percent by dry weight as the maximum concentration of volatile solids for nonpolluted sediments. This criterion suffers from the same difficulties as the other bulk criteria in that it is impossible to utilize bulk composition as a measure of the potential environmental impact of materials as diverse as natural water sediments. In domestic wastewaters, particularly in the activated sludge tanks, the volatile solid content is an estimate of the organic content of the particulate matter present. However, with sediment the volatile solids are an undefined mixture of organic and inorganic compounds. Some of the organics present in natural waters would be resistant to volatilization. A substantial part of these organics are highly refractory, being the residues left after bacterial degradation. There is certainly no relationship between this organic residue and the oxygen demand of the sediment. In high carbonate sediment some carbonate species are lost through decomposition at the temperature of the volatile solids test. In sediment with large amounts of reduced iron, manganese, and sulphur, the fixed solids will increase in weight due to the oxidation of these species to their corresponding oxides in the volatile solids test. There is no rational basis by which it is possible to establish the relationship between volatile solids and the environmental impact of dredged material disposal.

Oil and Grease

Extraction of a sample of sediment with an organic solvent such as hexane and determination of the weighable dry residue gives a measure of the oil and grease present in the sediment. While it is generally agreed that the presence of tar or oil residues in sediment is undesirable, essentially no information is available on the relationship between such residues and

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degradation of water quality. Recently, the EPA[8] has proposed
that the maximum concentration of hexane-extractable substances
in air-dried samples not exceed 1000 mg/Kg. However, no ra-
tional basis was presented for selecting this value. Research
is needed on the relationship between the oil and grease con-
tent of sediment and the adverse effect of the sediment on
water quality before a rational limit may be placed on the ex-
tractable organic matter present in sediment.

From an overall point of view, it is strongly recommended
that parameters such as volatile solids, COD, or Kjeldahl
nitrogen not be used in developing dredged material disposal
criteria until such time as it can be demonstrated that there is
a relationship between a particular concentration of each of
these parameters and the environmental impact caused by the
disposal of dredged sediment containing this concentration.

FACTORS AFFECTING THE ELUTRIATE TEST RESULTS

In an attempt to develop a more technically sound approach toward dredged material disposal, the EPA and the Corps of Engineers have developed the Elutriate Test which has been published in the "Federal Register."[9,10] This test is an attempt to develop a leaching test which could be used as a basis for estimating the potential significance of chemical contaminants present in sediment to be dredged. The revised criteria are more realistic since a release of potentially significant dis- solved solids must occur before dredged material is classified as polluted. Dredged sediment must produce less than a 50 per- cent increase for any parameter in the disposal site water after being mixed in a ratio of 1:4 volume to volume with disposal site water in order to be non-polluting.[9,10] Although this approach is superior to the bulk-analysis approach, it does not cover all of the possible problems that could be encountered in dredging and dredged material disposal in natural water systems. A small volume of discharged dredged material would have a very different impact on the receiving water than a larger volume. However, although the old bulk criteria and the present Elutriate Test criteria acknowledge that volume of dredged material must be con- sidered, neither approach specifies how the volume of dredged sediment to be discharged should be used or interpreted. Also, there was no specified limit on the volume of dredged material that could be discharged at one time or one place. The same comments apply to the volume of water available at the disposal site for dilution. Both sets of criteria mention this factor but do not discuss how to evaluate the importance of this param- eter. Third, the combination of disposal site water and a one- half hour shaking time and a one-hour settling time may not be

sufficient to assess significant release. The first two points can be compensated for in the interpretation of the test results and the third point can be compensated for by modifying the test to some type of exchange procedure. This approach is further discussed in a subsequent section.

A major difficulty of interpretation of the standard Elutriate Test is the use of the 1.5 factor. This problem becomes clear by considering three different situations: one concentration so low that the levels are just detectable (cadmium in Lake Superior), an intermediate concentration (alkalinity in Lake Mendota) or a high or near-saturation concentration (chloride in the ocean). The intermediate level may be the only case where the 1.5 factor is workable. At higher concentrations, saturation may restrict reaching a value of 1.5 times the disposal site's ambient water concentrations. Also, a factor smaller than 1.5 may be desired at high concentrations since a 50 percent increase can be sizeable at higher initial concentrations. The problem becomes slightly different in the extremely low concentrations. If the initial level can not be determined with any degree of accuracy, it becomes impossible to determine a 50 percent increase.

It is possible that a disposal site could be selected based on the 1.5 factor currently in effect which would allow a greater deterioration of water quality than would occur if this factor were not utilized. A key part in the 1.5 factor is the ambient concentration of selected chemical species in the disposal site water. It is possible that, by selecting a water with a high ambient background for a particular chemical species released in the Elutriate Test, disposal of dredged material would cause the waters in the disposal region to exceed the critical concentration for certain forms of aquatic life but not 1.5 times the ambient concentration. However, if the disposal took place in a region where there was a low ambient level, and the sum of the ambient

and the dredged material release concentrations are less than the critical value, then there would be no adverse effect on water quality. It is clear that the 1.5 factor should not be used as a rigid standard, but used to detect potential problems.

In addition to there being several potentially important problems in interpretation of the Elutriate Test results, there are also potential problems with the test itself. The results obtained may, under certain circumstances, be highly dependent on test conditions. In order for a test of this kind to be useful, the results should be essentially independent of minor modifications of the test procedure.

The factors that can affect the leaching test are listed in Table 1. The importance of these factors will be discussed in the subsequent sections.

The authors have recently completed a comprehensive study of the factors influencing the release of chemical constituents from taconite tailings.[11] Taconite is a low grade iron ore which typically contains 20-30 percent iron. The Reserve Mining Company of Silver Bay, Minnesota, derives its ore from the eastern end of the Mesabi Iron Ore Range. This ore is transported to Silver Bay on the shores of Lake Superior where it is wet ground, and the iron is removed by magnetic extraction. The residue is called taconite tailings and consists of various iron-magnesium-silicate minerals such as cummingtonite and silicates such as quartz. These tailings contain trace amounts of heavy metals and aquatic plant nutrients. The Reserve Mining Company applied for and received permits to discharge these tailings in a density current to Lake Superior. Recently, questions have risen about the effect of the possible release of various chemical constituents from taconite tailings on water quality in Lake Superior. In order to ascertain whether such a release was possible, a study has been conducted by the authors on the release

TABLE 1

FACTORS INFLUENCING ELUTRIATE TEST RESULTS

1. Amount of solid (solid-liquid ratio)
2. Time of contact
3. pH
4. Dissolved oxygen concentration
5. Agitation
6. Particle size
7. Handling of solids
8. Characteristics of water
9. Solid-liquid separation

of various chemical constituents from taconite tailings in a variety of laboratory conditions designed to simulate on-land and in-water disposal. Since the situation with respect to the release of chemical constituents from taconite tailings is somewhat similar to dredged material, it is felt that it would be appropriate as part of this discussion to summarize the results of the taconite tailings study in order that some inference might be gained about the possible factors that could influence the release of chemical constituents from dredged material. It should be emphasized that there are significant differences between taconite tailings and grossly contaminated dredged material such as occurs near urban centers arising from the improper treatment of industrial and municipal wastes. Taconite tailings are relatively inert silicate minerals which contain trace amounts of various chemical constituents that could be significant in natural waters. Some dredged sediment, on the other hand, contain large amounts of industrial and municipal organic sludges which could, under improper disposal, have an adverse effect on environmental quality.

Solid-Liquid Ratio

The solid-liquid ratio could influence the results of a laboratory leaching study. When a high initial dissolved solid concentration exists in the disposal site water, the release from dredged material may be limited by saturation concentrations. Should some constituent reach saturation levels, then the addition of more dredged material could not produce a proportionate increase in the test solution even though the constituent may be readily available. Thus, there are conditions under which the Elutriate Test would yield low estimates of available chemical contaminants in dredged material.

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There is also another effect of the solid-liquid ratio even though concentrations may not reach saturation levels. In the taconite study,[11] increasing the weight of tailings in suspension increased the cumulative release of dissolved solids, but the release per gram of material was not the same. Using calcium as the example, the cumulative releases were 11 mg Ca/5 g tailings, 28 mg Ca/20 g tailings and 46 mg Ca/35 g tailings. The calculated release per unit weight was 2.2 mg/g, 1.4 mg/g and 1.3 mg/g. The same response was observed for dissolved solids (specific conductance), alkalinity, sodium, copper, zinc and manganese.

Lotse et al.[12] report that the solid-liquid ratio is the most significant variable in the degree of sorption of lindane by lake sediment. Luh and Baker[13] found that for a fixed amount of clay, the amount of pyridine desorbed was directly related to the volume of water. Huang and Liao[14] 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 doubles. Thus, although higher solids concentrations will result in a greater change in the aqueous concentration of the compound in question, lower solids concentrations will result in higher uptake or release of a compound per gram of sediment. This phenomenon was also observed in a taconite study.[11]

The reason for this type of response is probably related to the fact that any solid surface has a wide variety of sorption sites for chemical constituents. As the amount of solids per unit volume increases in the leaching solution, it would be expected that less materials would be released per unit weight of solids due to sorption on the surface. The Elutriate Test utilizes a 4:1 liquid-to-solid ratio based on volumes in an attempt to simulate the liquid-to-solid ratio that occurs in hydraulic dredging. It is clear, however, that shortly after the release

of the dredged material to the environment in open-water disposal, the liquid-to-solid ratio of various types of dredging, including hydraulic dredging, could be markedly different from the 4:1 ratio. Since there is little or no information available today on the effect of the liquid-solid ratio on the release of chemical contaminants from sediment which is subject to be dredged, a study should be conducted in which a wide variety of sediments taken from various locations in the U.S. are subjected to leaching with liquid-to-solid ratios representing the conditions that may be encountered in dredging operations and dredge material disposal.

Time of Contact

Time of contact is another important parameter that will affect the results of the Elutriate Test. Figure 1 represents the type of release patterns observed in a leaching study with taconite tailings.[11] Depending on the parameter selected, the cumulative release curves showed an asymptotic release, an exponential release, an initial release and a loss from solution or no release. Another possibility is a net loss from solution due to sorption or precipitation. For the first case, 50-75 percent of the eventual release occurred in the first sampling period, then the release leveled off and approached some value asymptotically. This pattern was observed for the readily soluble material such as total dissolved solids (specific conductance), calcium, sodium, magnesium and alkalinity. The second type of pattern was exhibited by silica. Silica concentrations were initially very low, followed by a sharp increase in concentration after 100-200 days. Another break in the silica release curves was thought to be due to instantaneous silica concentrations reaching saturation levels. The slow release of silica compared to the constituents mentioned for type-one release is due to the necessity of some type of hydrolysis step for the release of

FIGURE I
Types of Release Patterns

(1) Asymptotic Release

(2) Exponential Release

(3) Release followed by loss from solution

(4) No Release

CONCENTRATION

TIME
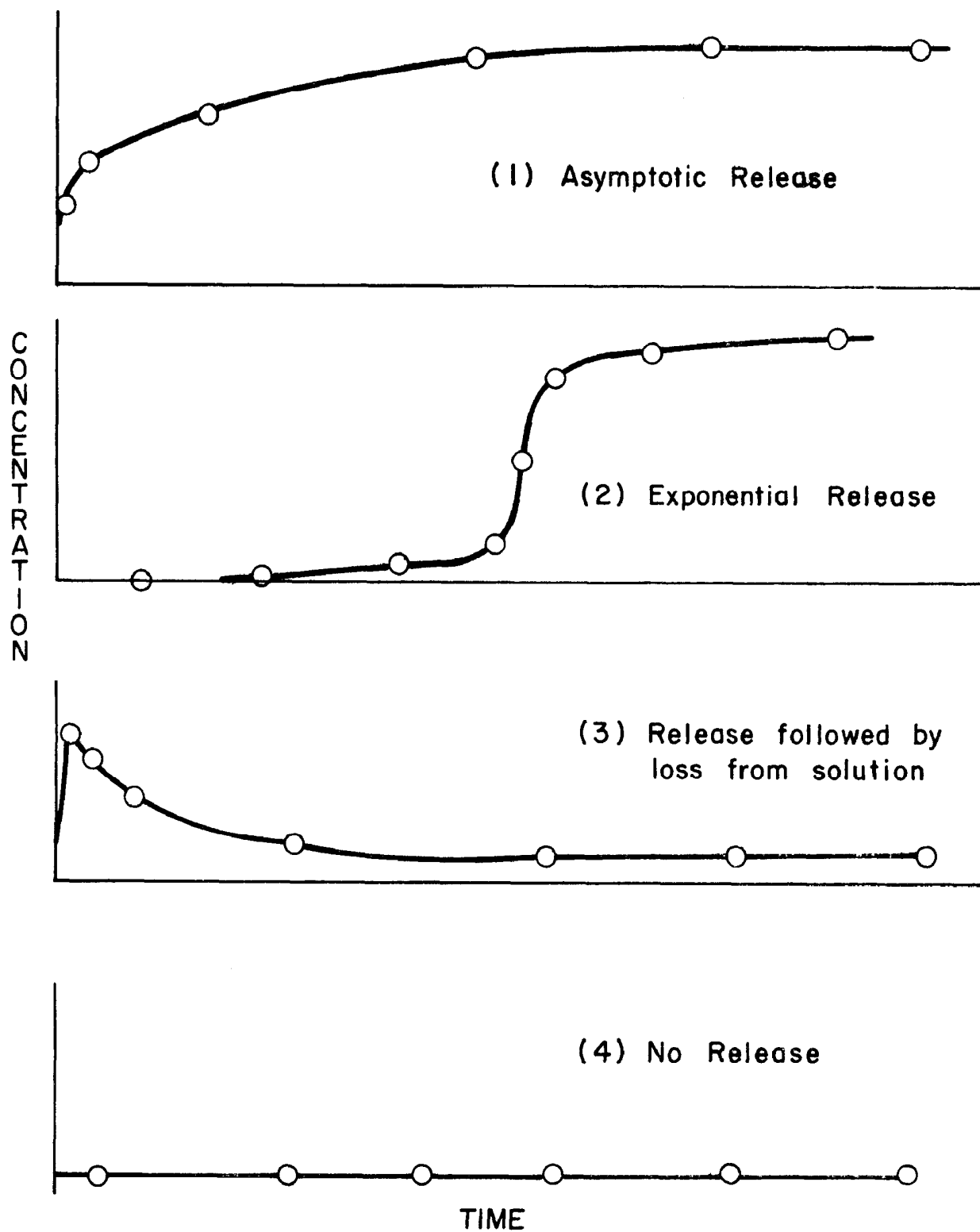
silica to occur. A different type of release pattern was observed in the copper and zinc data. Both of these metals showed an increase in the first sampling period. For the duration of the study, the concentration and cumulative release of each metal decreased. The probable cause for the net loss from solution is the process of sorption. The initial release was attributed to low initial pH, lack of agitation and pretreatment of tailings. A fourth type of pattern occurred in the cadmium, lead, phosphate, nitrate and ammonia data. These parameters did not change with time in the test suspensions, and within the errors of the analytical procedures there was no cumulative release of these materials.

The different release patterns are not unique to taconite tailings. Windom[5,15] observed changing concentrations of phosphate, nitrate, ammonia and trace metals in dredged material suspensions with time. This demonstrates that the amount of material leached from dredged material in a standardized leaching period will be a function of the length of time selected and the chemical parameters measured.

Most investigators report that sorption and desorption of pesticides on sediment occur rapidly and that there is little change in concentrations after two to three hours.[14,16,17,18] However, Rowe et al.,[19] in a sorption-desorption study of dieldrin on natural sediment, report that maximum sorption occurs after three days and that after this time desorption begins to dominate. They found that most of the originally sorbed dieldrin was released after seven days. These results are difficult to explain (unless some change occurred in pH or dissolved oxygen concentrations) but they point out the necessity of carrying out long-term leaching studies.

Because of the extremely limited amount of data on the effect of contact time on the release of chemical contaminants from dredged material, studies should be initiated to evaluate the reasonableness

for the 30 minute leaching period which was selected for the standard Elutriate Test. Particular attention should be given to longer periods of time in order to ascertain whether any potentially significant chemical contaminant present in the sediment subject to dredging could be released within the period of time that dredged sediment is likely to be suspended in the water column at the dredging and disposal sites. In addition to studies on the relationship between time of contact and contaminant release, studies are needed on the range of times that dredged material would be suspended in the water column at the dredging and disposal sites. There is little or no point in running long-term leaching tests in excess of the time periods expected under normal contact in normal dredging operations. It should be emphasized that the Elutriate Test is primarily designed to detect potential problems that could occur in the water columns of the respective areas during dredging and disposal. This test should also detect any potential problems that may occur because of resuspension of the dredged material at the disposal site. It will not readily detect problems associated with dredging which are related to the physical effects of solids deposition on aquatic organisms, nor will it detect, to any significant extent, problems associated with dredging that arise from the presence of chemical contaminants to benthic organisms. The environment that exists in the dredged sediment of the disposal site will likely be markedly different from the environment that exists in the water columns at the dredging and disposal sites.

It is recommended that in order to detect potential problems associated with chemical contaminants in dredged material which could have an adverse effect on benthic organisms, bioassay procedures be conducted for selected sediments which are subject to dredging using representative benthic organisms from the various dredged material disposal sites available in the U.S.

It is proposed that relatively simple tests be used in which the benthic organisms are placed in contact with a column of the dredged material where the organisms would have an opportunity to burrow into the sediment and swim above it. In any test situation which shows toxicity to benthic organisms under these conditions, tests should be made of the interstitial water composition in order to determine what compound(s) could be responsible for the toxicity. It is possible that, should the bioassay tests show that dredged material is highly toxic to a wide variety of benthic organisms and that this effect is judged to be significant to overall water quality in the area, a modified leachate test could be developed in which attempts would be made to simulate situations in interstitial waters in the dredged material disposal area. This modified test would have to investigate the importance of time of contact over long periods of time since this is the situation where long periods of contact (months to years) would be important to aquatic organisms.

pH

Another important factor that will have to be controlled or evaluated in the Elutriate Test is pH. In general, solubilities tend to increase with decreasing pH. For example, the less than 44μ size tailings had a calculated solubility of 0.8 percent in quiescent distilled water and a solubility of 3.0 percent at a pH of 4.7. This is a 400 percent increase in solubility. However, the effect was not the same for each parameter. In the taconite tailings study,[11] alkalinity leached from tailings doubled at the lower pH, but copper and iron increased by 100 fold.

pH can also influence the transfer of organic compounds from suspended solids. Luh and Baker[13] found that m-aminophenol

and 2,4-diaminophenol were sorbed at an acidic pH but not
at a basic pH by montmorillonite and kaolinite; while phenol,
m-cresol, 2,4-dichlorophenol, valeric acid and n-hexanoic acid
were not sorbed at any pH. It was also found that maximum
desorption of pyridine from clay occurred at pH's of 1 and 11
and minimum sorption occurred at a pH range of 4.0 - 5.5.
In general, it appears that ionizable molecules are desorbed
to the greatest extent at pH values that favor ionization.
The effect of pH on sorption and desorption of neutral organic
molecules is not very clear. Boucher and Lee[17] report that pH
values normally found in an aquifer had no significant effect
on the sorption of lindane and dieldrin by unconsolidated
aquifer sands. Huang[16] found that the sorption of dieldrin
by montmorillonite was slightly decreased with an increasing pH
within the range of 6.0 to 10.0. Rowe et al.[19] investigated
the sorption and release of dieldrin from estuarine sediments
and found uptake was dependent upon time and pH (Table 2).
Although the effect of pH on the sorption and release of neutral
organic compounds is probably slight within the pH range usually
found in natural water, the study of Rowe et al.[19] indicates
that it should be further investigated.

pH of the Elutriate Test will be determined by the buffer
capacity of the water and sediments used. It is possible that
minor changes in the pH, in the neutral pH range, could have a
pronounced effect on the contaminants released from dredged
material.[20] It is recommended that no attempt be made to control
the pH in the Elutriate Test by addition of acidic or basic
materials to the test. Instead, the pH of all Elutriate Test
solutions should be measured and recorded. If it is anticipated
that there is a markedly different pH prevailing in the water
column at the dredging area or the disposal area, a series of
Elutriate Tests should be run in which the pH of the solutions is

TABLE 2

SORPTION OF DIELDRIN ON ESTUARINE SEDIMENT

AS A FUNCTION OF TIME AND pH*

pH range/time	1 hour	72 hours	168 hours
3.8 - 4.2	25	60	10
6.7 - 7.1	25	60	25
7.8 - 9.0	<5	60	<5

Values are percent of dieldrin added to solutions that were
sorbed.

* after Rowe et al.[19]

adjusted to essentially the same pH that prevails in the
environments under consideration.

Dissolved Oxygen Concentration

The presence or absence of dissolved oxygen can influence
the release of dissolved solids from dredged material. In
general, the oxidized forms of several elements are less mobile
and have lower solubilities than the reduced forms. It has
been well documented in many lake studies that the removal of
oxygen from the hypolimnion of a lake can be followed by
increases in iron, manganese, phosphate, ammonia and sulfide.
It has also been suggested by May[3] that dissolved oxygen may
control the release of dissolved solids from dredged material.
Care must be exercised in running and interpreting the Elutriate
Test because dredged material could have a direct effect on
dissolved oxygen concentrations. The high concentration of
solids used in the Elutriate Test could deplete the oxygen if
the sediments are reducing which would create more favorable
conditions for reduced species from dredged sediment. However,
if dredged material disposal does not produce an oxygen depletion
at the disposal site due to dilution or some other factor,
then the laboratory test will not reflect the effect of dredged
material disposal on the environment. A high concentration of
trace metals or some other species in the Elutriate Test may only
be a secondary effect of the oxygen demand of dredged sediment
and may not properly reflect the situation that may prevail in
the dredged material disposal area.

The cycle of hydrous metal oxides can result in a co-
precipitation or flocculation of organic compounds. Sridharan and
Lee[21] reported that iron flocculation would partially co-
precipitate phenol, citric acid and glycine from natural fresh
water and distilled water but would not remove dextrose,

alkylbenzenesulfonate or formaldehyde. There was a positive cor-
relation between the organic content of the water and the amount
of phenol precipitated; a negative correlation existed for citric
acid; and there was no apparent correlation for glycine. Floc-
culation with ferric hydroxide has been shown to be able to
also partially remove soluble COD[22] and DDT and dieldrin.[23]

Another effect of redox conditions is observed in the
degradation of organic compounds since some compounds degrade
more rapidly in oxic environments than in reducing sediments.
For example, Hill and McCarty[24] demonstrated that DDT, lindane
and aldrin degrade less rapidly in anaerobic than aerobic
conditions, while heptaclor epoxide and dieldrin were persis-
tent in both environments. Thus, if a sediment containing DDT
was removed from an anaerobic environment and placed in an
aerobic one, the persistence of DDT and similar compounds might
be increased.

As will be pointed out in the literature review section of
this report, dredged material leaching studies that have been
conducted thus far show that very little if any of the chemical
contaminants present in dredged sediment are released to the
aqueous phase. It has been postulated that the primary reason
for this was the presence of hydrous iron oxide in the test
system. Lee[25] has presented a comprehensive review of the
potential role of hydrous metal oxides on the transport and
transformations of heavy metals and other trace contaminants in
natural water systems. Because of the highly significant role
that hydrous metal oxides could play in release of contaminants
from dredged material, care must be exercised to ensure that the
Elutriate Test maintains essentially the same oxygen status
as will prevail at the dredging and disposal sites since the
oxygen status of the test system will determine, to a major extent,
the presence or absence of hydrous metal oxides in the test system.
If it is found that the oxygen demand of dredged sediment is
sufficiently great based on the liquid-solid ratio used to deplete

the dissolved oxygen in the test but not deplete the oxygen
content in the water column in the disposal area, then it may
be necessary to aerate the test solution in order to maintain
the oxygen status similar to that which may occur in the
disposal site environment.

Since the oxygen demand of sediment may be sufficient
to deplete the oxygen content of the water at the dredging
and/or disposal site, it is recommended that a special form of
the Elutriate Test be developed in which a known amount of the
sediment and the dredging site water in one test and disposal
site water in another test are mixed together under conditions
of continuous agitation. The oxygen demand of the sediment in
the respective waters should be measured by determining the
oxygen content as a function of time in a closed container. It
is suggested that a relatively simple system of a BOD bottle
which is placed on a magnetic stirrer stoppered with an oxygen
membrane electrode be considered for use. It is felt that a
standardized test of this type could be developed where the rate
of oxygen consumption would be empirically correlated with the
actual oxygen demand that occurs at the dredging and disposal
sites for various types of physical settings and dredging opera-
tions.

Bella[26] has discussed the factors influencing the oxygen
demand of estuarine sediment. He developed a conceptual model
to demonstrate these relationships and discusses how dredging
and dredged material disposal could influence oxygen demand of
sediment.

Agitation

Another factor that will have to be standardized in the
Elutriate Test is agitation. In the taconite tailings study,
Plumb[11] found the solubility of less than 44μ size tailings in
constantly agitated suspensions was 0.9-1.2 percent. The

same size and weight of tailings had calculated solubilities of 0.7-0.9 percent under quiescent conditions. The general pattern found for the uptake or release of chemical constituents from natural water sediments is one in which the release rate is dependent on agitation at lower degrees of agitation. At higher rates of agitation the rate of release becomes independent of the degree of agitation with some types of solids, especially those that are loosely agglomerated. The rate of release becomes dependent again on the degree of agitation at very high agitation levels where the degree of agitation is sufficient enough to break up the particles.

There are basically two conditions in which there is concern about the degree of agitation in dredging and dredged material disposal. One of these is the completely suspended condition in which the rate of release of constituents from the surface of the particles is not influenced by the degree of agitation. The other is the quiescent and semiquiescent conditions that prevail prior to dredging and once the dredged material has settled to the bottom. As discussed previously the Elutriate Test does not provide an environment which is designed to simulate the latter conditions of dredged material disposal. This test does, however, simulate to some extent the conditions that will prevail in the water column at the dredging and disposal sites. Therefore, the degree of agitation in the Elutriate Test should be sufficient in order that the rate of release of any constituents from the particles is not controlled by the agitation. Normally a gentle shaking of the suspension is adequate for this condition.

Particle Size

Particle size would be expected to be important because solution is a surface phenomenon and smaller size particles have a greater exposed surface area than the same weight of larger size particles. This factor was examined in the taconite tailings

study[11] and the magnitude of the effect varied with the parameter
of concern. For example, cumulative specific conductance values
were 275 μmhos/cm/20 g of less that 44μ size tailings, 210
μmhos/cm/20 g for 105-149μ size tailings and 170 μmhos/cm/20 g
for 350-500μ size tailings. The differences were much less
for calcium, as the measured values were 32 mg Ca/20 g of less
than 44μ size tailings, 30 mg Ca/20 g for 105-149μ size tailings
and 29 mg Ca/20 g for 350-500μ size tailings. Although Slotta
et al.[27] have shown that the size distribution of dredged sedi-
ment may change during disposal, it may not be necessary to
control particle size for the Elutriate Test because all the
material is usually discharged at one location. However, considera-
tion may have to be given to particle size effects at on-land
or in-diked areas of disposal as commonly practiced today where
the fine particles are allowed to return to the water course
within a relatively short period of time after disposal. Under
these conditions, it would be appropriate to modify the Elutriate
Test so that only those particles which have not settled in a
period of time similar to those used in a disposal practice would
be tested.

The phenomenon of particle agglomeration noted by Slotta
et al.[27] would be expected under any circumstance in which the
salinity of the water in contact with the dredged material has
increased markedly. This is a well-known phenomenon where the total
salts in solution cause a flocculation of the clay particles. This
type of situation would be frequently encountered in estuarine
dredging where the dredging takes place in fresh or low salinity
waters and disposal takes place in high salinity waters. The
standard Elutriate Test considers this situation to some degree
as a result of using water from the disposal site as the elutriate
solution. However, it should be noted that the degree of floc-
culation in the test may not be the same as that which occurs
at the disposal site because of differences between the two conditions.

Handling of Solids

Another factor that could influence leaching studies with dredged material is the treatment and handling of solids prior to the Elutriate Test. If a delay occurs between sediment collection and the Elutriate Test, a partial oxidation of the material could result. This would have the effect of changing the solubility and availability of constituents. Another step that should be avoided is drying of dredged material before use. Drying could change crystal structure and solubility. Plumb[11] found that drying taconite tailings prior to leaching caused a release of copper from the tailings which did not occur if the tailings were maintained in their wet condition prior to the leaching test. As discussed by Lee,[20] the drying step probably caused a change in the surface characteristics of the hydrous iron oxide, which usually coats the surface of the taconite particles, to have less sorption capacity for copper than the non-dried tailings. Support for this hypothesis is found in the fact that an ammonium acetate leaching of the dried and non-dried taconite tailings showed a much greater leachable copper from the dried tailings.

This type of phenomenon could be important with respect to on-land disposal of tailings and dredged material in that the normal desiccation that occurs with this type of disposal could result in a greater release of potentially significant chemical contaminants to the environment than would occur with direct water disposal. Any on-land disposal system must ensure that the dried sediments are not carried by wind or water to nearby water courses.

Additional discussion of the factors such as oxidation, temperature, freezing, etc. that should be considered in handling of the sediments prior to the Elutriate Test is presented in the literature review section of this report which should be consulted for additional information on this topic.

Another variable that may have to be evaluated during
the study is the effect of the sample bottle type. In partic-
ular, the use of a plastic bottle could create spurious values
for some organic compounds such as phthalates, since these
compounds are frequently used in the manufacture of plastics.

Characteristics of Water

Consideration must be given in any Elutriate Test to
ensure that the characteristics of the leaching water are
similar to the waters in the region of the dredged material
disposal operations and the dredging site. The standard
Elutriate Test specifies that a liquid-to-solid ratio of 4:1
on a volume-to-volume basis be used where the liquid phase is
obtained from the disposal area. As noted above, the 4:1
ratio is derived from the typical liquid-solid ratio in hydraulic
dredging. This condition would prevail from the time the
sediment is picked up in a hydraulic dredge until it was
discharged. However, after discharge occurs the liquid-solid
ratio will change significantly due to dilution with disposal
site water. It is important that studies be conducted on the
significance of liquid-solid ratios on a variety of dredged
material. At the same time, studies must be conducted on
the influence of the type of water on the release of chemical
contaminants from dredged sediment. It is possible that the
type of water used may have little or no effect on the release of
chemical contaminants from most dredged material provided that
certain conditions such as pH and oxidation state maintained during
the test are the same as those occurring at the disposal site.
It is also possible that the bulk composition of the water and
its physical characteristics, such as temperature, might have
a significant effect on the release of some constituents. Should
this situation occur, it would be necessary to modify the

Elutriate Test to use waters representative of the dredging and disposal sites in order to evaluate the potential contaminant release in both areas.

This situation is much more complex in river, river mouth and estuarine dredging where water composition can change markedly with time and depth necessitating utilization of each of the water types in the Elutriate Test.

Because of the complexity of this situation, it may be more appropriate to develop a standardized Elutriate Test in which one or two standardized waters are used as the leaching solutions. Such an approach would eliminate the necessity of going to the anticipated disposal site to collect water for the Elutriate Test as currently required.

An alternate approach that could possibly be used to evaluate the potential environmental impact of the chemical contaminants present in dredged material is the use of a leaching solution which would not resemble either the dredging or disposal site waters but would be designed to estimate the amount of "available" constituents present in the sediments. This approach has been used in the soil fertility field in an attempt to determine what part of a particular nutrient is available for aquatic plant growth. For a review of these various procedures, consult Black.[28] The most frequently mentioned reagents in the technical literature for accomplishing this purpose are water, ammonium chloride, ammonium acetate, dilute hydrochloric acid and a dilute sodium hydroxide. Each of these procedures would be used basically for inorganic ions.

The use of water as an extraction reagent would be similar to a short-term leaching study. The same problems of time or rate of release would occur. The use of ammonium chloride would give an estimate of exchangeable material in dredged material.

With this method, a high concentration of ammonium ions is used to act as a driving force and replace the cations associated with the solids. The cations can then be determined in the leachate. Ammonium acetate is similar to ammonium chloride and appears to be used more frequently than ammonium chloride. This is also an exchange procedure in which a high concentration of ammonium acetate is used to force a replacement of ions associated with the sediments. Released ions are then determined to calculate the amount of available material and the exchange capacity of the sediments. The use of a dilute acid such as 10 percent hydrochloric acid or dilute sodium hydroxide would subject the sediments to harsher conditions and generally produces higher results. The result is an undefined measure of exchangeable and potentially available material associated with sediments. This would include metal oxides and other materials sorbed onto or entrapped in the metal oxides.

The value of the exchange procedures approach is that the absence of exchangeable material should be a good indicator of a lack of potential problems for that element. For example, iron, cadmium and lead associated with taconite tailings were not exchangeable. No release of the metals was observed in a long-term leaching study and no problems have been reported in Lake Superior[11] due to the presence of these elements in the taconite tailings discharged to the lake.

The results of an exchange procedure are not a measure of environmental changes. The results are only a measure of some fraction of the exchangeable or available material and must be interpreted in terms of the volume of water available for dilution. Another weakness of the exchange procedures is that they do not reflect the chemistry of each element in the environment. A high concentration of available copper and zinc was indicated in the taconite tailings study, but the long-term

leaching study clearly indicated a small initial release followed by a gradual loss from solution, probably by sorption.[11] The same discrepancy would result if the released material is lost by oxidation and precipitation as is possible for iron and manganese.

The primary value of these exchange leaching tests derived from the soil's field has been in the area of estimating soil fertility. While some success may have been achieved in estimating the amount of phosphorus present in a soil sample that will become available to terrestrial plants, little or no success has been achieved in utilizing the same or modified procedures to estimate the amount of phosphorus or other chemicals present in sediment that may become available in the water column. In the opinion of the authors, however, there is still some potential for this approach in evaluating the potential environmental impact of the disposal of dredged material. It is clear, however, that such an empirical approach will have to be developed in conjunction with large scale field studies in which an empirical correlation can be derived between the laboratory leaching test and the environmental impact of dredged material disposal. This topic will be discussed further in the section on the interpretation of the Elutriate Test results.

It is clear from the discussion that study is needed on the role of water composition and characteristics before a satisfactory leachate water can be developed to meet the needs of the majority of the dredging situations that occur in the U.S.

Throughout this report frequent reference has been made to the behavior of taconite tailings as a somewhat model system which could be used to draw some inference on the possible role of the various factors that could influence the release of trace elements from solid materials. Because of the large amounts of data available on laboratory leaching studies, intake-discharge studies at the taconite ore beneficiation plant and measurements

from Lake Superior, fresh samples of taconite tailings were obtained from Reserve Mining Company, Silver Bay, Minnesota, and subjected to the presently accepted form of the Elutriate Test. Also, samples of Duluth Harbor sediment and Lake Superior open-water sediment were subjected to the Elutriate Test for purposes of comparison with the taconite tailings results. A 4:1 suspension of disposal site water with tailings was prepared by mixing 1800 ml of Lake Superior water with 450 ml of taconite tailings collected from the Reserve west launder. The suspensions had a total solids concentration of 1.9 g total tailings per liter. These suspensions were shaken for thirty minutes on a rotary action shaker, allowed to settle for one hour and then filtered through presoaked 0.45μ pore size Millipore filters. The Duluth Harbor and Lake Superior sediments were diluted to the same approximate suspended solids concentration and treated in an identical manner.

The filtrate from the Elutriate Test was analyzed for 21 parameters including nutrients and trace metals. These results for taconite tailings are presented in Table 3. An examination of the data in Table 3 reveals a very good agreement between replicate Elutriate Test results for taconite tailing samples except for a single zinc analysis (sample A). Because of the difference between this sample and the other replicate samples, it is probable that this sample was contaminated as part of the test procedures. This type of problem is frequently encountered in working with low levels of zinc.

Elutriate Test results with taconite tailings[29] are also in good agreement with a long-term taconite tailings leaching study conducted by Plumb.[11] The greatest release in both studies occurred with alkalinity and calcium. Another similarity between the two studies is that an 18 fold increase in manganese occurred in the Elutriate Test (Table 3), and Plumb[11] observed that

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TABLE 3

ELUTRIATE TEST RESULTS WITH TACONITE TAILINGS*

	Units	Filtrate from Tailings and Lake Superior Water			Initial Lake Superior Water
		A	B	C	
Ca	mg/l	14.4	14.6	14.4	13.2
Mg	mg/l	3.00	2.96	2.96	2.81
Na	mg/l	1.51	1.57	1.57	1.43
K	mg/l	0.79	0.96	0.96	0.62
Alkalinity (as $CaCO_3$)	mg/l	45.75	46.50	46.72	41.99
SO_4	mg/l	4.6	4.2	3.8	4.2
Cl	mg/l	1.4	1.4	1.4	1.2
Si	mg/l	3.4	3.4	3.6	2.4
$O-PO_4-P$	µg/l	1	1	1	<1
Fe	µg/l	4	6	5	5
Mn	µg/l	18	18	17	1
Cu	µg/l	1.7	1.4	1.5	1.9
Zn	µg/l	9	0.7	<0.2	1.6
Ni	µg/l	<1	<1	<1	<1
Cd	µg/l	<0.2	<0.2	<0.2	<0.2
Pb	µg/l	1	1	1	<1
Co	µg/l	<0.5	<0.5	<0.5	<0.5
NH_3-N	µg/l	4	3	3	6
NO_2^--N	µg/l	13	16	11	5
NO_3^--N	mg/l	0.26	0.23	0.24	0.17
pH		7.70	7.70	7.71	7.43
Spec. Cond.	umhos/cm	94	92	99	90
Dis. solids**	mg/l	57	56	60	54

*After Wagner[29]

**Calculated as 0.605 x specific conductance

A, B and C are replicate samples treated in an identical manner

manganese was the only trace metal to be released from taconite tailings under conditions similar to those to be expected in Lake Superior. Although manganese is more available than other trace metals associated with taconite tailings, the discharge of tailings to Lake Superior has not caused a change in lake manganese concentrations.[30] Probable reasons for the lack of concentration changes in Lake Superior are the expected oxidation and precipitation of manganese in the oxidizing conditions of Lake Superior and the large volume of dilution water available.

The results of this study on taconite tailings show that the Elutriate Test as currently designed yielded an accurate prediction of the potential long-term release of various elements from this type of sample and therefore support in principle the potential use of short-term Elutriate Tests as a possible tool to detect longer-term release in the environment.

For comparison purposes, the taconite tailings Elutriate Test results are compared to the results obtained with this test for samples of sediment taken from Lake Superior and Duluth Harbor. These results are presented in Table 4.

Three parameters in tailings suspensions, zinc, manganese and nitrite, exceeded the arbitrary 50 percent increase limit (1.5 times the ambient water concentration) in the dredged material evaluation procedure. As explained above, the 206 percent value for zinc is the result of one high, unreplicated value. The other two tailings samples suggest a loss of zinc from solution (Table 3, samples B and C). Manganese release during the Elutriate Test has been found in other investigations.[11] However, the relatively large increase, 1800 percent, has not produced any locally detectable change in manganese concentrations.[30] Elutriate Test results with taconite tailings also suggest nitrite is available, but no changes have been observed

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TABLE 4

EFFECT OF TACONITE TAILINGS, LAKE SUPERIOR SEDIMENT AND
DULUTH HARBOR SEDIMENT ON DISSOLVED SOLIDS IN LAKE SUPERIOR WATER*

Percentage of ambient concentration

	Taconite Tailings[1]	Lake Superior Sediment[2]	Duluth Harbor Sediment[3]
Ca	110	97	92
Mg	106	97	99
Na	108	102	116
K	145	93	101
Alkalinity (as $CaCO_3$)	110	100	92
SO_4	100	94	109
Cl	116	108	136
SiO_2	146	108	128
$O-PO_4-P$	-	-	>233
Fe	100	107	613
Mn	1800	5000	22,500
Cu	79	179	103
Zn	206	94	44
Ni	-	-	-
Cd	-	-	-
Pb	>100	-	-
Co	-	-	-
NH_3-N	50	39	260
NO_2^--N	266	206	200
NO_3^--N	141	84	125
pH	-	-	-
Spec. Cond.	106	100	97
Dis. Solids	106	100	97

The calculated percentage increases are the averages of three
  replicate samples: 1) 1.9 g/l taconite tailings, 2) 2.5 g/l
  lake sediments, 3) 2.6 g/l harbor sediments.

- no ratio possible because initial value was less than detection
  limit -- no concentration change was measured

* After Wagner[29]

in the lake as a result of Reserve Mining discharge operations.[30]

Open lake sediments exceeded Elutriate Test criteria for manganese, copper and nitrite; harbor sediments exceeded criteria for phosphate, iron, manganese, ammonia and nitrite. Both types of sediment produced a greater increase for manganese (5000 percent and 22,500 percent) than taconite tailings (1800 percent) (Table 4). The results suggest that Duluth Harbor sediment are under more reducing conditions because of the higher release of manganese, iron, ammonia and nitrite. Zinc results from both Lake Superior sediment suspensions tend to support the position that the one tailings sample (Table 3, sample A) was contaminated because zinc was removed from solution by Lake Superior sediment and Duluth Harbor sediment during the test. Plumb[11] also observed that tailings have the capacity to remove zinc from solution by sorption.

Several problems are apparent from these data with the use of a percentage increase as a standard criteria. First, when the final concentration is measurable but the initial concentration is not, it is impossible to determine the percentage change (lead with taconite tailings and phosphate with Duluth Harbor sediment). The same problem occurs when neither concentration is measurable, i.e., less than detectable limit (Ni, Cd and Co in Table 4). The most serious problem is that at this time there is no relationship between percentage change in the laboratory test and actual environmental change. This point was discussed previously with respect to manganese where an 1800 percent increase was measured in the test but no change was measured in the lake. These results amplify the fact that it is important not to attach any across-the-board significance to the Elutriate Test results with regard to the tendencies of a particular sediment without carefully considering the characteristics of the receiving waters for the sediment. As shown in the studies with taconite tailings, the fact that a particular

element exceeds the 1.5 criterion should not be used as the sole criterion to determine the potential effects of that element on the environment. Because of the characteristics of the Elutriate Test, it is possible for certain elements to show release under the conditions of the test and yet show no measurable change in the receiving waters due to the high assimilative capacity of a water. Also, for those elements that tend to occur in the reduced oxidation state in the sediment, such as manganese, there is a high probability that they will be oxidized by dissolved oxygen in the receiving waters and precipitate as an insoluble species.

It is interesting to note that the natural Lake Superior sediment which has not been contaminated by the activities of man also showed release of a number of chemicals that was approximately equal to or sometimes exceeded the release from taconite tailings. The open waters and sediment of Lake Superior would be considered as being some of the cleanest water and sediment in the world as a result of having very low ambient concentrations of chemicals and being virtually unaffected by the activities of man. These results further amplify the need for realistic interpretation of the Elutriate Test results.

Solid-Liquid Separation

The standard Elutriate Test requires that the sample be filtered or centrifuged prior to analysis. The conditions of either procedure are not specified. Generally, in the water pollution field two types of filters are used. The glass fiber filter frequently used normally has a highly diverse pore size distribution with a mean size in the order of 5 μ . The other type of filter that is receiving a wide spread use is the

membrane filter with a relatively narrow pore size distribution with a mean near 0.4 - 0.5 μ. It is commonly accepted in the aquatic sciences that filters of this type may be used to differentiate between soluble and insoluble chemical species. There was little rationale from a chemical point of view for selecting these filters. Originally these filters were designed for sanitary bacteriological work since they would retain most of the enteric pathogenic organisms and other indicator species that cause waterborne disease. Their use in chemical analysis stems primarily from the fact that they were available at moderate cost and that a reasonable volume of filtered water could be collected in a relatively short period of time. The porosity of these filters represents the upper end of the colloidal size range. Therefore, it is conceivable that large amounts of particulate matter could pass through these filters and be measured as "soluble" species. The element that probably causes more problems in this regard than any other is iron. Ferric hydroxide tends to form particles with a diameter less than 0.5 μ. This behavior could be of importance in dredged material disposal since ferric hydroxide would be expected to form in the Elutriate Test as a result of the oxidation of the ferrous iron normally present in sediment. Since ferric hydroxide is a very efficient scavenger for many trace compounds, it is possible that dissolved species in the sediment's interstitial and disposal site water may be removed from solution during the Elutriate Test. Since the particle size of ferric hydroxide is dependent on a wide variety of factors that are poorly understood at this time, it is possible that some of the contaminants which are removed from solution by ferric hydroxide would appear in the filtrate as soluble species as a result of forming particles less than 0.5 μ in diameter.

The use of centrifugation as an alternate to filtration in the Elutriate Test should only be done where it can be shown that particles with a specific gravity slightly greater than water

and a diameter of 0.5 μ can be removed in the centrifuge. In this way, the centrifugation and filtration would yield somewhat comparable results. In any situation where it appears that large amounts of contaminants in an apparently soluble form are present in the elutriate, high speed centrifugation should be employed to determine whether or not the apparently soluble species are in true solution. If it is found that the majority of the materials present in apparently soluble form are in fact in colloidal form, then bioassays should be performed in order to determine whether the colloidal forms are toxic to selected forms of aquatic life.

One of the most severe problems with filtration compared to centrifugation is the contamination of the test solution by chemicals present in the filter. It is essential that a blank solution be carried through the Elutriate Test utilizing distilled water in place of the dredged material in order to determine if any significant contamination has occurred in the test. If contamination problems become significant, then it may be necessary to wash the filters prior to use with distilled water and in some instances a dilute HCl solution. The most severe problems of this type are encountered with zinc and phosphate. Often, it is almost impossible to clean up the filters to the degree necessary to avoid zinc contamination. Under these circumstances it may be necessary to resort to high speed centrifugation as an alternative to filtration.

Another problem that has been encountered by the authors in utilization of the Elutriate Test is the fact that some sediments are sufficiently cohesive so that it is impossible to filter the required volume of water within the 1.5 hour total time period allowed in the standard Elutriate Test. At this point in time, it is impossible to determine the significance of this problem in that no information is available on the effect of leaching time on the release of chemical contaminants

from sediment. It is recommended that the individual conducting the Elutriate Test investigate the effect of time on release where this type of situation is encountered. From this type of information, it should be possible to ascertain the significance of not being able to keep the contact time to the 1.5 hour total time period specified. It has been found that a combination of centrifugation and filtration may reduce the total time of contact for sediments difficult to filter. The centrifuge would be used to remove the bulk of the solids. The supernatant would then be filtered to provide the sample for analysis.

The standard Elutriate Test does not specify the overall volume of the elutriate solution. It does specify the ratio of sediment to disposal site water that is to be used. For certain of the chemical analyses, such as chlorinated hydrocarbon pesticides, the total volume used in the test will have to be very large in order to obtain the amount of elutriate solution needed for these analyses. This situation may cause even greater problems in the filtration step due to the large volumes involved. In order to eliminate problems of this type, it may be necessary to filter the sample in multiple filters and combine the filtrates. An investigator should be aware of the fact that this could amplify possible contamination problems. Another approach that has proven to be of value in filtering large volumes of difficult to filter suspensions involves the use of pressure filtration rather than the more commonly used vacuum filtration.

PRACTICABILITY OF THE ELUTRIATE TEST

An essential feature of any Elutriate Test designed to
determine certain aspects of the environmental impact of
dredged material disposal is that the test must be able to be
performed in a reasonable period of time at a reasonable cost.
One of the reasons why the bulk-analysis approach has been
used for dredged material disposal is the fact that the chemical
tests could be performed in the laboratory in a reasonable time
period and at a reasonable cost. In addition to these analyses,
costs must be added for performing the Elutriate Test itself.
While the total funds that should be spent for dredged material
analyses is a highly subjective figure, it is important to keep
in mind that any modifications of the Elutriate Test which
cause a significant increase in cost should be minimized. It
should also be recalled that the alternative to the Elutriate
Test in many instances is a more expensive means of disposal
with possibly little or no improvement in water quality.

It is felt that the current cost associated with conducting
the Elutriate Test is reasonable and that this test can be
performed by technically trained personnel and equipment
normally available in analytical laboratories. It is further
felt that an Elutriate Test that does not exceed a several day
period is a reasonable requirement.

The implementation of any meaningful Elutriate Test requires
that procedures be developed to obtain representative samples
of natural water sediment that is scheduled for dredging. Since
these types of sediment tend to be highly variable in composition,
very large numbers of samples may be needed in order to obtain
a representative sample of the area. It is beyond the scope of
this report to discuss in detail the procedures that should be
used except to say that the sampling program developed for any

particular area should be based on the spatial variability of the results of the Elutriate Tests for that region rather than some arbitrary grid which does not consider the characteristics of the system under investigation. Lee[31] has recently discussed the use of this type of approach in water-quality studies on the Great Lakes.

INTERPRETATION OF THE ELUTRIATE TEST RESULTS

The current Elutriate Test has established a 1.5 factor as a critical value for the release of contaminants from sediment that is scheduled to be dredged. This factor allows a 50 percent increase above receiving water background for dissolved solutes in the elutriate water. The basis for this figure is not that an increase of this magnitude would necessarily mean that the disposal of the dredged material would have an adverse effect on the water quality in the region of disposal. Instead, this figure is used to flag potentially significant situations that deserve further study.[32]

The arbitrary application of the 1.5 factor to determine whether or not a particular sediment is "polluted" is no more technically sound than using bulk analysis. The proper interpretation of the Elutriate Test results requires consideration of the existing concentrations of each of the water-quality parameters of concern in relationship to the amount of increase in concentrations that would occur in the disposal area. The sum of these two must be examined in light of the critical concentrations of the parameter for aquatic life of the receiving water.

The EPA has recently proposed water-quality criteria for many chemical parameters for both marine and fresh waters.[8] In general, the parameters listed in the proposed criteria are based on soluble species and chronic exposure of the aquatic organisms. For a few chemical constituents, bioassays have been conducted in order to determine the relationship between acute lethal concentration (LC_{50}) and the chronic sublethal detrimental concentration such

as impairment of reproduction. It has generally been found that an application factor of 10 to 1000 relates these two concentrations. The EPA[8] has chosen an application factor of 100 for those situations where no information is available to relate acute lethal to chronic sublethal effects. Neither the EPA-proposed water-quality criteria based on chronic sublethal effects nor the acute lethal concentrations which via an application factor serve as a basis for these criteria should be applied to most dredged material disposal situations.

The adverse effects of chemicals to aquatic life are generally a time-concentration dependent process. Aquatic organisms can tolerate very high concentrations of many chemicals for short periods of time. As the time of exposure increases, the critical concentrations decrease until the EPA water-quality criteria based on chronic-continuous exposure is reached. Criteria of the type proposed by the EPA[8] are applicable to situations in which there is a continuous discharge of the chemical to the environment in such a manner that organisms present in the water columns could and do permanently reside in an area which has excessive concentrations of soluble solutes of the same chemical species as used in the bioassay tests which served as a basis for the criteria.[33] With few exceptions dredged material disposal does not create this type of situation since dredging is generally of an intermittent nature and there is little opportunity for organisms present in the water column to receive chronic exposure to any chemical constituents which may be released from the solids. Further, the areal and volume extent of both dredging and dredged material disposal are generally rather limited compared to the area and volume of the receiving waters. This situation can result in the rapid dilution of any adverse chemical contaminant released from dredged sediment. From an overall point of view, an organism present in the waters receiving

dredged material under the normal situation where a large load
is dumped at a specific site would be exposed to a continuously
changing concentration of any released contaminant due to
dilution occurring in the water column. It is reasonable to
expect that in many instances the rate of dilution would
invalidate the use of the 96-hour LC_{50} as a valid criteria for
adverse effects of chemicals released from dredged material. As
noted above, aquatic organisms may tolerate much higher concen-
trations than the EPA LC_{50} provided the time of exposure is less
than the 96-hour period.

The basic question that must be resolved in application of
the Elutriate Test is what criteria should be used in order
to determine whether or not an excessive release of one or more
chemical constituents will occur. The Elutriate Test will give
a numerical value which will indicate the amount of chemical
release which can occur in the dredged material disposal area
per unit volume of dredged material. Under conditions where
large scale potentially significant constituent release occurs,
this information must then be combined with information from
the expected amount of dilution in the disposal area in order
to develop a time-concentration relationship for the chemical
constituents of concern. From a time-concentration-toxicity
relationship for the chemical constituent based on short-term
bioassays for selected organisms of the disposal region and the
time-concentration-dilution relationship developed above, it
would be possible to ascertain whether the release of a chemical
constituent from dredged material could have an adverse effect
on the aquatic life in the water column.

Water-Quality Criteria for Particulate Species

The water-quality criteria recently proposed by the EPA[8]
are only directly applicable for the chemical species that were
involved in the bioassay test used to establish the criteria.

Chemical compounds exist in natural waters in a wide variety of forms. There is substantial information which shows that there is a markedly different toxicity for many chemical forms. The greatest differences are often found between the soluble aqueous species and a wide variety of particulate forms that can exist in natural waters. However, even the soluble or apparently soluble species show differences in toxicity in different forms. For example, copper-II aqueous species is highly toxic to many algae and forms of aquatic life. Some organic complexes of copper show little or no toxicity to various forms of aquatic life. A specific example of this type of situation is the copper-II complex with EDTA. The copper-II citrate complex shows toxicity to many forms of aquatic life. Further, this complex is not stable as a result of bacterial degradation where the citrate part of the molecule is utilized as a source of energy.

The EPA-proposed water-quality criteria[8] recognized a variable toxicity dependent upon chemical species and water characteristics in that many of the criteria are based on a 96-hour LC_{50} with an application factor used to relate acute lethal to chronic sublethal effects. There is a potentially significant problem with this approach in that the application factors have been, in general, based on the relative toxicity of the aquo species. Essentially no work has been reported on application factors which are applicable to different forms of the same compound. It is highly questionable whether the application factor approach can be used for solid species of particular compounds. This situation is further complicated by the fact that the forms of particular elements or compounds are somewhat interchangeable with the result that the toxicity of natural water samples may change with time because of chemical and biochemical reactions that

may occur in this system. While reactions of this type would tend to reduce toxicity, there are conceivable situations where an increase in toxicity could occur. One example of this type can be postulated which involves a partial degradation of an organic compound where the parent is nontoxic and the daughter is toxic. Very little work has been done thus far on toxicity of complex organic mixtures as a function of time.

As discussed by Lee,[25] the toxicity of a particular compound from a specific source is likely to be controlled to a major extent by transport mechanisms that exist in natural water systems. This would be especially true for the relative toxicities of particulate versus dissolved species. Studies on the chemical forms of a particular element or compound conducted in the absence of aquatic organisms may not yield realistic results because the aquatic organism creates environments which are markedly different from the bulk water environment. For example, the intestinal tract of zooplankton and fish may have a markedly different pH and organic content than the bulk solution. It is possible that a release of potentially significant chemicals present in particulate form may occur within the organism's intestinal tract which would not occur to any extent in the bulk water. It is important to emphasize that such a release should not be interpreted as being adverse to the organism per se. Experiments in which the solid forms of elements are made radioactive and then exposed to fish may yield results indicating the radioactive species became incorporated in the fish tissue. This result should not be used to infer detrimental effects on the organisms. It is entirely possible that the magnitude of transfer is sufficiently small so that no adverse effect results.

It is evident that before any generalizations can be made on the toxicity of contaminants in dredged material and other

solid forms, substantial study has to be conducted in this area. It is unlikely, however, that substantial toxicity would occur in either the dredging or disposal site due to particulate forms of the compounds present. Based on information available today, it appears that in general, the formation of a particulate form would tend to reduce toxicity rather than enhance it. This means that as far as the respective water columns are concerned at the dredging and disposal sites, the Elutriate Test should be designed to measure soluble or apparently soluble species that are released from these sediments or dredged material. If the amount and rate of release is less than the critical toxicity threshold for key organisms in the area, then it is reasonable to propose that little or no adverse effect would be found due to the chemical contaminants in the dredged sediments.

As noted previously in this report, concern about dredging and dredged material disposal is not restricted to the water columns but extends to the deposited sediment. Normally, little concern is voiced about problems of this type at the dredging site since from a geological point of view this area is an environment where the boats and current-induced mixing provide an unsuitable habitat for many forms of aquatic life. Therefore, the concern about the chemical contaminants is for the deposited sediment in the region of dredged material disposal. As noted previously, it is improper to apply existing water-quality criteria to this environment. The only approach that may be used to determine an adverse effect in this situation is to conduct bioassays using representative benthic organisms from the disposal area. It is possible that the toxicity under these conditions would be correlated empirically with the chemical characteristics of the interstitial water. Studies are needed to determine whether or not such a relationship exists.

There is a situation which could exist where contaminated dredged material would not show an adverse effect on benthic organisms, yet could be adverse to higher forms of life. This situation stems from the fact that it is possible that aquatic benthic organisms that exist in contaminated dredged material may have a much higher concentration of chemical contaminants than the same organism living in non-contaminated areas. Since some fish derive a substantial part of their food from benthic organisms, it is conceivable that fish of this type could acquire sufficient contaminant levels to be adverse to their well-being. Also, such a situation could be adverse to man in that the concentrations of contaminants in fish may not be adverse to the fish, yet be sufficiently high to exceed the FDA limit for the use of the organism as a foodstuff for man. Several of the EPA-proposed criteria[8] were established based on the concentrations in an aquatic environment that, while not adverse to aquatic organisms, limit the usefulness of certain parts of the food web by man. Prime examples of this situation are mercury, DDT and PCB's. It should be emphasized that these examples are not based on a mechanism in which the concentration in the solids or interstitial waters are used to determine food web buildup. They are based on forms present in the water column. It is unlikely that sufficient concentrations of these chemicals could buildup in the food web arising from dredging and dredged material disposal unless there was substantial release of these compounds to the water column. This is another area which deserves further study.

Mixing Zone

Open-water disposal of dredged material represents a prime example where the mixing-zone concept should be used. This concept allows for different water-quality standards in the

region of the discharge than in the bulk receiving waters.
While there is still considerable controversy on the proper
size of mixing zones,[34] there is no question that mixing zones
are a reality and should be considered in any discharge or
disposal of contaminants in natural water systems. The mixing-
zone concept generally allows some degradation of water quality
in the region of discharge. It is generally assumed that it is
in the interest of the public to allow for a mixing zone in
order to utilize to some extent the contaminant assimilative
capacity of natural water systems. The basic question that
must be resolved for each particular region is the size of the
mixing zones that can be allowed for a particular receiving
water without causing significant overall degradation of the
water quality. As noted above, the implication of a mixing-
zone concept to dredged material disposal is somewhat different
than the application to industrial and municipal discharges.
Because of the intermittent nature of dredged material disposal,
even a larger mixing zone can be tolerated without having
significant impact on the aquatic ecosystem of the receiving
waters. The basic problem with the mixing-zone approach is
a lack of understanding between the significance of a partial
degradation of a limited region of the receiving waters and the
overall functioning of the aquatic ecosystem. In order to prop-
erly develop dredged material disposal criteria, it is necessary
to conduct research on this relationship. Once this information
is available it should be reviewed by the public to determine
whether it is in the best interest of society to change the
size of a mixing zone in a particular area.

   It is suggested that an equation of Lerman and Brunskill[35]
be modified for estimating the environmental impact of dredged
material disposal. They presented a formula for calculating
the effect of sediments on overlying bulk water composition

which is

$$C_{L'} = \frac{C_L}{1 + h/H} \left\{ 1 + \left(\frac{C_b}{C_L}\right) \left(\frac{h}{H}\right) (P + K[1-P]) \right\}$$

where $C_{L'}$ = predicted concentration

C_L = previous concentration

h = thickness of sediment being mixed with water

H = mean depth of water column

C_b = interstitial water concentration

P = porosity of sediment

K = exchangeability factor.

This approach considers relative concentrations in water and sediment, availability of ions associated with solids and the depth of the sediment mixing zone. The term $C_L H$ is an approximation for the total ions in the water column which results in units of mg/m/l. Remaining terms are attempts at evaluating dissolved ion sources in the sediments. The term $C_b hP$ approximates ions from interstitial water. The term $C_b h[1-P]K$ approximates exchangeable ions from the solid phase assuming the availability of ions from solids is proportional to the interstitial concentration. For both of these factors, the total ion balance is approximate since the units are mg/m/l.

The equation can be modified for use in dredged material disposal by substituting volumes for depths resulting in an equation such as

$$C_L' = C_1 + \frac{XK + V_i C_i}{V}$$

where C_L' = predicted water concentration

C_1 = present water concentration

X = amount of dredged material

K = exchange ability factor

V_i = volume of interstitial water

C_i = concentration of interstitial water

V = volume of receiving water.

Because some investigators have found that the distribution of ions can be influenced by the procedures used to determine availability from solids and interstitial water concentrations,[7] it may be better to reduce the term $(XK + V_iC_i)$ to XK' where K' is total sediment availability (available solutes + interstitial water concentrations). It may also be advisable to define V as the volume in a specified mixing zone rather than total volume of water available. A starting point would be to use the 100 yard radius value that is used by EPA for ocean dumping[10] and to assume some spreading with depth such as a conservative estimate of 1:1. Using the 100 yard radius figure and a 1:1 depth dispersion value, it can be shown that the volume available in the mixing zone for point source dumping is:

$$V' = 1/3 \; \pi \; (r+d)^3$$

where   d = depth

r = discharge radius.

If a moving discharge source is used, the dilution volume would be:

$$V'' = 1/3 \; \pi \; (r+d)^3 + x \; (200d+d^2)$$

where   d = depth

r = discharge radius

x = distance barge moves during dumping.

A working equation would then take the form of:

$$C_2 = C_1 + \frac{XK'}{V''} \; .$$

An equation such as this would consider the amount of solutes discharged, the availability of solutes in dredged material and the volume of water available for dilution. In addition, the criteria could be expressed in terms of environmental concentrations which may be more meaningful than percentage increase.

It is important to clearly distinguish between mixing-zone toxicity to planktonic organisms and toxicity to higher forms. Generally during spring, summer, and fall, algal growth is limited by one or more chemical species. The zooplankton population is often limited by the phytoplankton population. Under these conditions, the addition of toxic compounds to the water column at either the dredging or disposal site which would be adverse to phytoplankton and/or zooplankton does not normally represent a potentially significant adverse effect on the over-all ecosystem. This is the result of the fact that the population density outside the zone of toxicity may be increased to a sufficient extent as to completely overcome the reduced growth and reproduction that occurred in the mixing zone. It is also important to note that many algal toxicants do not kill the organisms but merely prevent their reproduction so long as the concentration is above some critical value. There is increasing evidence that natural waters have a certain zooplankton-carrying capacity with the result that any reduction in numbers in the disposal site area is readily made up outside of this area due to the high reproductive capacity of these organisms.

PREVIOUS DREDGED MATERIAL STUDIES

Studies on Biological, Biochemical, and Turbidity Problems

A recent publication by May[3] summarized dredged material studies for the period 1938-1972. It is clear from the literature review section of his review that past studies concentrated on biological and turbidity problems. The studies seem to indicate that a wide variety of species can tolerate dredged material disposal and that any changes are reversible.

The principal potential physical problems causing concern in open-water disposal of dredged material are turbidity increases and sediment accumulation. A turbidity increase resulting from the mixing of dredged solids with disposal site water would be considered an aesthetic deterioration. In addition, a turbidity increase would contribute to reduced light penetration, interference with photosynthesis, interference with heat transfer, flocculation of algae, disruption of spawning beds and burial of bottom fauna and macrophytes. The literature on these topics has been reviewed by Plumb.[11] Turbidity problems are usually of short-term duration[3] and tend to be more severe in flowing systems such as rivers and streams rather than lakes.[11]

In the review by May,[3] turbidity received the greatest attention of any single water-quality parameter. In one study a measurable turbidity plume was detected 3.1 miles down current from the discharge location.[3] This appears to be an unusual case, however, as the turbidity plume generally becomes indistinguishable within 2000 feet of the discharge site. Also, reported turbidity increases are within normal fluctuations at each site at sampling locations greater than 400 feet from the disposal operations.[3]

The duration of the turbidity increases is rather short with some of the studies reporting background levels two hours after dredged material disposal stopped.

The most significant changes occurred when disposal of dredged material was sufficient to cause burial of the existing population. The population usually reestablished itself although at a lower species diversity. Most of the biological problems reported in the literature are concerned with benthic fauna reductions.[3] Not all species were destroyed but population reductions of 65-70 percent have been reported. Recovery times ranged from six months to two years.

A sequence of studies discussing the effect of dredged material on fish were summarized by May.[3] Sediment concentrations of one percent were reported to be toxic to salmon smolts in the laboratory. No effect was demonstrated in the environment, although a fright response was postulated. In a second study no damage was observed to fish and crustaceans within 75-150 feet of an active dredge. In yet another study in Chesapeake Bay, no gross effects were observed on microscopic plants, aquatic animals, eggs and larvae of fish, adult fish captured in the dredging area or fish held in traps in the dredging area.[3]

The organisms mentioned in the literature that may be influenced by dredging activities include fish, phytoplankton, oysters, mollusks and rooted aquatic vegetation. Reported effects are highly variable. Ingle et al.[36] demonstrated that a suspension of dredged solids was toxic to fish in the laboratory, but could not detect any changes in the environment although it was suggested that fish would exercise some type of avoidance reaction in the natural environment. Others have reported no adverse effect on various life stages of fish and,

in one case, have even reported increased numbers of fish in the vicinity of active dredges.[3]

May[3] studied the effect of dredged material from shell dredging, ship channel dredging and intracoastal dredging in Mobile Bay. Samples were collected in a radial grid pattern with the discharge located at the center. They were analyzed for turbidity, suspended solids, volatile solids, nutrients, trace metals and pesticides. Turbidity data suggests that a turbidity plume existed in the down current direction. The plume extended 400-1200 feet depending on wind velocity and type of dredging. Suspended solids data demonstrated that some down current transport of discharged solids was occurring. However, suspended solids concentrations were less than 100 mg/l at distances greater than 400 feet from the source. Both sets of data indicate that more than 90 percent of the dredged material settled quickly and created a mud flow along the bottom of the channel. May[3] felt the turbidity increases had a limited deleterious effect even though the average depth in Mobile Bay is approximately ten feet.

An oxygen depletion was observed at the interface of the mud flow. This was attributed to the oxygen demand of reduced inorganics in the dredged solids.[3] The reasons given for this conclusion were the following: 1) volatile solids were not released from dredged material and 2) the rate of oxidation of volatile solids was small compared to settling time and the chemical oxygen demand (COD) of the sediment.

Very little change occurred in the chemical parameters as a result of dredging and dredged material disposal.[3] Total zinc, total chromium and total COD increased within 100 feet of the disposal site. However, there was no change in pH and dissolved oxygen away from the mud flow, or soluble forms of phosphorus, nitrogen, heavy metals (Hg, Pb, Zn, Cd, Cr), COD or pesticides (DDT). This was demonstrated by a lack of change in filtered samples collected before, during, and

after dredging activities. May[3] concluded that the concentration of material in sediments did not determine the effect of dredged material on water quality. Instead, release will be regulated by the effect of dredged material on conditions such as pH and dissolved oxygen levels that regulate exchange processes. Because the system remained aerobic, organic and inorganic constituents remained insoluble or absorbed on the high concentration of sediment.

Windom[15] also studied the environmental impact of dredging. Dredged material can decrease the Eh (redox conditions) and increase the sulfide levels in sediment. These conditions favor the reduced form of each species. The reduced species can migrate to the oxidized layer at the sediment water interface where they are concentrated by processes of oxidation and precipitation. These sediment changes can endure for a long time if the accumulation of dredged solids is great enough.

Despite the changes produced in the sediments by accumulation of dredged material, no significant changes in water quality occurred during or after dredging activities except possibly for mercury.[15] In fact, the concentration of metals in the dredge discharge pipe was considerably lower than either river water or the weir effluent from a diked area receiving the dredged material. Metal concentrations were observed to increase with time (five days) back to ambient river levels. The proposed mechanism accounting for the observed changes in metal concentrations was related to the iron cycle in natural waters. It is postulated that reduced iron is released from dredged material, oxidized in the water and precipitated with the precipitate carrying other metals to the bottom by sorption and/or entrapment. When the iron is re-reduced in the sediments, the metals are freed and the original concentrations are re-established.

The lack of trace metal increases is not surprising because Windom[15] reported an increase in pH and dissolved oxygen. These conditions would not favor higher metal concentrations. This is an agreement with May[3] in that an increase would not be expected unless the conditions controlling exchange reactions are altered. Windom,[15] like May,[3] also stated that the effect of dredged material on water quality is not determined by the composition of the sediment being dredged.

In another report, Windom[5] discussed the potential effects of hydraulic dredging in several southeastern estuaries. Turbidity was monitored in order to assess any effects on water quality. In addition, nutrients and trace metals were monitored to determine whether the dispersion of dredged material resulted in a chemical exchange from the sediments to the water.

Increased turbidity levels caused by dredging activities are not thought to be a significant water quality problem.[5] It is a transient condition that only exists in a limited area around a dredging operation and may last only a few hours. This is especially true in estuaries and the open ocean where the fine particles will tend to agglomerate or flocculate due to the high ionic strength resulting in faster settling rates.

Windom[15] observed an initial release of ammonia with concentrations approaching 8 mg/l-N following dispersion of dredged solids. The source was thought to be the ammonia present in interstitial water. In some cases, concentrations were reduced to less than 1 mg/l-N in 10 to 20 days. The lower ammonia concentrations were caused by biological utilization as shown by increasing oxygen and chlorophyll concentrations and by nitrification as evidenced by increasing nitrate concentrations.

A variable phosphate release was measured in each of the four estuaries studied.[5] The initial release in two estuaries was 10-40 percent above ambient and gradually increased to 30-75

percent above ambient in two weeks. Sediment from a third
estuary produced a 300 percent increase in phosphate that
dropped to less than 100 percent in 10 days. Phosphate levels
in the fourth sediment - water system fluctuated around a 200
percent increase. Phosphate releases are thought to be less
significant than nitrogen in coastal waters because nitrogen
apparently limits production in these areas.

Dispersion of sediment with overlying water in proportions
similar to dredging operations resulted in variable concentra-
tions of iron, zinc, copper, lead, cadmium and mercury.[5] An
initial release of iron and zinc was observed followed by a
decrease for a period of a week and a subsequent increase to
concentrations three times ambient levels. The other metals
fluctuated between 100 and 300 percent above ambient levels.
The smallest fluctuations were seen in the mercury data.
Windom[5] suggested that the observed metal concentrations were
controlled by the iron cycle and the amount of metal complexing
organic matter present in the dredged sediments.

Gustafson[37] conducted a limited leaching study of dredged
sediment from the San Francisco Bay area. One hundred grams
of sediment were shaken with one liter of bay water for 20
minutes, allowed to settle for 30 minutes and analyzed. The
data (Table 5) indicate that four of the five metals had a lower
concentration after mixing with sediment. It was emphasized
that no replicates were run but the results suggest that sus-
pended sediment would tend to remove metals from solution prob-
ably by sorption rather than release metals to solution. It
was also reported that the concentration of pesticides and PCB's
in San Francisco Bay water decreased after the addition of
sediment.

The chemistry of trace metals in sediment was discussed
briefly by Saila et al.[38] in a report on the disposal of dredged
material in Rhode Island Sound. Although metals were found in

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TABLE 5

EFFECT OF SEDIMENT ON TRACE METAL CONCENTRATIONS

IN SAN FRANCISCO BAY WATER*

Metal	Sediment Concentration	Bay Water Concentration	Water + Sediment	Concentration Change-Percent
Mercury	NA	0.0014	0.00003	-97.4
Lead	310	<0.02	<0.0024	-88.0
Zinc	NA	<0.02	0.0024	-88.0
Copper	NA	<0.04	0.0121	-69.8
Cadmium	130	<0.02	0.0290	+45.0

All concentrations in mg/l

NA - No analysis

*After Gustafson[37]

dredged material and sediment in the disposal area, they were
not found in the overlying water. The transfer of material
to the water was controlled by the physicochemical state
of the metals in the sediment-water system that regulated or
limited metal availability.

Hydrocarbon distribution in sediment was also discussed
in the same report.[38] The hexane extractable material was 0.2
to 0.76 percent of the sediment (dry weight basis) and was
similar in characteristics to aged petroleum. Certain oils
could also be released that could possibly interfere with the
sensing ability of some marine organisms. The oils would also
selectively concentrate non-polar chemicals such as DDT and
PCB's. Concentration factors for these compounds of one million
have been reported.[39]

The results of an acid-iron waste disposal study in the
New York Bight have some application to a study of dredged
material. It was shown that the addition of the waste resulted
in the formation of an iron hydroxide precipitate.[40] The iron
precipitate concentrated seven other trace metals and carried
them to the bottom (Table 6). These results demonstrate that
the addition of a metal, even in a soluble form, does not mean
that it will be utilized by a biological population and also
gives support to the iron cycle influencing the chemistry of
other elements. Each of the metals in Table 6 was concentrated
2 to 27 times above levels in the effluent. Vaccaro et al.[40]
concluded that the fate of heavy metal additions in the New
York Bight area is entrapment in the sediments. They also implied
that a source of the metals is sewage sludge and dredged material
discharged in the area.

Hansen[41] presented a general discussion of dredging on the
Great Lakes. He notes that there is an awareness that nutrients
and other materials may transfer from suspended solids to water

TABLE 6

CONCENTRATION OF METALS IN AN ACID-IRON WASTE

AND A SEAWATER PRECIPITATE OF THE WASTE*

Metal	Concentration in Raw Effluent	Seawater ppt Dried
Fe	52,500	335,000
Ca	<0.5	83
Zn	25	520
Pb	5	120
Cr	5	140
Co	7	190
Ni	4	55
Cd	--	3

All concentrations in mg/l

*After Vaccaro et al.[40]

and that dissolved oxygen concentrations may be reduced as
a consequence of the exchange process. However, he states that
pollutants that remain fixed in sediment will not affect water
quality. The problem is to determine what fraction of the
dredged material is available for exchange. It was suggested
that this must be done on an individual basis.

Several dredging projects across the United States were
reviewed by O'Neal and Sceva.[42] Their report discusses the
effect of dredging on turbidity, dissolved oxygen and toxicity.
Significant turbidity problems were listed at an Inland Steel
landfill lagoon on southern Lake Michigan, at the mouth of the
Cuyahoga River on Lake Erie and along the Detroit River. The
magnitude and duration of the changes were not discussed.
Oxygen depletions ranged from 2-3 mg/l in New York harbor, to
25-35 percent of saturation in Cleveland Harbor, to 16-83 percent
of saturation in Arthur Kill, New Jersey, to 100 percent of
saturation in a mud flow at Bellingham Harbor, Washington. The
effect of these changes was not discussed. Releases of oil
and grease, ammonia, organic nitrogen, total phosphorus, BOD,
COD and iron were listed at several locations but no data were
given.

Hopper dredging in Oregon was the subject of an investi-
gation by Slotta et al.[27] The investigators concentrated on
physical and biological changes resulting from dredging and
demonstrated changes in median grain size, porosity, volatile
solids and hygroscopic moisture content at the dredging and
disposal site. The observed changes generally followed
expected changes. Some reductions in bottom fauna populations
were observed but these changes were thought to be minor in Coos
Bay, Oregon. It was postulated that the fauna has adapted to
short-term turbidity increases because of the relatively shallow
draft and the heavy marine traffic. The sampling program was

not sufficient to distinguish between acute and chronic turbidity effects or various sources of turbidity.

The chemical aspects of the Coos Bay study were limited to turbidity, temperature, salinity, dissolved oxygen and pH in the water and sulfate, total sulfide, chloride, total Kjeldahl nitrogen, soluble organic carbon and volatile solids in sediment interstitial water.[27] Dissolved oxygen reductions and turbidity increases were observed which agrees with other studies. However, the study is not useful for determining the effect of dredged material disposal on chemical water quality because more detailed analyses were not run. Changes observed by Slotta et al.[27] in sediment interstitial water as a result of dredging activities are not indicative of changes in overlying water because sediment is influenced by different conditions of pH, dissolved oxygen and redox potential.

An investigation of Great Lakes harbors' sediments was conducted at the University of Wisconsin[43] to determine the treatability and possible biological significance of dredged material. Samples were collected from nine harbors scattered throughout the lower Great Lakes region and subjected to physical examination, chemical analyses and biological testing. The physical examination was limited to particle size analysis, settling studies and filtration studies. Considerable variation was observed in the data, and treatment of the dredged sediment (aeration and digestion) had no uniform effect on settling or filtration characteristics.[43] The data varied from harbor to harbor and within one harbor.[43]

The chemical data from the Wisconsin study[43] included total analysis for phosphate, ammonia, organic nitrogen, chemical oxygen demand and volatile solids. The same analyses were run on supernate samples from the settling studies. Total analyses data was tabulated but not discussed except for the general observation that higher concentrations were observed in river samples compared to outer harbor samples.[43]

Chemical data from the settling studies would be similar to short-term (two hours to four days) leaching of dredged material. The observed range of concentrations was 20-1260 mg/l for volatile solids, 4.4-69.3 mg/l ammonia nitrogen, 5.5-57.2 mg/l Kjeldahl nitrogen and 0.15-11.40 mg/l phosphorus.[43] However, the data cannot be used to assess the effect of dredged material on water quality. First, suspensions for the settling study were prepared at a concentration of approximately 20 percent total solids. Since the exact concentration was not reported, the chemical changes cannot be related to the total mass of solids present. Second, Madison, Wisconsin, city tap water was used in the tests. The composition of this water varies with time but was not reported in the investigation which makes it impossible to determine exact concentration changes. Third, there is no mention of a filtration step which implies that the analytical results are a total analysis. This means that the reported results include dissolved solids present in the tap water, solids leached from the harbor sediments and suspended solids that did not settle. Consequently, data from the University of Wisconsin[43] investigation possibly overestimates the release of dissolved solids from dredged sediment.

As part of the dredged material investigation at the University of Wisconsin,[43] a series of bioassay experiments were conducted using benthic fauna, algae and Cladophora as test organisms. This resulted in the definition of five sediment categories[44,45] that are discussed elsewhere in this report. The methods that provided the most information and would be suitable for additional sediment studies were the benthic fauna viability and selectivity tests and algal bioassays using carbon-14 uptake as an indicator of algal activity.[43,45]

Algal bioassays using direct algae counts or light scattering methodology were meaningless.[43] The principal reason for the lack of results was a clumping or flocculation that occurred between

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the algae cells and the sediment particles. The <u>Cladophora</u>
bioassay results were also difficult to interpret.[43]

The use of carbon-14 to determine algal response avoids the
problems of algal flocculation. However, the data presented
in the University of Wisconsin report[43] and discussed by Gannon
and Beeton[45] do not support the position that algae were stimu-
lated by dredged sediment. An increased incorporation of carbon-
14 into algal cells was observed during the four day bioassays,
but the rate of carbon-14 incorporation actually decreased
between day 1 and day 4. If stimulation were occurring, the
population would increase, causing an increase in the rate of
incorporation. When the carbon-14 data is corrected for time of
contact, the algal population photosynthetic activity is
decreasing. This observation is true for each of the five
categories delineated by Gannon and Beeton.[45] Although the
carbon-14 procedure can be used to monitor the response of algae
to imposed experimental conditions, a great deal of care is
required in the presentation of such data to ensure proper
interpretation.

The carbon-14 procedure is based on the conversion of
CO_2 to cellular organic matter during the photosynthetic process.
By adding radioactive labeled $^{14}CO_2$ and knowing the amount of
$^{12}CO_2$ in the sample, the total amount of carbon fixation can be
calculated by measuring the carbon-14 uptake of the cells.
However, there are several factors that will influence the
uptake and should be specified in the data presentation. These
factors include the concentration of carbon-14, the number of
algal cells and the incubation time. In addition, the type of
algae may also be important. It is recommended that carbon
fixation be expressed as a rate based on a relatively short contact
time such as counts/minute/4 hours. It should be stressed that
counts/minute is the rate of decay of carbon-14 and as such is

only a measure of the amount of carbon-14 present and not of the rate of carbon-14 incorporation into cell matter.

Posner and Weber[46] determined the distribution of eight trace metals in three operationally defined fractions of sediment collected from selected Great Lakes' harbors. A soluble fraction was defined as the metals present in water squeezed out of the sediment. An acid leachable fraction was defined as the amount of metal released from sediments after a six to eight hour treatment with 10 percent hydrochloric acid and hydrogen peroxide at 90°C. The third fraction consisted of water soluble metals released during a 56-day anoxic leaching period. The range of values observed for each metal in each fraction is presented in Table 7. In general, the highest concentrations for each metal occurred in the acid leachable fraction. Also, the metals released to the greatest extent in any one fraction were iron and manganese.

There was no apparent relationship between the water soluble fractions and the acid leachable fraction.[46] The ratio of the water soluble fraction (R) to the acid leachable fraction (L) varied from metal to metal and from harbor to harbor. In fact, the only consistent pattern was the observed loss of copper from solution during the 56-day anoxic leaching experiments.

Because of similar sampling stations in the University of Wisconsin study[43] and the Posner and Weber investigations,[46] the classification of sediments based on bioassay results was compared to trace metal availability in each of the three operationally defined sediment fractions. The biological suitability increased in the following sequence: Cleveland: Buffalo: Toledo: Green Bay;[43] and trace metal availability in the acid leachable fraction decreased in the sequence of Cleveland: Buffalo: Toledo: Green Bay.[46] The apparent relationship between trace metal availability and biological suitability may be more fortuitous

TABLE 7

TRACE METAL AVAILABILITY

IN GREAT LAKES HARBORS' SEDIMENT*

	L	S	R
Cu	8.1-33.8	0.37-7.3	0.32-5.80
Cd	0.22-2.50	0.002-0.04	---
Pb	9.16-183	0.01-0.32	0.00-0.250
Zn	13.0-160	0.11-0.71	0.16-0.75
Fe	565-1340	1.1-12	5.9-11.0
Mn	26.3-168	0.71-1.9	0.7-8.1
Cr	7.6-42.7	0.0036-0.13	0.011-0.11
Hg	0.161-0.348	0.0066-0.05	---

L = acid leachable in 10 percent HCl for 6-8 hours at 90°C.

S = water in association with sediments ("pore water").

R = water leachable after 56 days under anoxic conditions.

All concentrations in mg/g.

*After Posner and Weber[46]

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than real because of the harsh conditions used in the acid leachable procedure. Trace metal availability in the sediment water (S) and water leachable fractions (R) followed a different order and decreased in the general sequence of Cleveland: Green Bay: Buffalo: Toledo. Part of the reason for the discrepancy between the metal release sequence and the biological suitability sequence, provided such a relationship does exist, is that composite samples were used in the metal study[46] compared to individual samples in the Wisconsin study.[43] It is known from several studies that the chemical characteristics of harbor sediments are highly variable from one location to another. This type of situation could readily explain the differences between the University of Wisconsin and the Posner and Weber studies.

Chemical studies have been conducted with material dredged from the Lake Erie ports of Buffalo[6] and Ashtabula.[47] Both reports give rather complete analyses of dredged material and the results are useful as an indicator of the variability of dredged material composition. However, the results of Ritchie and Speakman[6] are of little value because all chemical analyses were for total solids and a distinction must be made between total, soluble and available chemicals in order to assess the potential effect of dredging activity on water quality. The same is true for the data in the Leonard and Dahm[47] report except for the information presented in Table 8. An examination of Table 8 reveals that the effect on water quality is not a simple function of dredged material composition. This is shown by the fact that the percentage of soluble material (defined as passing a Whatman No. 541 filter) is not a constant percentage of the total analysis. There was a variation from sample to sample and from parameter to parameter for the same sample (percentage column, Table 8).

According to May,[3] a potential problem at dredging sites that has not received proper attention is the indirect effect

TABLE 8

CHARACTERISTICS OF DREDGINGS

COLLECTED AT ASHTABULA HARBOR, OHIO*

Parameter	SAMPLE 2A			SAMPLE 3A		
	Initial	Filtered	Percentage	Initial	Filtered	Percentage
pH	7.14	--	--	7.38	--	--
BOD	3,100	--	--	700	--	--
COD	14,900	39	0.26	4,100	48.5	1.18
Coliforms/100 ml	<10	--	--	600	--	--
Total Solids	600,000	320	0.05	206,300	240	0.11
Suspended Solids	599,510	--	--	206,060	--	--
Dissolved Solids	490	490	100	240	240	100
Volatile Solids	24,900	--	--	37,340	--	--
Turbidity -JTU	87,500	39	0.04	15,340	20	0.13
Oil and Grease	565	--	--	135	--	--
Nitrate Nitrogen	0.10	0.03	30	0.08	0.03	37.5
Kjeldahl Nitrogen	259	16	6.1	98	19	19.4
Ortho-Phosphate	--	0.12	--	--	0.03	--
Total Phosphate	8.0	<0.01	<0.12	16	<0.02	0.12
Phenol	--	<0.01	--	--	<0.01	--
Surfactants as LAS	--	--	--	--	<0.01	--
Chlorides	--	22.5	--	--	20	--
Sulfate	--	10	--	--	30	--
Sulfide	--	<1	--	--	<1	--
Iron	10,500	1.8	0.017	2,680	12.5	0.46
Mercury	0.068	--	--	0.044	--	--
Chromium	60	<0.3	0.5	14.0	<0.3	<2.1
Cadmium	<0.6	<0.01	1.66	0.2	<0.01	<5
Arsenic	<0.5	--	--	<0.5	--	--
Zinc	90	<0.1	<0.11	27	<0.1	<0.37
Lead	60	<0.5	<0.83	20.6	<0.5	2.4
Sodium	--	7.5	--	--	7.5	--
Calcium	--	52.5	--	--	45.0	--
Manganese	270	2.0	0.74	82	0.5	0.61
Copper	8.0	<0.5	<6.2	4.1	<0.5	<12.2
Nickel	<6.0	<0.1	<1.66	2.1	<0.1	<4.7
Weight of Sample, g/l	1,210	--	--	1,238	--	--

Initial--Composition of initial sample; Filtered--Passes Whatman No. 541 Filter; All Values in mg/l unless otherwise specified. *After Leonard and Dahm[47]

of physical modification. Dredging and disposal of dredged material
could conceivably alter water circulation and the extent of
salt water intrusion, which in turn may have a significant
effect on the estuarine ecosystem. Physical modifications could
alter the release of chemical contaminants from the sediments in
the region of dredging and dredged material disposal.

The potential physical effects of dredging on water quality
would not necessarily be adverse to the ecosystem. Since in
many harbors the areas that are dredged are often areas receiving
large amounts of municipal and/or industrial wastes and as a
result have degraded water quality, dredging which results in
an increased water circulation in these areas could produce
improved water quality by increased dispersion of the waste.

The discharge of dredged material can produce biological
changes at the disposal site. This may be caused by chemical
contaminants in the dredged sediments or the physical presence
of increased amounts of suspended solids. Several papers on
dredged material and suspended solids will be discussed to sum-
marize the type of biological problems to be expected at a
dredged material disposal site.

Flemer et al.[48] observed the biological response to dredging
and dredged material disposal in upper Chesapeake Bay. Samples
were collected along a sampling grid and examined for several
species of fish, clams, snails, worms and algae. It was found
that one species of snail, Congeria leucophaeta, was decreased
from several thousand organisms/0.1 m^2 to zero organisms/0.1 m^2
as a result of dredging activities. Dredged material disposal did
not have a measurable effect on any other organisms counted.
There was no difference in the abundance and distribution of adult
fish, fish eggs or fish larvae. In addition, fish placed in
cages at the dredging site had the same mortality as control fish
and no histological changes were observed in the gill structures.

It was felt that field studies at the time of dredging would only indicate the presence or absence of extreme damage to the ecosystem.[48] The authors also suggested that year round field studies and laboratory studies are required to rationally determine the biological effects of dredged material disposal. For example, a 33 percent reduction in productivity that lasted a few hours was observed in Chesapeake Bay. However, a 300 percent diurnal variation was observed in productivity and laboratory bioassays demonstrated the sedimentary material to be non-stimulatory and non-inhibitory. It was concluded that dredged material was not exerting a significant effect on algae. It was also pointed out that factors such as salinity and the natural mortality patterns would influence the distribution of various life stages of many aquatic organisms (fish, clams, worms). This type of variation must be considered in evaluating the effect of the disposal of dredged sediments.[48]

Pratt et al.[49] felt that it is difficult to run bioassays on waste solids discharged into the ocean because of the unknown factors of diffusion of dissolved solids out of deposits and the resultant dilution with overlying water. It was also suggested that the toxicity of interstitial water to bottom fauna may be more important than the toxicity of released solids that are diluted in the overlying water. Results indicate that waste solids would be toxic to cunner (in flow through bioassays but not batch bioassays) and shrimp but not to barnacles, crabs, mussels and quahogs. The toxic component was hydrogen sulfide.

Laboratory bioassays were conducted on sediment dredged from nine Great Lakes' harbors.[44] The test organism selected was Pontoporeia affinis, a pollution intolerant amphipod that is common in the Great Lakes. One of the studies was a selectivity test in which sediments were placed in containers and then randomly placed in an aquarium. Pontoporeia were randomly placed in the

aquarium. After 48-60 hours, the distribution of living and dead
Pontoporeia was determined. The organism indicated a preference
for open lake sediment (34 percent) and control harbor sediment
(32 percent). Sediments from industrialized areas such as
Cleveland, Toledo, Detroit and Indiana Harbor were avoided. The
second test consisted of placing six Pontoporeia in individual
containers with each type of sediment for 24-48 hours. There
was no mortality in the control sediment and the greatest
mortality occurred in Rouge River and Indiana Harbor sediment.
It was generally observed that dead amphipods were covered with
oil.

Gannon and Beeton[44] suggested that future studies should
utilize native organisms and be conducted under conditions
that closely approximate the natural environment.

Additional bioassays were conducted on the Great Lakes
sediment samples using midge larvae, Cladophora, phytoplankton,
unialgal cultures, zooplankton and Daphnia.[45] Based on the
effects of sediment on test organisms, the authors defined
five categories to classify sediment. These categories are:

1. sediment toxic, avoided by benthic animals, did not
   stimulate phytoplankton or Cladophora;

2. sediment toxic, stimulated phytoplankton or
   Cladophora;

3. sediment somewhat toxic, stimulated phytoplankton
   or Cladophora;

4. sediment not toxic, algae not stimulated;

5. sediment not toxic, phytoplankton stimulated.

As discussed previously, the distinction between these categories
may be poorly defined because of a possible error in the inter-
pretation of carbon-14 productivity data. Even so, Gannon and
Beeton[45] found no direct correlation between bioassay results and
any single chemical or physical analysis of the sediments. However,
chemical oxygen demand (COD), volatile solids, phosphate and
ammonia exhibited a collective trend of decreasing from category
1 to category 5.

The cause of mortalities in the bioassays was not known. Possible mechanisms are toxic components present in the sediment or oxygen depletion resulting from the oxygen demand of the sediment as inferred by high COD analyses. The authors[45] recommended that future studies utilize biological and chemical testing to evaluate possible effects of dredged material disposal and define relationships between chemical analyses and observed mortalities.

Carlisle[50] investigated fish populations in an area influenced by sewage discharges. A total of 705 bottom tows were completed in a six-year period and it was concluded that fluctuations in the population of 104 species of fish could not be related to the discharge of sewage effluent to Santa Monica Bay. It was acknowledged that no one species of fish could be used as an indicator organism.[50] The discharge reduced populations of mollusks, echinoderms and crustaceans within one-half mile of the sewage outfall. The organisms had not recovered seven years after the discharge was stopped. It was also pointed out that sedimentation and increased turbidity resulting from sewage disposal operations reduced the giant kelp growth in Santa Monica Bay.

Several literature reviews are available summarizing the biological effects of suspended solids. This information has been discussed in terms of type of effect[51] and type of organism.[52,53] According to Cairns[51] the mechanisms of sediment interaction are:
1. mechanical or abrasive action,
2. blanketing action or sedimentation,
3. reduction of light penetration,
4. availability as a growth surface for bacteria and fungi,
5. adsorption and absorption of chemicals,
6. reduction of temperature fluctuations.
The significance of these mechanisms will be determined by the concentration of suspended solids, the type of suspended solid,

the length of exposure, the presence of other toxic materials, the condition of the exposed organism and the phase in the life cycle of the organism.[51]   Because of the variation in these factors and uncertainties in the mechanisms of interactions, it was suggested that rigid turbidity standards not be set.

Several examples of the variation mentioned by Cairns[51] are discussed by Hollis et al.[52] and Cordone and Kelley.[53] For example, several species of adult fish can tolerate 100 g/l of suspended solids without apparent harm while turbidity levels of 2500 mg/l can cause total mortality of eggs. It was concluded by Cordone and Kelley[53] that siltation is one of the most important factors limiting natural reproduction of salmonoids in streams. Another potential effect of turbidity increases is to cause a shifting of species composition from game fish to rough fish.[52]   Changes of this type require long-term changes in turbidity levels and may be reversible if the turbidity is reduced at a later date.

Benthic fauna populations are also susceptible to change as a consequence of suspended solids additions to a lake, river, estuary or ocean.[11,52,53]   The magnitude of the change will be influenced by the type of solids being discharged since organic sludge blankets tend to affect species diversity provided the solids are nontoxic and there is sufficient oxygen present. However, blanketing caused by inorganic sediments tend to alter all forms of life at high rates of sedimentation.

A major problem in assessing the effect of suspended solids on bottom fauna is that essentially nothing is known about the sensitivity of organisms to increased rates of siltation. It would be expected that increased sedimentation would favor burrowing animals such as Tubificiae and Chironomids.[11]   However, the critical rate of sedimentation that each organism can tolerate has not been determined. A similar problem that has received

some attention is the response of organisms to the stress caused
by increased turbidity. Suspended solid concentrations of 750
mg/l retarded egg development and the growth of shellfish.
At slightly higher concentrations, egg development and growth
stopped.[11] In another study,[54] suspended solids concentrations
of 100 mg/l reduced the feeding rate of oysters. It has generally
been observed that normal activity resumes when the organisms
are removed from the turbid water.

Although it is intuitively obvious that increased sedimenta-
tion can reduce bottom fauna populations under the proper condi-
tions, it is very difficult to determine population changes in the
environment with any degree of statistical reliability. Cordone
and Kelley[53] concluded that 21 to 715 samples must be collected
and counted to estimate the mean number of organisms in sediment
at a specific site with a 95 percent confidence of being correct.
In another study, it was calculated that over one thousand
samples would have to be analyzed to determine whether the
discharge of 67,000 tons per day of taconite tailings to Lake
Superior was reducing the population of Pontoporeia by more than
25 percent.[55] Smaller numbers of samples would only indicate
the major species present in the samples. The large number of
samples are necessary because of the high variation in the
natural population.

Sherk[56] suggested that the lack of correlation between
suspended solid studies and biological changes may result from
the fact that the biological response is due to the shape, size,
density or number of particles rather than the concentration of
suspended solids. In addition, surface coatings and sorptive
properties may also be more important than concentrations. It
was concluded that concentration standards may be insignificant
from the standpoint of assessing biological effects of suspended
solids.[56] Sherk[56] also felt that resuspension of sediment by

wind, currents and tide interfere with the determination of threshold concentrations for suspended solids. Based on a literature review, Plumb[11] observed that the most severe effects of suspended solids were usually seen in high energy locations such as streams and rivers where the sediment is continually resuspended and moved down current.

Dredging activities are a major source of the solids discharged to open waterways. However, based on the summary of the literature presented above, studies on the effect of dredged material disposal on chemical water quality are limited. Available data indicates that dredged material is very heterogeneous but does not differentiate between soluble, available and total forms of an element. This distinction must be made in order to assess the potential effect of dredged material on water quality. Most studies indicate that dredged material disposal can result in reduced oxygen concentrations that can potentially affect the transfer of several elements from dredged sediment to water. Unfortunately, past studies were not carried out in enough detail to assess the significance of potential elemental transfer from dredged material.

Studies of dredging operations indicate that a turbidity increase occurs during disposal operations. Disposal of large amounts of solids and turbidity increases can create several potential biological problems. These problems are primarily physical in nature and not dependent on the chemical characteristics of the dredged material.

Studies on Bulk Properties of Dredged Material and Sediment

Numerous studies are available in the technical literature discussing the relationship between sediments and quality of overlying water. Approaches, results and limitations of these

studies will be discussed as they may be applicable to the disposal of dredged material.

One of the previously used approaches is to classify sediment according to some overall characteristics. This approach has been taken by several investigators in which some bulk properties of the sediment were measured such as bulk chemical analysis and cation exchange capacity.

Oliff et al.[57,58] have collected and analyzed nearshore sediment off the coast of Natal. They were able to correlate their results with industrial and municipal inputs in the area and propose pollution criteria for sandy beaches[57] and for other nearshore sediment.[58] Parameters for pollution were established by the authors at 60 µg/g Kjeldahl nitrogen and a bottom fauna density of 300 organisms/0.66 ft^3 for a sandy beach. Suggested limits for nearshore areas were 1.0 mg/g permanganate oxidation value, 1.0 µg/g dehydrogenase acitivity, 1.0 mg/g humic acid and a bottom fauna density of 2000 organisms/350 ml of surface sediment.[58]

The criteria proposed by Oliff et al.[57,58] were based on differences between average background levels and the analyses of samples collected near zones of discharge. The studies were designed to determine the extent of the area affected by the discharges based on changes in sediment characteristics. The authors[58] noted that no universally applicable criteria are possible because sediment composition changes from time to time at one place and from place to place. However, relative changes may be used to judge the nature and magnitude of changes that occur in sediment as the result of a localized input. There was no attempt to relate sediment composition to the quality of the overlying water.

The organic matter content of sediment was the basis of a sediment classification system developed by Ballinger and McKee.[59]

Organic matter was divided into organic-C and organic-N fractions. Organic-C was determined using the chemical oxygen demand (COD) wet oxidation procedure developed for soil and industrial waste analysis and assuming that all carbon is converted to CO_2. As noted in another section of this report, there are significant problems in attempting to utilize wet oxidation (COD) as a measure of organic matter in sediment. Organic-N was defined as Kjeldahl-N minus ammonia-N. Four sediment categories were used to classify the sediment. These are the following:

I.   0-5% org.-C; 0-0.2% org.-N   Inorganic or aged sediment, stabilized organic deposits.

II.   5-20% org.-C; 0-0.2% org.-N   High carbon, little nitrogen contribution; slow oxygen demand.

III.   0-5% org.-C; 0.2-1.0% org.-N   Nitrogenous sediment, further stabilization likely.

IV.   5-20% org.-C; 0.2-1.0% org.-N   Actively decomposing sediment, high potential nitrogen release and high oxygen demand.

Ballinger and McKee[59] introduced the concept of an organic sediment index (OSI) defined as the product of the concentrations of the organic-C and the organic-N. The OSI values and sediment types are:

I.   OSI = 0.0-0.5   Sand, clay, old stable sludge

II.   OSI = 0.5-1.0   Organic detritus, peat, partially stabilized sludge

III.   OSI = 1.0-5.0   Sewage sludge, decaying vegetation, pulp and paper wastes, sugar beet wastes

IV.   OSI = 5.0-   Actively decomposing sludge, fresh sewage, matted algae, packinghouse wastes.

The OSI concept was tested on the Red River (N.D. and Minn.), Kanawha River (W. Va.), Mississippi River (Minn.), Raritan Bay (N.J.), Charleston Harbor (S.C.), Lake Sebasticook (Me.) and

and Waterville Reservoir (Tenn.). It was generally successful in locating pollution sources and recent dredging sites.

As with the Oliff et al.[57,58] studies, Ballinger and McKee[59] made no attempt to correlate sediment composition with water quality. Changes in sediment composition were only used to locate pollution sources.

Trace metal concentrations in the sediment of the Rhine River and its tributaries were studied by Hellmann.[60,61] Some metals such as zirconium, strontium and rubidium were constant between Lake Constance and the German-Dutch border. Concentrations of others such as copper, lead and zinc varied from place to place. The concentrations above normal background levels were due to the discharge of wastewater. Hellman[60] suggested that trace metal concentrations could be used to classify sediment and determine its background.

Another bulk property that has been used in an attempt to classify sediment is exchange capacity. Toth and Ott[62] determined cation exchange capacities (CEC) and exchangeable cation status (ECS) for sediment collected from rivers, bays, estuaries and impoundments along the East Coast and observed wide variations in their results. Factors that influenced their results were organic content, clay content, pH, nature of displacing cation, age of sediment and moisture content. The authors expressed the opinion that CEC and ECS values could be used to determine the extent of salt water intrusion and pollution effects.

The cation exchange capacity of sediment is a function of particle size.[63] The actual exchange process is rapid and limited by in-stream diffusion. A slug of pollution will be removed quicker by passage over fine sediment than over cobblestones. Exchange is a reversible process and pollution would be flushed out of fine sediment more easily.

Lenhard et al.[64] considered sediment to be nothing more
than soil that had developed under water-logged conditions and
used modified soil techniques to study and attempt to classify
sediment from the Apies River. The analyses completed in order
to characterize the sediment included 1) the determination of
operationally defined water extractable, ammonium chloride extract-
able and 10 percent hydrochloric acid extractable ions; 2)
ion adsorption and exchange capacity; 3) water holding capacity;
4) humic acid content and degree of humification; and 5) dehydro-
genase activity.

The sediment extracts were analyzed for calcium, magnesium,
sodium, potassium, iron, copper, chromium, aluminum, manganese
and phosphate. At each of the eleven sampling stations, the lowest
results were obtained in the water extractable fraction and the
highest results were obtained in the acid extractable fraction.
According to these authors water soluble ions are considered
immediately available, ammonium chloride extractable ions are
considered a reserve for physiological processes and acid
extractable ions represent the ions that may become available
during future working of the sediment. Unfortunately, the river
water was not completely analyzed and it is impossible to
determine the significance of the various extractable fractions
of the sediment as they may influence water quality.

Each of the other techniques was also defined in relation
to potential effect on water quality.[64] The ion adsorption and
exchange capacity is thought to be a measure of the sediments'
ability to "purify" overlying water.[64] Water holding capacity
determines the amount of river water that comes in direct contact
with the exchange surfaces of the sediment and influences the
purification ability of the sediment. The degree of humification
was taken as an estimate of carbon resistant to further biological
degradation. Dehydrogenase activity is a measure of general bio-
chemical activity in the sediment. The lowest values for

Kjeldahl nitrogen, humic acid content and degree of humification occurred in the stretch of stream sediment receiving a municipal discharge. An insufficient amount of stream analysis data was collected to determine any possible correlation between sediment and water composition.

The first proposed criteria for the regulation of dredged material disposal was based on a Great Lakes survey.[65] Seven parameters were specifically mentioned and the limits are given in Table 9. These values are total concentrations based on a dry weight analysis. If the analysis of a sample of dredged material exceeded any of the seven values, the material was classified as polluted and was not acceptable for open-water disposal. If the proposed limits are not exceeded, the proposed disposal operations must be evaluated on a case by case basis according to 1) volume of dredged material, 2) existing and potential quality and use of the water in the disposal area, 3) depth and currents at the disposal site, 4) time of year, 5) method of disposal and alternatives, 6) physical, biological and chemical characteristics of the dredged material and 7) the number of disposal requests for the same discharge area. The criteria did not consider frequency distribution of results or specify the numbers of samples necessary. In addition, it was pointed out by Boyd et al.[1] that there was no technical basis for the proposed criteria although Gannon and Beeton[45] observed a general relationship between chemical analyses of dredged material and biological stimulation. Also, no guidelines were given for applying the seven additional factors if dredged sediment passed the chemical analysis criteria.

Criteria for the disposal of dredged material have appeared in several technical reports.[4,38] These criteria are the same as the FWQA criteria given in Table 9. Windom[5] cites criteria with a lower mercury standard that conceivably indicates concern

TABLE 9

DREDGED MATERIAL DISPOSAL CRITERIA

DEVELOPED FOR FWQA*

Parameter	Maximum Percent Dry Weight
Volatile Solids	6.0
Chemical Oxygen Demand	5.0
Total Kjeldahl Nitrogen	0.10
Oil and Grease	0.15
Mercury	0.0001**
Lead	0.005
Zinc	0.005

*Cited in Boyd et al.[1]

**A value of 0.001 appeared in the original report which was a typographical error.[66]

that was expressed about mercury in the environment in the late 1960's (Table 10). This set of standards also increased the allowable concentration for zinc and listed copper and cadmium for the first time. However, these criteria are for Region IX EPA only.

Another set of criteria that was accepted by the EPA Water Quality Office in 1970 was presented by O'Neal and Sceva.[42] These authors listed the same factors as Boyd et al.[1] for evaluating dredged material pollution. However, the chemical criteria varied and were presented as a function of the degree of pollution (Table 11). Because the accepted criteria were based on bulk chemical analyses, it was suggested that a separate set of dredged material water-quality standards be adopted. The information given by O'Neal and Sceva[42] indicates the chemical variability to be expected in dredged sediment but does not specify disposal standards.

In 1973 the Corps of Engineers and the EPA reached an agreement on new dredged material disposal criteria applicable to ocean dumping. The new criteria were based on the release of dissolved solids from dredged material under standardized conditions and existing concentrations in disposal site water. The test requires mixing one volume of dredged material with four volumes of water for one-half hour. If a ratio of the concentration of any soluble constituent after the test exceeds 1.5 times the initial concentration, the material is classified as polluted and is not considered acceptable for open-water disposal.[9,10] This procedure is better than a bulk-analysis approach since it recognizes that elements may be in different states of availability. However, it fails to consider the amount of material to be discharged and certain factors at the disposal site (dilution, changing redox potential). The importance of these factors will be discussed in another section of this report.

TABLE 10

U.S. EPA REGION IX DREDGED MATERIAL DISPOSAL CRITERIA*

Parameter	Maximum Percent Dry Weight
Volatile Solids	--
Chemical Oxygen Demand	--
Total Kjeldahl Nitrogen	--
Oil and Grease	--
Mercury	0.00005
Lead	0.0050
Zinc	0.0075
Cadmium	0.0002
Copper	0.0050

*Cited by Windom[5]

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TABLE 11

CRITERIA FOR DETERMINING ACCEPTABILITY OF DREDGED MATERIAL DISPOSAL
INTO OPEN WATERS*

Parameter	Units	Lightly Polluted		Heavily Polluted	
		Mean	Range	Mean	Range
Total Volatile Solids	Percent	2.9	0.7 – 5.0	19.6	10.2 – 49.3
Chemical Oxygen Demand	g/Kg	21	3 – 48	177	39 – 395
Kjeldahl Nitrogen	g/Kg	0.55	0.01 – 1.31	2.64	0.58 – 6.80
Total Phosphorus	g/Kg	0.58	0.24 – 0.95	1.06	0.59 – 2.55
Grease and Oil	g/Kg	0.56	0.11 – 1.31	7.15	1.38 – 32.1
Initial Oxygen Demand	g/Kg	0.50	0.08 – 1.24	2.07	0.28 – 4.65
Sulfides	g/Kg	0.14	0.03 – 0.51	1.70	0.10 – 3.77
Redox Potential	MV	+0.05	-0.18 – +0.41	-0.13	-0.22 – +0.11

*Cited by O'Neal and Sceva[42]

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A common feature of the bulk-analysis papers is that changes
in sediment composition could often be used to locate pollution
sources. This usually requires extensive sampling to determine
background levels in the region. The EPA-proposed criteria for
determining whether a particular sediment is polluted or not
based on bulk sediment composition do not properly consider the
variability of background levels. Windom[5] found that several
samples exceeded the EPA bulk criteria even though the source
of the samples was an unpolluted estuary. Another weakness of
the bulk properties approach is that no universally applicable
criteria are possible.[57,58] Fluctuations in background levels
will vary from place to place and limit the usefulness of the
criteria.

A major difficulty of the bulk-analysis approach is that
it does not indicate whether water-quality problems exist in
the overlying water or the extent of the water quality problems
when they do exist. This is because changes in concentration
in the water column will be influenced by the amount of water
available for dilution and the rate of release of dissolved
solids which will be influenced by chemical and biological
conditions in the overlying water and solubility and availability
of material in sediment. The combination of these factors is
more important than the presence of a constituent in the
sediment.

According to Windom,[5] the amount of transfer of chemical
constituents from the sediment to the overlying water is not
dependent on bulk analysis in any simple, readily discernible
manner. In fact, several papers discussed above suggest that
the direction of transport is from water to the sediment.
Windom[15] reported a decrease in dissolved metal concentrations in
a dredge material suspension. Ritchie and Speakman[6] observed
a small increase in apparently dissolved metals in a dredged
material suspension, but the percentage of each parameter released
fluctuated widely and varied from sample to sample.

Sediment leaching studies also fail to establish a correlation between material released from solids and bulk composition. This is shown with data taken from a taconite tailings solubility study by Plumb.[11] An inspection of Table 12 reveals that dissolved solids leached from tailings were not in proportion to their presence in the tailings. For example, 106 percent of the sodium was released under agitated conditions, but iron, phosphate, or lead were not released. This is interesting in the case of iron because it accounts for 15 percent of total tailings. Also, calcium and magnesium are present to a similar extent in tailings, but five to eight times as much calcium is released.

The fact that no iron was released from tailings even though they were composed primarily of a series of iron magnesium silicate minerals is due to the precipitation of ferric iron in the laboratory and natural water systems. There is little doubt that the ferrous iron present in the minerals is, to some extent, released from the crystalline lattice. However, upon contact with the water containing dissolved oxygen, the ferrous iron is rapidly oxidized to ferric iron which precipitates as ferric hydroxide. Ferric hydroxide is a very efficient scavenger for many trace elements in natural water systems. Lee[25] has recently reviewed the potential role of the hydrous metal oxides in the environmental chemistry of heavy metals and other contaminants in natural waters. The results with taconite tailings and numerous other studies with natural water sediment indicate that a bulk analysis is not a reliable indicator of water-quality changes as a result of sediment solubility. This position is strengthened by the fact that a physical parameter such as stirring will affect the amount of material released from tailings, but the magnitude and direction of the change is not the same for all chemical species.

TABLE 12

RELEASE OF DISSOLVED SOLIDS FROM TACONITE TAILINGS

SUSPENDED IN DISTILLED WATER FOR 512 DAYS**

Tailings Component	Percent in Tailings	Wt of Component Added To Flask - mg	Release from 20 g Tailings/10 l (stirred)	Percent of Amount Added To Flask	Release from 20 g Tailings/10 l (quiescent)	Percent of Amount Added To Flask
Si	33.59	6718	51 mg	0.76	14 mg	0.20
Fe	14.93	2986	~0 mg	0.00	0 mg	0.00
Ca	1.67	334	28 mg	8.3	32 mg	9.6
Mg	1.96	392	6 mg	1.53	4.6 mg	1.17
Mn	0.37	74	1.47 mg	1.99	1.1 mg	1.48
P	0.026	5	0 mg	0.00	0 mg	0.00
Na	0.040	8	8.5 mg	106	2.0 mg	25.00
Pb	0.007	1.4	0 mg	0.00	0 mg	0.00
Zn	0.004	0.8	0.105 mg	13.1		
Cu	0.004	0.8	0.066 mg	8.25		
C	0.11	22	16.8 mg*	76	13.2 mg*	60

*Based on alkalinity release expressed as $CaCO_3$

**After Plumb[11]

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The weakness of a bulk analysis is further demonstrated by
the studies of Peterson and Gschwind[67] who investigated the
effect of sewage sludge on the quality of acidic mine spoil
leachate. The composition of the leachate varied with the
amount of sludge added to the mine spoil and the degree of
homogenation. The distribution of elements among dissolved,
settleable and colloidal fractions was studied by Heukelekian
and Balmat.[68] The percentage of each element in the different
phases was highly variable from sample to sample.

Sediment water interaction will produce dissolved solids
concentrations independent of the suspended solids concentra-
tions. This is demonstrated by data summarized by Oschwald[69]
and presented in Table 13. The ratio of dissolved solids to
suspended solids in various rivers was variable across the
United States.

The bulk composition of sediment is dependent not only
on the flux of chemical contaminants that become associated
with the solids but also on the flux of non-contaminant
solids such as detrital minerals, etc. It is improper to think
of concentrations in sediment in a manner similar to that
commonly used for concentrations of pollutants in water. In
the aqueous phase the chemical characteristics of the bulk
material-water are constant and serve as a useful reference point
against which to determine the concentrations of a particular
chemical species. In sediment, however, a concentration on a
weight per weight basis does not have the same meaning as in
the aqueous phase since the bulk material, i.e., the sediments,
have a variable composition.

Studies by Lee[70] on the chemical characteristics of sedi-
ment in Wisconsin lakes have shown that the northern lakes with
the most oligotrophic (least fertile) waters have the highest
concentration of aquatic nutrients. The southern Wisconsin lakes

TABLE 13

VARIATION IN SUSPENDED SEDIMENT AND DISSOLVED SOLIDS

IN RIVER BASINS

IN DIFFERENT REGIONS OF THE U.S.A.*

Region	Suspended Solids Concentration	Dissolved Solids Concentration
New England	< 300	<100 - 300
Southeast	< 300 - 2,000	<100
Central Corn Belt	300 - 5,000+	300 - 700
Lake States	< 300	<100 - 700
Great Plains	300 - 30,000	300 - 2,600
Southwest	2,000 - 50,000	300 - 2,600
Pacific Northwest	< 300	<100 - 300

Concentrations in mg/l
*After Oschwald[69]

which are highly fertile have lesser concentrations of nitrogen and phosphorus in the sediment. If one attempted to use the bulk characteristics of the lake sediment for northern and southern Wisconsin lakes, it would be found that a completely erroneous conclusion would be developed with respect to the fertility of the overlying waters. This situation arises from the fact that the northern Wisconsin lakes are soft water lakes with little or no calcium carbonate precipitation. The southern Wisconsin lakes, on the other hand, are hard water lakes with 30-40 percent of the sediment being composed of calcium carbonate. The high calcium carbonate content of the sediment dilutes the aquatic plant nutrients which are deposited in the sediment so that the bulk composition of nitrogen and phosphorus is less for the more fertile waters. Even though the bulk composition is less in the southern Wisconsin lakes, the rate of release of phosphorus to the overlying waters is higher, indicating that the phosphorus in the sediment is more available to affect the water quality of the lake. Studies by Bortleson and Lee[71] have shown that a good correlation exists between phosphorus sedimentation intensity ($mg/cm^2/yr$) and degree of fertility of the Wisconsin lakes.

Interstitial Water Composition

The lack of correlation between bulk analysis and overlying water quality does not mean that leaching of solutes does not occur. In fact, an exchange can occur as demonstrated by several interstitial water studies.

Disposal of dredged material has produced changes in the interstitial water composition at the disposal site.[57,58] The changes observed by Windom[15] are generally related to increased concentrations of reduced species caused by a lowering of the

redox potential in the sediment. The chemical species that increased were sulfide, iron and manganese. The magnitude and duration of the changes are influenced by the accumulation of dredged material in the sediment, but the changes are reversible.

Numerous papers are available on the subject of interstitial water, and they all generally indicate that dissolved constituents are enriched in interstitial water compared to overlying bulk water. The concentration of constituents in interstitial water is strongly influenced by redox potential, pH and oxygen penetration into sediment. Because of the number of factors that affect interstitial water composition, concentration profiles are seldom homogeneous. Also, the profiles are not the same for individual elements. For example, according to Brooks et al.,[72] phosphate, iron and nickel concentrations increase with depth in reduced marine sediment while zinc, cadmium, copper and cobalt are enriched at the mud-water interface. The surface maximum for the last group of elements is thought to be due to biological concentration of organic detritus. The type of fluctuations possible in interstitial water is further illustrated by the magnesium data which was uniform throughout the cores but less than seawater concentrations.

The higher concentrations of dissolved solids generally existing in interstitial water compared to concentrations in overlying water create a concentration gradient that would often favor the movement of ions out of the sediment. The upper 30 cm of the sediment may participate in this exchange process.[73] Non-reactive (conservative) elements such as chloride will move in response to mixing caused by currents and biological organisms and to diffusion. While these factors will influence the movement of reactive elements as well, the transfer in some instances is controlled by chemical reactions and rates of reaction.

Because of uncertainties of controlling chemical reactions, the transfer of reactive chemical species out of sediment cannot be accurately modeled at this time.[73]

At least one attempt has been made to establish interstitial water criteria to assess the pollution status of beaches.[74] Oliff et al.[74] proposed critical levels for dissolved oxygen and several forms of nitrogen and phosphate. The data on which the criteria are based are unusual in that interstitial concentrations are similar to seawater concentrations rather than being greater. This was attributed to the high porosity of the sediment which allowed seawater to penetrate and flush the upper sediment layers. The authors concluded that knowledge of dissolved oxygen concentrations, pH, ammonia concentration and oxygen absorbed would give a good indication of conditions in the sediment.[74]

Several aspects of oceanic waste disposal, including the buildup of dissolved solids concentrations in interstitial water, were investigated by Pratt et al.[49] The waste lowered the redox potential as evidenced by the decreased oxygen concentrations and the increased concentrations of sulfide, ammonia and ferrous iron. Assuming diffusion from the sediment is directly proportional to concentration gradient, the waste would generate 10 to 100 times as much ammonia as an equal area of aerobic sediment. It was pointed out that this would be inconsequential in the open ocean but could be important in nearshore waters.[49]

Laboratory studies may overestimate the diffusion of dissolved solids from sedimentary deposits.[49] Experimental conditions may produce a measurable change in the laboratory, whereas dilution may prevent detectable changes in the environment. It is important to note that this dilution is part of

the contaminant assimilative capacity of natural water systems.
The fact that there is some release of chemical contaminants
from sediment does not necessarily mean that this release is
having an adverse effect on water quality. In general, chemicals
have an adverse effect on water quality based on the concentra-
tions of the chemicals present in the aquatic phase. For every
chemical constituent present in natural waters, there is a
critical concentration above which the chemical is thought to
have an adverse effect on aquatic ecosystems or on some beneficial
use of the water by man. Concentrations less than this amount
are judged to have no adverse effect on water quality. There-
fore, unless the release from the contaminated sediments
causes the concentrations to exceed the critical concentration,
the release does not have an adverse effect on water quality but
does utilize some of the contaminant assimilative capacity of
the overlying waters. It was suggested that molecular diffusion
coefficients might be used to estimate sediment release of
contaminants based on the concentration gradient that exists
between the interstitial water composition and the overlying
water composition. The primary problem with this approach is
that it is most likely to grossly underestimate the flux of
the chemicals to the overlying waters due to the fact that the
mixing processes in the sediment caused by currents and organism
stirring will cause a much more rapid release.

Sullivan[75] criticized molecular diffusion as a method of
dissolved solids transfer from sediments. A rapid transfer of
solutes requires a high degree of agitation. Suggested mechanisms
influencing the exchange of solutes are wind induced currents,
eddy diffusion, internal seiches and convectional streaming caused
by temperature differences and organism movement. Basin morphology
will affect the importance of each mechanism listed above and
influence the effect of bottom sediment on water quality.

Lee[70] prepared a literature review of the factors affecting the transfer of materials between sediment and water and discussed many of the mechanisms listed by Sullivan.[75] The processes were classified as exerting physical control or chemical control over the rate of leaching from sediment. Because of the higher concentrations usually observed in interstitial water, Lee[70] concluded that hydrodynamic factors of mixing exert a greater control over the transfer of dissolved solids from sediment to overlying bulk water.

A detailed sampling program is necessary in order to study the transfer of dissolved solids from the sediment phase to the water phase.[70] One such study was conducted by Glass[76] and illustrates the scope of sampling necessary and problems in data interpretation. Glass[76] collected sediment cores and water samples from a 400 square mile area of Lake Superior sediment covered with taconite tailings and compared results with a similar set of samples collected in a control area of similar size. Water samples were collected at several depths between 3 cm and 30 m above the sediment. Interstitial water samples were collected at depths of 1.3 cm, 3.8 cm and 6.3 cm below the sediment-water interface.

Glass[76] observed a higher concentration of most elements (Ca, Cu, Mn, Mg, K, SiO_2) in interstitial water in both sampling areas. Because higher concentrations were observed in the tailings deposit compared to lake sediment, it was concluded that material was diffusing out of the tailings and affected water quality. However, the lake water data indicate there is no difference in water composition at either location. This situation arises from the fact that the rate of mixing of any materials that are released from the sediment with the overlying waters is sufficiently rapid that no differences in concentrations are observed in the water immediately above the sediment-water interface even though

the interstitial water in the tailing area has higher concentrations of many of the chemicals studied. This situation is an example of how the release of chemical constituents from sediment may occur without having adverse effects on water quality.

Glass[76] investigated the possibility of lake currents masking any change in water quality due to ions diffusing out of sediment by incubating a set of cores in the laboratory. Interstitial water from the tailings cores had higher concentrations of Cu, Fe, Mn, SiO_2 and P than sediment cores from the control area. However, the concentration of dissolved solids in the overlying water was the same above both sets of cores except for a small magnesium increase above tailings and an iron increase above lake sediment. Even in the absence of lake currents, higher concentration gradients for many chemicals in the interstitial waters compared to the overlying waters in tailings' cores did not produce measurable concentration changes in lake water.

Glass' study[76] appears to demonstrate the usefulness of laboratory investigations. Interstitial water had higher concentrations in laboratory incubated tailings' cores than sediment cores incubated under the same conditions. This agreed with results obtained with the environmental samples taken from Lake Superior. Also, no changes were observed in the bulk water in the lake itself or over the laboratory incubated cores.

Extreme caution must be exercised in attempting to utilize the effect of interstitial water composition on water quality in the overlying waters. From studies conducted thus far, there appears to be little or no relationship between the chemical characteristics of the interstitial and overlying waters. There are several problems related to sampling of interstitial water. Sediment is generally under lower redox potentials, and the

reduced form of several species, particularly iron and manganese, are favored under these conditions. If care is not exercised during filtration steps, these metals may be oxidized and their concentrations will be reduced by precipitation. A second problem of equal magnitude is that iron will be removed by precipitation as a hydrous oxide which will reduce the concentrations of phosphate and other metals by scavenging and co-precipitation.

Not only must caution be exercised in determining the chemical characteristics of the interstitial waters, but care must be taken in handling the sediment samples in order to avoid changes in the form of the chemical constituents and physical characteristics present in the sediment and the dredged material. This topic will be discussed in another section.

Studies on Release of Materials from Sediment

Even though transport of material out of sediment is complex and affected by a large number of parameters,[70] several studies are available to demonstrate that the migration of dissolved solids does occur in sediment and across the sediment-water interface. These studies will be discussed in the following groups: oxygen, nutrients, heavy metals and organic compounds.

Oxygen

One of the most significant chemicals that could affect the release of contaminants from dredged material is oxygen. Fillos[77] has shown that bottom deposits will take up oxygen at a rate which is independent of the oxygen concentration for oxygen levels greater than 2 mg/l. The uptake was dependent on the bottom sediment for depths up to four inches. As long as the residual oxygen concentration remained above 2 mg/l, the nutrient flux from the sediment to the overlying water was reduced.[77,78] Mortimer[79,80] has concluded that chemical exchange from sediment

in the Great Lakes may exert a measurable but a quantitatively unimportant influence on the chemistry of overlying waters as long as oxygen concentrations at the sediment interface remain above 1 to 2 mg/l.

Stein and Denison[81] investigated the oxygen demand of cellulose enriched sediment. It was observed that undisturbed sediment exerted a greater oxygen demand than disturbed sediment. The explanation given for the difference is that undisturbed sediment maintained their animal burrows which increased the surface area available for oxygen transfer. McKeown et al.[82] also observed that the oxygen demand of benthal deposits was proportional to the surface area. In addition, it was observed that the oxygen demand increased with mixing, decreased with time, and was proportional to sediment depths up to one foot. The oxygen demand was reduced if the deposit was covered with a lower oxygen demand material such as sand.

A controversy exists regarding the interaction between sediment and dissolved oxygen. Fair et al.[83] suggest that the cause of oxygen depletion is the diffusion of reduced material across the sediment-water interface. However, Mueller and Su[84] concluded that oxygen changes above sedimentary deposits are due to oxygen diffusion into sediment with subsequent utilization. Support for the latter position is available from the observation of oxidizing layers at various depths in sediment that are visible because lighter colored oxidized layers contrast with darker reduced sediment.

Conway[85] has reviewed the literature on the oxygen demand of sediment and has developed a generalized mathematical relationship that can be used to formulate oxygen-depth profiles in the hypolimnion of Lake Mendota. The formulation involves a two-component model in which the oxygen demand of the sediment is exerted in the first few meters above the sediment-water interface.

The oxygen demand of the water above this depth is primarily due to the biochemical oxygen demand of algae and other bio-degradable organics derived from the surface waters.

Penetration of oxygen into sediment could be a dominant factor in the transfer of material across the sediment-water interface. Gorham and Swaine[86] have classified sediment as reducing mud, oxidizing mud, and oxidate crust and have demonstrated that certain trace metals are differentially con-centrated in these zones. Metals such as Fe, Mn, P, Mo, Sr and Ba had higher levels in oxidized mud and the oxidate crust; and Zn, Co, Pb, Ti, Rb and Li were enriched in the oxidate crust. Although several of these elements do not enter into redox reactions in natural waters, they are concentrated by co-precipitation and sorption when iron and manganese are oxidized to produce hydrous oxides. Thus oxygen concentrations will determine the chemical form of some elements which will influence the migration of other ions.

Oxygen consumption by sediment is dependent upon the depth and age of the sediment.[87] Also, as discussed earlier, the oxygen consumed by disturbed sediment will be less than undisturbed sediment.[70] However, oxygen consumed by undisturbed sediment such as collected in a core is similar to in situ measurements of oxygen consumed by sediment.[88,89]

Nutrients

The release of nutrients from dredged material or sediment is of concern because an influx of nutrients could stimulate biological growth. Net transport of phosphate is generally to the sediment.[70] However, dissolved phosphate is often trans-ported to water. The direction of dissolved phosphate transport is a complex function of physical, chemical and biological inter-actions in the environment.

Pomeroy et al.[90] investigated the exchange of phosphate
from estuarine sediment. The transfer was a two-step process
with half times of 15 seconds and approximately 30 minutes.
The addition of formalin decreased the amount of exchanged
phosphate by 50 to 100 percent which was taken as a measure
of the magnitude of biological fixation. The greatest effect
of formalin was seen in the quick exchange step. It was
estimated that the amount of phosphate transferred through the
surface of submerged, undisturbed sediment is on the order
of 1 μ mole PO_4/m^2/day. For sediment brought into suspension,
the exchange rate will vary with the time the sediment is
in suspension, the exchange capacity of the sediment, the
flushing time and mixing.

Spear,[91] Sridharan[92] and Bortleson[93] have found that in
a well-mixed system of lake sediments and water, there was an
appreciable release of phosphate. They found that the rate of
exchange varied with sediment type and was greater for anaerobic
environments. Gessner[94] observed that simulated Amazon River
sediment could release or remove phosphate from solution.

Pomeroy et al.[90] also attributed phosphate exchange to
bacteria. They found that in suspended sediment almost as much
phosphate was biologically exchanged as was exchanged inorganically
with clay minerals. Others[95,96] consider the biological influence
to be insignificant.

In an anaerobic environment there is an appearance of
soluble iron followed closely by dissolved phosphorus at the
sediment-water interface. When oxygen is introduced, the iron
is oxidized to iron III and it ties up the dissolved phosphorus.
Other processes occur in anoxic environments which can release
phosphate to the water column. Sulphate-reducing bacteria reduce
sulphate to sulfide which can react with ferrous iron and form
iron II sulfide. This reaction promotes the release of phosphate.

An important mechanism influencing phosphate concentrations in the water column is the tendency for phosphate to be adsorbed on sediment.[90,97,98] The sorption mechanism is highly pH dependent with maximum sorption occurring at pH's of 4 to 7. As the pH is increased or decreased, there is a rapid loss in sediment capacity.

Fillos and Molof,[78] Gahler,[99] and Mortimer[79,80] have reported that the release of phosphate from sediment is inversely proportional to the dissolved oxygen concentration. The greatest release of phosphate occurred into oxygen-deficient water. In addition, zero dissolved oxygen resulted in an immediate release of ammonia.[78] The fate of the released phosphate was dependent upon pH. In the pH range of 4.5 to 7.0, phosphate sorption would be favored.[100]

The effect of pH on phosphate release was also investigated by MacPherson et al.[101] Four types of lake sediment, acid bog, productive, moderately productive and unproductive, gave similar release patterns. Low concentrations were observed below pH 7 and increased at pH 8 and above. Acid bog and high productivity sediment released the most phosphate with lesser amounts leached from moderately productive sediment and unproductive sediment.

Phosphate that remains in the sediment is not equally available to algae. Bioassays of sediment were conducted by Golterman.[102] He concluded that algae (Scenedesmus) could only utilize a part of the phosphate. The available phosphate was not attributed to a well-defined chemical fraction; but it was similar to the phosphate extracted by 0.1 $\underline{N}$ NaOH or 0.5 $\underline{N}$ H_2SO_4. It was suggested that bioassays could be used to evaluate extraction procedures.

One method of investigating the flux of material across a sediment-water interface is to place isotopically labeled

material at known depths in the sediment and monitor the
overlying water for the active substance. Using this approach,
it was determined that diffusion of radioactive phosphorus
from sediment was negligible if initially placed deeper than
one centimeter in the mud.[103] The depth of sediment that
will prohibit transfer of dissolved solids to overlying water
is variable, and reported values range from one quarter of
an inch[104] (6.4 mm) to depths of 20 cm.[70] Factors that would tend
to increase the depth of the transfer zone are the fluidity of
the sediments,[70] direct biological effects,[70,90] indirect
biological effects[70] and turbulence.[70,104]

The direction of phosphate transfer is not always out
of sediment. Correll et al.[105] investigated the movement and
cycling of phosphate in an estuarine system using the radio-
isotope method. Phosphate was applied to the test area at
a rate of 43 mg P/m^2/day which produced a vertical migration of
phosphorus into the sediment at a rate of 4.3 µg/cm^2/day.
However, the phosphorus only penetrated 5 cm into the sediment
in a 20-day period. Once the isotopically labeled phosphate
entered the sediment, it migrated in a horizontal direction
in proportion to the concentration gradient that had been
created.

Migration of ions in interstitial water cannot be used
to predict the transfer of material across a sediment-water
interface. In one study,[96] radioactive phosphate was placed
at a depth of 4 cm in a laboratory incubated core and the move-
ment of the phosphate was followed with time. Migration in
interstitial water was proportional to the concentration of
isotopically labeled phosphate. However, the amount of radio-
active phosphate that was transferred to the overlying water
was less than would be expected based on concentration gradients.

Another point to be made is that ion migration is dependent upon chemical form and not total concentration.[106] During the time Lake Washington was receiving domestic sewage, a surface maximum developed in the total phosphate concentration in the sediment. Several years after the sewage was diverted around the lake, the phosphate maximum was still identifiable in sediment cores; however, it now occurred at a depth of 5 cm. That is, it did not diffuse to the interface or out of the sediment but was covered only by new sediment.

The chemical form will also determine the availability of the phosphate. Shapiro et al.[106] analyzed for seven operationally defined phosphate fractions in Lake Washington sediment and noted that the manner of phosphate-binding changed with time. Also, the largest fraction was acid extractable (65 to 80 percent) and the smallest fractions were water extractable (<1 percent) and phospholized phosphate (<1 percent). McKee et al.,[103] also discussed this point and mentioned that phosphate associated with ferric hydroxide is more available than phosphate bound as ferric phosphate. This was demonstrated by the fact that hydrogen sulfide, carbonic acid or calcium chloride would liberate phosphate in the first case but not in the second.

Additional information on the leaching of phosphate from sedimentary material is available from a series of marsh studies by Bentley,[109] Amundson[110] and Lee et al.[111] These authors studied Shakey marsh, a partially drained, partially fertilized and partially cultivated calcareous marsh in central Wisconsin. Bentley[109] and Amundson[110] both conducted laboratory leaching studies with soil samples from the cultivated and uncultivated areas of Shakey's marsh. The total phosphate release from undisturbed Shakey marsh soil was 1 mg/100 g dry sediment after day 24, and this value had not changed since day one.

However, total release from cultivated soil was 9 mg/100 g dry sediment on day one, 39 mg/100 g dry sediment on day 24 and the data indicated a release was still occurring.[109] This agrees with the fact that the cultivated soil was enriched with 210 lbs P/acre/yr. Amundson[110] observed similar rates of release from 500 g wet Shakey marsh sediment suspended in 20 l distilled water. An initial release of 0.17 mg P/g dry sediment was observed from the undrained sediment that decreased to less than 0.01 mg P/g dry sediment by day 17 and remained at that level for the next 40 days. Amundson[110] measured a total phosphate release of 0.35 mg P/g dry sediment from the cultivated area compared to Bentley's[109] value of 0.39 mg P/g dry sediment.

Amundson[110] also ran a short-term acid extraction of the marsh soil, and the results indicated a difference in phosphate availability. The calculated releases were 0.37 mg P/g dry sediment from sediment collected in the uncultivated area and 0.70 mg P/g dry sediment from samples collected in the cultivated area. These values were higher than the longer leaching studies using distilled water but still show a greater release from sediment that had been receiving nutrient supplements. Also, perhaps fortuitously, the difference between acid extractable phosphate in the two types of sediment (0.33 mg P/g) is essentially the same as the difference between water leached phosphate in the two sediments (0.34 mg P/g).

A nine-month field study conducted by Bentley[109] demonstrated that the laboratory studies reflected the natural environment. Greater concentrations of phosphate were measured in the drainage collected from the cultivated area which agrees with the known application of fertilizer and the laboratory results. However, a mass balance comparison is not possible because flow data were not given. It may be of interest to note that the ratio of

ortho-phosphate concentrations in the cultivated area to the uncultivated area was 12 to 1, and the ratio under laboratory conditions was 15 to 1. These ratios may be misleading because they are based solely on concentrations, and an actual mass balance ratio may be quite different because of the highly variable flow through a marsh. However, it is interesting to note that the laboratory and field results are of the same order of magnitude.

The marsh soil can act as a potential source of nitrogen compounds as well as phosphate. Results indicated that drained marshes would yield more than 50 times the amount of nitrogen usually associated with agricultural runoff. The process responsible for this large release was the solubilization of particulate organic forms of phosphorus and nitrogen.[110] This process is unusual in that most natural waters have low concentrations of organic phosphorus and organic nitrogen.

Cowen[107] and Sirisinha[108] have recently completed a study on the available phosphorus and nitrogen in the particulate and organic matter present in urban and agricultural runoff. They found using a variety of chemical, enzymatic, and biological tests that 20 to 50 percent of this phosphorus would likely become available in natural waters in periods ranging up to 100 days. The organic nitrogen species were essentially, completely converted to inorganic forms in a similar period of time.

It should be emphasized that this availability was determined under conditions where the rate of release for the particulate forms was determined by chemical-biochemical processes. In natural waters lesser amounts of available phosphorus and nitrogen would be expected due to the fact that the particulate forms of these elements would, to some extent, settle to the bottom of the water body and become incorporated in the sediment.

Nitrogen in sediment has not been as extensively studied as phosphate. However, the transfer of nitrogen from sediment to overlying water will also be influenced by chemical form, mixing and concentrations. Gahler[100] reported that mixing of sediment with overlying water resulted in measurable increases in ammonia and total Kjeldahl nitrogen.

The distribution and forms of nitrogen in Lake Ontario sediment were investigated by Kemp and Mudrochova.[112] Exchangeable nitrate plus nitrite and organic-nitrogen decreased with depth. Exchangeable ammonia and fixed ammonia increased with depth. Deeper sediment probably does not contribute to the nitrogen flux in Lake Ontario. However, an estimated 20 percent of the nitrogen entering the sediment is recycled to the lake from the top 6 cm. The mechanism of release is thought to be a combination of nitrification, denitrification and ammonification occurring at the sediment-water interface.

Byrnes et al.[113] observed the transport of ammonia through sediment under laboratory and field conditions. The ammonia release was linear for the first eight hours and reached a maximum concentration in 36 - 50 hours. More than 40 percent of the isotopically labeled nitrogen was transferred through the interface in this time period. Hynes and Greib[96] also reported that ammonia could readily move through 4 cm of undisturbed lake sediment in 70 days.

The release of nitrogen from lake sediment was studied by Austin and Lee.[114] The observed release was influenced by the solid-liquid ratio, stirring, pH and dissolved oxygen concentration. In addition, dissolved oxygen affected the form of nitrogen released. Under reduced conditions, soluble Kjeldahl nitrogen and ammonia increased for 100 days. In the presence of oxygen, the same forms were initially released but decreased to zero. Nitrate, which was released slowly, gradually increased for 200 days. The total nitrogen released was four times greater under aerobic conditions.

Windom[5] reported dredged material disposal increased
ammonia concentrations by 50 to 100 fold. This is potentially
significant because nitrogen is apparently the limiting nutrient
in coastal waters. It was also suggested that ammonia would
be a valuable parameter to predict the effects of dredging
operations on water quality because ammonia is soluble and the
initial release is instantaneous upon dispersion.

Heavy Metals

Dredging operations in San Francisco Bay have recently
been halted because of high trace metal concentrations in the
sediment.[115] It was feared that the heavy metals would create
problems of toxicity, biological concentration and public health
hazards at elevated levels.[116] However, the potential problems
due to metals are not related to total concentrations. This
was demonstrated in a solubility study of taconite tailings by
Plumb[11] in which it was shown that characteristics of the
water will control the release of metals. Iron, which comprises
15 percent of tailings, was not released in distilled water or
Lake Superior water. When the pH was lowered to 4.7, iron con-
centrations in the test suspension exceeded 1 mg/l. Also,
the addition of organic matter isolated from lake water increased
the soluble iron concentrations to several hundred micrograms
per liter.

Another important factor in the transfer of iron across
the sediment-water interface is the dissolved oxygen concen-
tration. In the presence of oxygen, the insoluble ferric form
is favored. However, the more soluble ferrous form is expected
under anoxic conditions. As a result, an iron increase occurs
in hypolimnetic waters during the latter stages of stratification
when oxygen concentrations have been reduced to zero. The total
iron increase is caused by the influx of reduced iron. This
distribution has been verified frequently in limnological and
oceanographic investigations.[117]

Other metals are influenced by the same factors that influence the iron and manganese cycles. The pH and redox conditions in sediment generally result in higher concentrations than occur in overlying water.[118,119] In addition, the iron and manganese cycles affect changes in other metal concentrations. Jenne[120] has discussed the significance of iron and manganese oxides as a controlling factor on the concentrations of Cu, Ni, Co and Zn in soils and water. Windom[5,15] also mentioned the importance of the iron cycle. Under reducing conditions, soluble metal concentrations, including iron, would be increased. However, on oxidation, iron would be precipitated as a hydrous oxide. The process would also reduce concentrations of other metals due to sorption, co-precipitation and entrapment.

Redox potential will also determine the distribution of metals in the sediment.[72,86] Mobilization of Mn, Ni, Co, Cr, V and U was a direct result of redox changes and P and La movement was indirectly determined by redox.[121] The only elemental mobility not affected was thorium. Mobilization of the elements resulted in a concentration of Mn, Ni, Co, P and La in the upper oxidized zone of the sediment and an enrichment of Cr, V, U and S in the lower reduced zone. Gorham and Swaine[86] investigated the distribution of 24 elements in white clay, reducing mud, oxidizing mud, and the oxidized crust of sediment. The elements Fe, Mn, P, Mo, Sr, Ba, Zn, Co, Pb, Ti, Rb and Li were enriched in the oxidized portion of the sediment. The enrichment of Ba, Sr, Mo, P, Pb, Zn and Co was thought to be due to sorption on oxidized sediment. Brooks et al.[72] reported similar results.

The relationship between high metals content of bottom sediment and metals concentration in the overlying water was studied by Lopez[122] in Torch Lake. This lake, located in the copper mining area of Keweenaw Peninsula near Lake Superior, has received large amounts of copper mine tailings. As a result

the sediment of the lake consist of very fine material primarily derived from tailings containing from 0.13 to 0.38 percent copper and from 4 to 16 percent iron. High levels of copper (in the range of 25-100 µg/l) are found in Torch Lake water.

Leaching studies were performed where the sediment was suspended in lake water in a jug and aerated. Similar suspensions were stripped of oxygen by bubbling nitrogen gas. The metals concentration in the water was monitored with time for 46 days. Copper was released at a rate of 1.5 µg/l per day in the aerated jug as compared to 0.8 µg/l per day in the anoxic jug. These results point to the sediment and copper mine tailings of Torch Lake as the potential source of large quantities of copper found in the water.

Although the laboratory results cannot be completely extrapolated to the natural environment, it is clear that the massive discharge of tailings that occurred over the past 100 years in Torch Lake caused and maintained high levels of copper in these waters. Waters of similar chemical quality in the Torch Lake area but which have not been in contact with copper mine tailings have low levels of copper. The chemistry of copper in Torch Lake water appears to be controlled by hydrous oxides of iron and manganese.[122] Apparently copper in Torch Lake exists in a relatively nontoxic form since relatively moderate to large amounts of phytoplankton and fish thrive in the lake[123,124] even though concentrations of copper far exceed those known to cause deleterious effects on aquatic life.

The addition of solid material to sediments can produce a change in interstitial water composition without affecting overlying water quality. The interstitial concentration of several metals in Lake Superior sediment increased in the

zone of taconite tailings discharge.[76] Even though the
tailings affected sediment covering 400 square miles, no
measurable change occurred in lake water concentrations within
a few centimeters of the interface. This suggests that dif-
fusion out of the sediment is of minor importance or the oxygenated
conditions in Lake Superior are controlling trace metal trans-
port, or mixing and dilution are masking any transport out of
the sediment.

Pratt et al.[49] summarized the literature on the leaching
of 16 metals from sediment. The conditions providing the
greatest transfer are reducing conditions in the sediment and
anoxic conditions in overlying water (Co, Cr, Fe, La, Mn, and
Ni). However, Jernelöv and Asell[125] report that anaerobic and
sulfide-containing water at the surface of the sediment is
likely to cause a considerable reduction in the rate of
formation and release of methylmercury, one of the most toxic
forms of mercury. If oxygen is added, the released metals be-
come unstable and may be carried to the sediment unless some
other mechanism keeps the metals in solution. The mechanism
most often cited is organic matter that can complex with
Cu, Fe, Hg and Zn. It has been suggested that this mechanism
could influence the release of metals from dredged material.[5]
Several other investigators have shown that organic matter
will increase the transfer of dissolved solids from sediment
to bulk water.[126,127,128]

Another process that could be locally important in deter-
mining the release of metals from dredged material is complexa-
tion and ion pair formation. Several metals, aluminum, iron,
manganese and chromium, would be expected to be present as
hydroxides.[129] However, other metals such as lead, mercury
and cadmium tend to form complexes with chloride. The high
concentration of chloride in seawater could produce an increase
in the metal complexes resulting in higher concentrations of
certain dissolved metals.

Another method of trace metal migration that has been recently considered and could be locally important is cycling through aquatic plants.[130] The plants studied absorbed metals through the root system and expelled the metals into the bulk water. Seger[130] has suggested that aquatic plants and macro-algae cycle a minimum of 0.5 percent of the annual iron loading and 29 percent of the annual cadmium loading in a subtropical estuary. The significance of this mechanism will be influenced by the number of plants, the type of plants and the availability of metals in sediment.

Higher organisms can also contribute to metal cycling. Burrows of benthic fauna increase the surface area through which transfer may occur.[70] Fish have also been observed to increase turbidity;[70,131] and in one case turbidity caused a reduction in soluble phosphate by sorption.[131] It is also possible that the solids could sorb or leach metals depending on other conditions in the water (pH, DO, redox, salinity). Cross et al.[132] investigated this problem and reported that oligochaetes increased the transfer of trace metals from sediment.

It has been reported that more than 90 percent of the mercury in biota consists of methylmercury, although methyl-mercury usually represents only a small fraction (<1 percent) of the mercury present in an aquatic system.[125] This is the result of methylmercury's high affinity to organic matter in general and the efficiency with which it is retained by organisms. The effect of stirring and suspending of sediment on the biological methylation rate of mercury was studied in the laboratory by Jernelöv and Asell.[125] Mercury was added as $HgCl_2$ at a concentration of 10 ppm (wet weight); two types of lake sediment were incubated in 250 ml Erlenmeyer flasks for 20 days. One group of flasks was placed on a shaking table and

another group was kept stable. Results are presented in
Table 14. Methylation rates were considerably higher when
the mercury contaminated sediment was kept in suspension.

Jernelöv and Asell[125] simulated the effects of dredging
in mercury contaminated sediment using a mathematical model
that described methylmercury formation and transport in
a simplified ecosystem consisting of three trophic levels.
The methylmercury concentration in the top carnivore in this
model ("pikes") increases shortly after the dredging and
begins to decrease after approximately one year. The increase
in methylmercury concentration is a result of stirring and
turbulence of the sediment, as simulated by an increased
volume of "active" sediment (top 5 cm where methylation of
mercury takes place) during the dredging period.

Another possible mechanism through which organisms can
affect the transfer of material from sediments is bio-accumulation.
For example, Cross et al.[132] determined that the concentration of
trace metals in polychaetes collected from two different stations
in a coastal plain estuary did not reflect the differences in the
trace metal content of the sediment. It was suggested that the
organisms were capable of regulating their trace metal composition
to some degree. However, an alternate explanation is that the
trace metals associated with the sediment are not chemically
available to the organism. Data collected by Chipman et al.[133]
demonstrating that the polychaeta Hermione hystrix could accumu-
late ^{54}Mn from labeled organic detritus added to sediment but
not ^{54}Mn labeled MnO_2 support this position. Cross et al.[132]
also reported that tubificid worms could not remove radioactive
metals from Columbia River sediment.

TABLE 14

EFFECT OF SHAKING ON THE RATE
OF BIOLOGICAL METHYLATION OF MERCURY*

Type of Sediment	Increase in CH_3Hg amounts during 20 days ng/g		Increase of methylation rate in shaking table factor
	Shaking	No Shaking	
Eutrophic lake (Lake Langsjön)	555.0	22.2	25
Oligotrophic lake (Lake Djupkärra-Dammsjö)**	57.0	9.2	8

*After Jernelöv and Asell[125]

**It appears that the number
9.2 under the No Shaking
column might be a misprint and
that it should actually read
7.2 (8 x 7.2 = 57.6).

Sediment can serve as a sink for metals in natural water systems. Duke et al.[134] studied the distribution of zinc in a North Carolina estuary. Two cement walled ponds were established adjoining the estuary, and zinc concentrations were determined for the sediment, water, flora and fauna in each pond. A known quantity of radioactive zinc was then added to each pond, one of which was isolated from tidal influence (Pond I), and the movement of zinc-65 was followed for a period of 100 days. The major process was the accumulation of zinc-65 in the estuarine sediment. The zinc-65 distribution was essentially the same as that determined for stable zinc at the beginning of the experiment (Table 15). It is interesting to note that 95 to 99.8 percent of the stable zinc is in the sediment. Also, the added zinc-65 achieved the same distribution with 94 to 99.8 percent reaching the sediment within 100 days. Zinc-65 was not selectively concentrated by organisms even though it was added in the ionic form. This suggests that chemical reactions control the fate of added metals. Because sorption appears to control zinc, the bottom substrate type will influence the phase distribution. When the bottom is covered with sand, zinc becomes associated with suspended matter in the water rather than sediment.[135] Sorption can also control copper,[136,137] chromium[136] and cesium.[138]

Peterson[139] recently completed a study of the aqueous environmental chemistry of lead during which the distribution of lead was determined in lakes, rivers, rainfall, urban runoff and sediment. Lead concentrations in sediment cores collected from seven Wisconsin lakes show a rapid increase in the upper sediment of 10 to 525 µg/g dry weight indicating a recent input that was attributed to cultural development and the use of lead as an anti-knock component in gasoline. However, despite the recent input, dissolved lead concentrations in 16 lakes were

TABLE 15

ZINC DISTRIBUTION IN NORTH CAROLINA PONDS*

Pond I	Zinc	Zinc-65
Water	0.1	Background level
Macrobiota	0.1	0.2
Sediment (upper 6 cm)	99.8	99.8

Pond II		
Water	1	Background level
Macrobiota	4	5
Sediment (upper 6 cm)	95.0	94.0

Figures are in percent
*After Duke et al.[134]

usually less than 5 µg/l and frequently in the range of 1-2 µg/l in the water. Peterson[139] concluded that lead solubility was not the dominant mechanism controlling lead concentrations in natural waters unless sulfide was present. At other times lead concentrations in the water were limited by sorption.

Lead in urban runoff was transported quickly to lake sediment which act as a sink for the metal. This was shown by the short residence time calculated for lead that was on the order of 0.5 days for Lake Monona, Madison, Wisconsin. In addition, there were low lead levels in the runoff and a small dissolved lead to total lead ratio.

It was generally observed that lead transported within a water system is associated with a solid phase.[139] The reason for this is that lead is readily sorbed on solid phases which reduces lead concentrations below calculated equilibrium levels based on known solubility products for lead compounds. The importance of these results on a dredged material disposal criteria project is two fold. First, the identification of lead based on a bulk analysis of dredged sediment is not an indication of chemical availability. Second, lead mobility will be controlled by a physicochemical process of sorption in the same manner that redox reactions control the form and mobility of iron and manganese. Because a high suspended solids concentrations would be inherent in any dredged material disposal operation, a release of lead would not be expected.

Studies on the movement of metals from river sediment into the sea may shed some light on potential problems that could result from dredged material disposal at sea. Transport of heavy metals by rivers mainly takes place in solid form as part of the suspended materials.[140,141] In studies of the Rhine River, de Groot and Allersma[140] found that the metals remain fixed to the suspended matter until the river is influenced by the sea. According to these authors, downstream of the freshwater tidal

area of the river some of the metals are mobilized going into solution into the surrounding water partly as organo-metallic complexes. A high degree of mobility was observed with Cd and Hg followed by Cu, Zn, Pb, Cr, As and Ni. No solubilization of Sc, La, Sm and Mn occurred.

Evidence was obtained in the laboratory that the fulvic acid fraction resulting from decomposition of organic matter in the sediment, especially as far as the mouth of the estuary, are mainly responsible for the metals mobilization.[140]

The degree of mobilization depends on the stability constant of the metal under consideration with the organic ligand. Also, inorganic ions such as Cl^- can play a role in the mobilization processes. For example, mercury forms the very stable complexes $HgCl_2$ and $HgCl_4^{-2}$ with Cl^- ions.[129] De Groot and Allersma[140] estimate that large amounts of metals have been mobilized by these processes from the Rhine River sediment. The added amounts of metals are not found in the coastal water of the North Sea due to the large dilution of the river water with seawater.

Mobilization of large amounts of metals in the fashion described above can result from disposal at sea of dredged material from brackish and freshwater. This could be the case for harbors of large rivers and estuaries. The time and extent of dilution will depend on the volumes involved, of both dredged sediment and dilution water, and characteristics of the disposal site. Greater and faster dilution can be expected at sites with open water and swift currents as compared to small enclosed areas with little water movement. It appears that dilution of dredged material at the disposal site may be the single most important factor to determine the significance of potential pollutant concentrations to arise from dredged material disposal.

Observations on the dredging of mercury contaminated
sediments in Lake Trummen are reported by Jernelöv and Asell.[125]
By means of pump dredging, the sediment was stirred with
water and pumped into a sedimentation pond. The outgoing water
from this pond was precipitated with aluminum sulfate, and
after flocculation in a second pond, the water was returned to
the lake.

The mercury concentration of the lake water was within
the range 0.05 - 0.15 µg/l before and during the first dredging
operation. In the first sedimentation pond, the mercury con-
centrations of the water showed a mean of 0.6 µg/l, but after
settling and before precipitation the average concentration
was down to approximately 0.1 µg/l and remained at that level
during precipitation and flocculation until the water was back
in the lake. Thus, the mercury concentration of water had
decreased to background levels after the first sedimentation
process, and no further decrease in the mercury concentration
of the water was detected as a result of precipitation.

In addition, it was revealed that the mercury concentrations
of the drying dredged sediment decreased during the first
months on land. Mercury transport with drainage water was ruled
out as an explanation on the basis of water analyses. Laboratory
studies revealed a very rapid formation of volatile dimethyl-
mercury when mercury-contaminated wet, organic sediment was ex-
posed to air.[125] Thus, on-land disposal of mercury contaminated
sediment could result in rapid loss of the mercury to the atmos-
phere.

During the years between 1900 and 1950, large quantities of
copper sulfate were applied to Lake Monona, Wisconsin, waters
for control of aquatic vegetation growth. More than 1.5×10^6 lbs
of copper sulfate were introduced into the lake, yet present
copper concentrations in the water are about 4 µg/l or less.[142]

The bottom sediment of Lake Monona constitutes a natural sink for copper. Sanchez and Lee[143] have determined that the binding capacity of the sediment for copper is in the order of 26 mg/g of dry sediment. They suggest that copper ions in solution react with Ca and Mg carbonates in the sediment to form basic copper carbonate as part of the sediment, and in this way Ca and Mg ions are released to solution. Sediment cores of Lake Monona show that the maximum copper concentration is found 60 cm below the surface. The bulk of the added copper in this lake has been incorporated into the sediment and has become part of the permanent record of the lake. These results are similar to the results of a sediment phosphate study by Shapiro et al.[106] in which it was shown that phosphate added to Lake Washington accumulated in the sediment and was covered over by newer sediment and not leached out.

There is no wholesale release of metals from sediment and dredged material because total concentrations do not determine transfer across the sediment-water interface. The interface is usually in an oxidized state and acts as a barrier to soluble reduced species. When a release does occur, the concentration changes are determined by the individual behavior of the elements. Sorption-desorption and redox are the most important reactions in the process.[3]

Pesticides and Miscellaneous Organics

The least studied fraction in sediment is the organic compounds. The probable reason is that a relatively large volume of water is required for most organic analyses, and this volume is not readily available in interstitial water investigations. As a result, most reported sediment investigation data are expressed as total values.

1. Pesticides

One class of compounds that has been investigated is pesticides. Hughes and Lee[144] and Veith and Lee[145] studied the persistence of toxaphene in lakes. The pesticide was added to clear the lake of rough fish for restocking with game fish. Toxaphene accumulated in the fatty portion of the fish and was also removed from solution by sorption on suspended solids.[144] The toxaphene was transported to the sediment and migrated into the sediment. Because the vertical transport rates were a rather high 0.4 - 1.1 cm/day, it was suggested that the movement was due to sediment mixing and not molecular diffusion.

A similar study was conducted by Olney[146] in Rhode Island. Sediment, water and fish samples were collected from 32 lakes and analyzed for DDE, DDD, DDT, chlordane, dieldrin and PCB's. The pesticides were accumulating in the sediment.

Dixon et al.[147] studied the exchangeability of diquat from clay minerals. A direct relationship was observed between the amount of potassium-replaced diquat and the cation exchange capacity. Exchangeable diquat was also related to the amount of vermiculite in the soil samples.

A number of investigators have studied the interaction between pesticides and suspended solids or sediment. Boucher and Lee[17] observed that 70 percent of the lindane sorbed on natural aquifer sands was leached by three washes of distilled water but less than 20 percent of the sorbed dieldrin was released under the same conditions. Huang and Liao[14] found that 25 percent of the dieldrin sorbed on pure montmorillonite could be leached into distilled water, but very little DDT or heptaclor could be leached. It was further shown that natural sediment containing aldrin would sorb more of the pesticide rather than release it.[148] It should be pointed out that

organic material may be available to filter feeders while the dredged material is in suspension or to deposit feeders after it has settled on the bottom. However, the results suggest that bulk analysis will not indicate the amount of material that will be released into solution.

May[3] conducted a study around active dredging sites and found that pesticides were not released during dredging or dredged material disposal operations.

2. Oil and Grease

Another major class of compounds that has received attention is oil and grease. Most of the studies only identify oils in sediment.[149,150,151] In one case,[149] oil was identified several years after an oil spill. The concentrations were in the µg/g range in sediment, benthic species and lobsters.

Bengtsson and Berggren[152] and Hartung and Klingler[39] discussed several aspects of oil in sediment. Oil can create a paste-like consistency that may hinder benthic burrowing. This can have an indirect effect on redox potential because benthic fauna consume freshly settled material and older sediment material, pump oxygen-rich water through building tubes, aerate surface sediment with respiratory movements and move sediment thereby making it more available for aerobic microbial decomposition. Also, predators (fish) mix surface sediment in attempting to catch benthic fauna. However, no mortality was observed after two months when one volume of polluted sediment was mixed with three volumes of control sediment.

Another potential problem is the cyclic and aromatic compounds present in oil and grease that are difficult to degrade and may be toxic. In addition, PCB's and pesticides may be concentrated in oils. Hartung and Klingler[39] have estimated the partition coefficient for this transfer to be on the order of $1.08 \times 10^6 - 1.45 \times 10^6$.

Another major grouping of organic compounds is the natural organic matter. Keup et al.[126] reported that organic matter as measured by color was leached from sand, loam, mulch and leaf litter. The greatest release occurred from leaf litter. Hall[153] also investigated organic matter leached from leaves. The importance of this material is that it is capable of complexing with metals, thereby keeping them in solution and increasing their availability. The leaf extract isolated by Hall[153] caused a four fold increase in the release of zinc from taconite tailings, a ten fold increase in the release of iron and a 25 fold increase in the release of copper.[11] Faure[154] investigated the interaction between organic matter extracted from sediment and trace metals, and Plumb and Lee[155] studied the interaction between iron and organic matter.

Sever and Parker[156] identified long-chain alcohols thought to have resulted from the reduction of chlorophyll in sediment. Similar compounds were identified by Welte and Ebhardt[157] and Hites and Biemann.[158] In other studies, man-made compounds such as NTA[159] and 3, 4-benzopyrene and 3, 4-benzofluoranthene[160] have been measured. The effect of these materials in the environment is not known, but some of them could increase the solubility of metals (Fe, Ni, Zn, Mn, Co, Ca, Mg) by complexation[159,161] with a possible increase of algal activity.[162]

The influence of particulate matter on the incorporation of organic matter into sediment was investigated by Bader.[163] The study was conducted with isotopically labeled organic compounds (alanine, sucrose, fructose, oxalic acid and succinic acid) and purified minerals (montmorillonite, illite, kaolinite and quartz). The amount of a specific chemical that was removed during a 20-minute contact period with each mineral decreased in the order montmorillonite > illite > kaolinite > quartz. This sequence is identical with a listing of the cation exchange capacity of

the minerals tested (montmorillonite 80-150 meq/100 g, illite
10-40 meq/100 g, kaolinite 3-15 meq/100 g and quartz negligible)
suggesting that cation exchange capacity or mineral structure
is a primary factor in determining the amount of organic chemical
removed from solution.[163] It was also observed that the chemicals
tested displayed an order of preference for each of the minerals.
The degree of association decreased in the order alanine >
sucrose > fructose > succinic acid > oxalic acid. Major deter-
minants of this sequence are the types of functional groups
present and molecular weight of the organic molecule.[163]

Other factors such as chlorinity, pH, temperature and
surface area may alter the extent of organic matter - particu-
late matter association that occurs. However, these factors
did not change the preferential order of association that was
observed.[163] It was also pointed out by Bader[163] that physical
adsorption would not completely explain the uptake of organic
compounds on the selected minerals. In one case, 70 mg of alanine
was removed from solution by 20 mg of montmorillonite which
would require the formation of a coating approximately 65 molecu-
lar layers thick. Proposed mechanisms to account for the
observed uptake were the formation of a clay-organic complex,
entrapment of organic molecules or alteration of the organic
molecules.

An important aspect of the Bader[163] investigation is that
the formation of an organic-mineral complex would increase the
rate of flux of dissolved organic matter into the sediment.
Also, the association reaction was not reversible since only
20 percent of the organic matter could be removed by washing
the mineral. Thus, sediment would tend to be a sink for organic
matter rather than a source. In addition to being a sink for
organic matter, the clay organic complex may also be a sink for
trace metals and organic contaminants such as the chlorinated
hydrocarbons. The metals would tend to complex with the

organics which are sorbed on the surface of the clays. Also,
many organic contaminants may tend to be sorbed, i.e., "dissolve"
in the organic clay complex and thereby be removed from solu-
tion.

CONCLUSIONS

It is obvious from the above discussions that there is need for additional research in order to evaluate the environmental impact and the significance of this impact of dredged material disposal on man. It should be stressed that there is little or no evidence today to indicate that the highly conservative approach should be used where dredging would be halted until all the information is available. Since dredging represents a potentially significant economic gain to parts of society as a result of reduced costs of transporting goods and, in some cases, enhancing the recreational value of the water, those parts of society who gain from a particular dredging operation should contribute significantly to the funding of research needed to evaluate the environmental impact of dredging. It is likely that, as a result of the energy crisis, even greater emphasis will be placed on cheaper methods of transport in an effort to reduce energy consumption. Normally, water transportation is one of the most economical methods of moving large amounts of bulk material between urban centers with the result that even a greater emphasis will be placed on developing and maintaining deeper waterways for commercial traffic. Since such an approach is of benefit to a large part of society, a substantial amount of funds should be set aside in this area to ensure that significant detrimental environmental impact does not occur.

Techniques are available today to monitor dredging operations in order to detect large scale detrimental effects on environmental quality. Since there is little or no evidence that the chemical constituents in most dredged sediment have an effect on aquatic life and further, since there is little reason to believe that the chemical contaminants present in

sediment associated with normal dredging operations would have
a substantial detrimental environmental impact, it is recommended
that dredging and dredged material disposal continue provided
that funds are set aside for determining the environmental
impact at particular sites throughout the U.S.

As a result of this review, it is recommended that research
be undertaken in a number of areas which are important to
assessing the environmental impact of chemical contaminants in
dredged material. There is little doubt that under certain situa-
tions these contaminants could have an adverse effect on environ-
mental quality. It is likely that these situations would be
associated with the dredging of sediment undertaken in the
regions where there is discharge of large amounts of municipal
and industrial wastes which have not been properly treated. It
is clear that some type of predredging test(s) should be developed
to evaluate the potential environmental impact of the chemical
contaminants present in dredged material. This review has demon-
strated that the bulk-analysis approach is not a technically sound
basis for the development of a test of this type. Since one of
the primary potential modes by which the chemical contaminants
in dredged material could have an adverse effect on aquatic eco-
systems is through the release of these contaminants to the
water column at the dredging or disposal site, it is felt that
the Elutriate Test represents a potentially valuable tool which
could provide the information needed to assess water quality
problems in these areas. There are many factors, however,
that could influence the results of the Elutriate Test. It is
important that this test be relatively insensitive to minor
modifications in the operating procedures. It is therefore
imperative that studies be conducted on the factors influencing
test results. Based on these studies, which would include the
utilization of sediment representing the different types of

dredging situations that are encountered in the U.S., a modified Elutriate Test should be developed.

It is important to emphasize that the Elutriate Test is an empirical test. It does not duplicate the natural environment. It, like many other empirical tests used in the water pollution control field, provides an indication of potential problems. Empirical tests of this type become successful tools in environmental quality control when an empirical factor or factors are developed which relate test results to environmental situations. Therefore, a key part of the development of the Elutriate Test will be the utilization of this test or modification thereof, in conjunction with large scale field studies in which the environmental impact of a particular dredged material disposal operation is carefully evaluated. From a number of studies of this type, it should be possible to develop the empirical factors that relate the release of chemicals in the Elutriate Test to the environmental effect of these chemicals associated with dredging and dredged material disposal.

It is recommended that at a few selected sites across the country which are representative of normal dredging situations, the Elutriate Test be used to attempt to predict, prior to dredging, the environmental impact of the dredging. Subsequently, a detailed study should be conducted to determine the actual environmental impact of the operation at both the dredging and disposal site. In general, studies of this type would be of relatively short duration lasting a few weeks to a few months, depending on the situation. These studies which are designed to evaluate the potential adverse effects of dredging in the respective water columns should be followed up by long-term studies designed to evaluate the effect of the chemical contaminants present in the dredged material on benthic organisms at

the disposal site. It is recommended that in addition to utilizing the results of the standard Elutriate Test in these studies, laboratory and field studies be conducted to determine the chemical characteristics of the interstitial waters in contact with the dredged material. It is possible that an empirical relationship may be developed which could be used to relate these results to environmental impact. It is important to emphasize that it will likely take several years of intensive research before a satisfactory Elutriate Test is developed.

REFERENCES

1. Boyd, M.B., Saucier, R.T., Keeley, J.W., Montgomery, R.L.
   Brown, R.D., Mathis, D.B. and Guice, C.J. "Disposal
   of Dredge Spoil. Problem Identification and Assess-
   ment and Research Program Development." U.S. Army
   Engineer Waterways Experiment Station, Vicksburg,
   Mississippi, Technical Report H-72-8, 121 p. (1972).

2. Trimble, P.E. "Statement of Vice Admiral Paul E. Trimble
   at Lansing Meeting of Saginaw River Users Group with
   Federal and State Officials Concerned with Dredge
   Spoil Disposal." Lake Carriers' Association, Cleve-
   land, Ohio 4 p. September 19, 1973.

3. May, E.B. "Environmental Effects of Hydraulic Dredging in
   Estuaries." Alabama Marine Resources Bulletin 9:
   1-85 (1973).

4. Davis, J.D. "Dredge Spoil Disposal in Long Island Sound:
   A Coordinated Approach to a Power Project." Proceed-
   ings 19th Meeting, Institute of Environmental Sciences
   Anaheim, California 19: 167-174 (1973).

5. Windom, H.L. "Water Quality Aspects of Dredging and Dredge
   Spoil Disposal in Estuarine Environments." Skidaway
   Institute of Oceanography, Savannah, Ga. 19 p. mimeo
   (1973).

6. Ritchie, G.A. and Speakman, J.N. "Effects of Settling Time on
   Quality of Supernatant from Upland Dredge Disposal
   Facilities." U.S. Army Corps of Engineers, Buffalo
   District, Buffalo, N.Y. Presentation before 16th
   Conference on Great Lakes Research, Huron, Ohio (1973).

7. Murthy, A.S.P. and Ferrell, Jr., R.E. "Distribution of Major
   Cations in Estuarine Sediments." Clays and Clay Minerals
   21: 161-165 (1973).

8. Environmental Protection Agency "Proposed Criteria for Water
   Quality." Vol. I and II, U.S. EPA Washington, D.C.,
   October, 1973.

9. Environmental Protection Agency "Ocean Dumping Criteria."
    Federal Register 38(94): 12872-12877 (1973).

10. Environmental Protection Agency "Ocean Dumping Final
    Criteria." Federal Register 38(198): 28610-28621
    (1973).

11. Plumb, Jr., R.H. "A Study of the Potential Effects of the
    Discharge of Taconite Tailings on Water Quality in
    Lake Superior." Ph.D. Thesis, University of Wisconsin-
    Madison, 550 p (1973).

12. Lotse, E.G., Graetz, D.A., Chesters, G., Lee, G.F. and Newland,
    L.W. "Lindane Adsorption by Lake Sediment." Environ.
    Science and Tech. 2: 353-357 (1968).

13. Luh, M. and Baker, R.A. "Organic Sorption from Aqueous
    Solution by Two Clays." Proceedings 25th Ind. Waste
    Conference Purdue University, 534-542 (1970).

14. Huang, J. and Liao, C. "Adsorption of Pesticides by Clay
    Minerals." J. Sanitary Eng. Div., Am. Society Civil
    Eng. 96: 1057-1078 (1970).

15. Windom, H.L. "Environmental Aspects of Dredgings in Estuaries."
    J. Am. Society Civil Eng. 98 No. WW4: 475-487 (1972).

16. Huang, J. "Effect of Selected Factors on Pesticide Sorption
    and Desorption in the Aquatic System." J. Water Poll.
    Control Fed. 43: 1739-1748 (1971).

17. Boucher, F.R. and Lee, G.F. "Adsorption of Lindane and
    Dieldrin Pesticides on Unconsolidated Aquifer Sands."
    Environ. Science and Tech. 6: 538-543 (1972).

18. Wang, W., Lee, G.F. and Spyridakis, D. "Adsorption of Parathion
    in a Multicomponent Solution." Water Res. 6: 1219-1228
    (1972).

19. Rowe, D.R., Canter, L.W. and Mason, J.W. "Contamination of
    Oysters by Pesticides." J. Sanitary Eng. Div., Am.
    Society Civil Eng. 96: 1221-1234 (1970).

20. Lee, G.F. "Role of Phosphorus in Eutrophication and Diffuse
    Source Control." Water Res. 7: 111-128 (1973).

21. Sridharan, N. and Lee, G.F. "Coprecipitation of Organic Com-
    pounds from Lake Water by Iron Salts." Environ. Science
    and Tech. 6: 1031-1033 (1972).

22. Dornbush, J.N. and Ryckman, D.W. "The Effect of Physiochemical Processes in Removing Organic Contaminants." J. Water Poll. Control Fed. 35: 1325-1338 (1963).

23. Robeck, G.G., Dostal, K.A., Cohen, J.M. and Kreissl, J.F. "Effectiveness of Water Treatment Processes in Pesticide Removal." J. Am. Water Works Assoc. 57: 181-199 (1965).

24. Hill, D.W. and McCarty, P.L. "Anaerobic Degradation of Selected Chlorinated Hydrocarbon Pesticides." J. Water Poll. Control Fed. 39: 1259-1277 (1967).

25. Lee, G.F. "Role of Hydrous Metal Oxides in the Transport of Heavy Metal in the Environment." Proceedings of the Symposium on Heavy Metals in the Environment, Vanderbilt University (1973).

26. Bella, D.A. "Environmental Considerations for Estuarine Benthal Systems." Water Res. 6: 1409-1418 (1972).

27. Slotta, L.S., Sollitt, C.K., Bella, D.A., Hancock, D.R. McCauley, J.E. and Parr, R. "Effects of Hopper Dredging and In Channel Spoiling in Coos Bay, Oregon." School of Eng., School of Oceanography, Oregon State University, Corvallis, ·Oregon,133 p. (1973).

28. Black, C.A. (ed) "Methods of Soil Analysis." Part 2, Am. Society of Agronomy, Madison, Wisconsin (1965).

29. Wagner, D.M., Reserve Mining Company, Personal Communication to G. Fred Lee, January 8, 1974.

30. Wagner, D.M. and Wahlstrom, P.T. "1972 Permanent Station Water Chemistry Survey." Project 23-1108-1, Reserve Mining Company, Silver Bay, Minnesota, 39 p., October 1, 1973.

31. Lee, G.F. "Great Lakes Water Quality Monitoring Strategy." Presented at the CIC-CCIW Symposium on Water Quality Parameter Selection Measurement and Monitoring, Burlington, Ontario, Canada (1973).

32. Keeley J. and Engler, R. "Discussion of Regulatory Criteria for Ocean Disposal of Dredged Material: Elutriate Test Rationale and Implementation Guidelines." U.S. Army Engineer Waterways Experiment Station, Vicksburg, Mississippi, Miscellaneous Paper D-74-14 (1974).

33. Lee, G. F. "Chemical Aspects of Bioassay Test for Establishing Water Quality Criteria" Water Res. 7: 1525-1546 (1973).

34. Fetterolf, Jr, C.M. "Mixing Zone Concepts." Biological Methods
        for the Assessment of Water Quality ASTM STP 528 Am.
        Society for Testing and Materials, p. 31-45 (1973).

35. Lerman, A. and Brunskill, G.J. "Migration of Major Constituents
        from Lake Sediments into Lake Water and Its Bearing on
        Lake Water Composition." Limn. and Oceano. 16: 880-890
        . (1971).

36. Ingle, R.M., Ceurvels, A.R. and Leinecker, R. "Chemical and
        Biological Studies of the Muds of Mobile Bay." Rept.
        to Div. Seafoods, Alabama Dept. Conservation, University
        of Miami, Contrib. 139, 14 p. (1955).

37. Gustafson, J.F. "Beneficial Effects of Dredging Turbidity."
        World Dredging and Marine Construction 8: 44-52 (1972).

38. Saila, S.B., Pratt, S.D. and Polgar, T.T. "Dredge Spoil
        Disposal in Rhode Island Sound." Marine Technical Report
        No. 2, University of Rhode Island, 48 p. (1972).

39. Hartung, R. and Klingler, G.W. "Concentration of DDT by Sedi-
        mental Polluting Oils." Environ. Science and Tech.
        4: 407-410 (1970).

40. Vaccaro, R.F., Grice, G.D. Rowe, G.T. and Wiebe, P.H. "Acid-
        Iron Waste Disposal and the Summer Distribution of
        Standing Crops in the New York Bight." Water Res. 6:
        231-256 (1972).

41. Hansen, R.S. "Great Lakes Dredging - Problems and Remedies."
        World Dredging and Marine Construction 7: 16-20 (1971).

42. O'Neal, G. and Sceva, J. "The Effect of Dredging on Water
        Quality." World Dredging and Marine Construction 7:
        24-31 (1971).

43. The University of Wisconsin, "Investigation of Treatability
        and Effect on Biota of Dredged Materials from Selected
        Great Lakes Harbors." Center for Great Lakes Studies,
        the University of Wisconsin-Milwaukee, 249 p., September
        1968.

44. Gannon, J.E. and Beeton, A.M. "Procedures for Determining the
        Effects of Dredged Sediments on Biota-Benthos Viability
        and Sediment Selectivity Tests," J. Water Poll. Control
        Fed. 43: 392-398 (1971).

45. Gannon, J.E. and Beeton, A.M. "Studies on the Effects of
    Dredged Materials from Selected Great Lakes Harbors on
    Plankton and Benthos." Center for Great Lakes Studies,
    University of Wisconsin-Milwaukee, Special Report
    No.8,82 p. (1969).

46. Posner, J.C. and Weber, W., University of Michigan, Personal
    Communication to G. Fred Lee, 16 p., December 11, 1973.

47. Leonard, R.P. and Dahm, D.B. "Assessment of the Environmental
    Effects Accompanying Upland Disposal of Polluted Harbor
    Dredgings, Ashtabula Harbor, Ohio." Cornell Aeronautical
    Laboratory, Inc., Buffalo, N.Y., 25 p. (1972).

48. Flemer, D.A., Dovel, W.L., Pfitzenmeyer, H.T. and Ritchie, Jr.,
    D.E. "Biological Effects of Spoil Disposal in Chesapeake
    Bay." J. Am. Society Civil Eng. 94(SA4): 683-706 (1968).

49. Pratt, S.D., Saila, S.B., Gaines, Jr., A.G. and Krout, J.E.
    "Biological Effects of Ocean Disposal of Solid Wastes."
    University of Rhode Island, Marine Technical Report Series.
    No. 9, 53 p. (1973).

50. Carlisle, Jr., J.G. "Results of a Six-Year Trawl Study in
    an Area of Heavy Waste Discharge: Santa Monica Bay,
    California" California Fish and Game 55: 26-46 (1969).

51. Cairns, Jr., J. "Suspended Solids Standards for the Protection
    of Aquatic Organisms." 22nd Purdue Ind. Waste Conference
    Purdue University Eng. Bulletin 129: 16-27 (1968).

52. Hollis, E.H., Boone, J.G., DeRose, C.R. and Murphy, G.J.
    "Literature Review on the Effects of Turbidity and Silta-
    tion on Aquatic Life." Dept. Chesapeake Bay Affairs,
    Maryland Fish and Wildlife Admin., Annapolis, Md, 20 p.
    (1964).

53. Cordone, A.J. and Kelley, D.W. "The Influence of Inorganic
    Sediment on the Aquatic Life of Streams." California
    Fish and Game 47: 189-228 (1961).

54. Looseanoff, V.L. and Tommers, F.D. "Effect of Suspended Silt
    and Other Substances on the Rate of Feeding of Oysters."
    Science 107: 69-70 (1948).

55. Gay, J.C. "Bottom Fauna Study, Statistical Analysis." Reserve
    Mining Company, Silver Bay, Minn., Reserve Mining Company
    Report to the Minnesota Poll. Control Agency, Minneapolis,
    Minn., 15 p., February, 1970.

56. Sherk, Jr., J.A. "Current Status of the Knowledge of the Biological Effects of Suspended and Deposited Sediments in Chesapeake Bay." Chesapeake Sci. 13: S137-S144 (1972).

57. Oliff, W.D., Berrisford, C.D., Turner, W.D., Ballard, J.A. and McWilliams, D.C. "The Ecology and Chemistry of Sandy Beaches and Nearshore Submarine Sediments of Natal - I. Pollution Criteria for Sandy Beaches in Natal." Water Res. 1: 115-219 (1967).

58. Oliff, W.D., Berrisford, C.D., Turner, W.D., Ballard, J.A. and McWilliam, D.C. "The Ecology and Chemistry of Sandy Beaches and Nearshore Submarine Sediments of Natal - II. Pollution Criteria for Nearshore Sediments of the Natal Coast." Water Res. 1: 131-146 (1967).

59. Ballinger, D.G. and McKee, G.D. "Chemical Characterization of Bottom Sediments." J. Water Poll. Control Fed. 43: 216-227 (1971).

60. Hellmann, H. "The Classification of Sediments According to their Content of Trace Metals." Gewasserk, Mitt. 14: 160-164 (1970).

61. Hellmann, H. "Determination of Metals in River Sludge by Means of X-Ray Fluorescence and its Application in Practice." Anal. Chem. 43: 192-195 (1971).

62. Toth, S.J. and Ott, A.N. "Characterization of Bottom Sediments: Cation Exchange Capacity and Exchangeable Cation Status." Environ. Science and Tech. 4: 935-939 (1970).

63. Malcolm, R.L. and Kennedy, V.C. "Variation of Cation Exchange Capacity and Rate with Particle Size in Stream Sediments." J. Water Poll. Control Fed. 42: R152-160 (1970).

64. Lenhard, G., Ross, W.R. and duPlooy, A. "A Study of Methods for the Classification of Bottom Deposits of Natural Waters." Hydrobiologia 20: 223-240 (1962).

65. U.S. Army, Office, Chief of Engineers, "Disposal of Dredged Materials" Engineering Circular 1165-2-97, U.S. Government Printing Office, Washington, D.C., May 12, 1971.

66. Keeley, J.W. Army Corps of Engineers, Vicksburg, Mississippi, Personal communication to G. Fred Lee, February 6, 1974.

67. Peterson, J.R. and Gschwind, J. "Leachate Quality from Acidic Mine Spoil Fertilized with Liquid Digested Sewage Sludge." J. Environ. Quality 1: 410-412 (1972).

68. Heukelekian, H. and Balmat, J.L. "Chemical Composition of the Particulate Fractions of Domestic Sewage." Sewage and Ind. Wastes 31: 413-423 (1959).

69. Oschwald, W.R. "Sediment - Water Interactions." J. Environ. Quality 1: 360-366 (1972).

70. Lee, G.F. "Factors Affecting the Transfer of Materials Between Water and Sediments." University of Wisconsin, Eutrophication Information Program, Literature Review No. 1, 50 p., July (1970).

71. Bortleson, G.C. and Lee, G.F. "Chemical Characteristics of Wisconsin Lakes (in press) (1974).

72. Brooks, R.R., Presley, B.J. and Kaplen, I.R. "Trace Elements in the Interstitial Waters of Marine Sediments." Geochim. et Cosmochim. Acta 32: 397-414 (1968).

73. Bricker, III, O.P. and Troup, B.N. "Sediment-Water Exchange in Chesapeake Bay." Presented at the Second Internatl. Estuarine Conference, Myrtle Beach, S.C., 42 p., October 1973.

74. Oliff, W.D., Gardner, B.D., Turner, W.D. and Sharp, J.B. "The Chemistry of the Interstitial Water as a Measure of Conditions in a Sandy Beach." Water Res. 4: 179-188 (1970).

75. Sullivan, W.T. "Chemical Composition of the Mud - Water Interface Zone, with the Description of an Interface Sampling Device." Proceedings 10th Conference Great Lakes Res. 10: 390-403 (1967).

76. Glass, G.E. "A Study of Western Lake Superior: Surface Sediments, Interstitial Water, and Exchange of Dissolved Components Across the Water-Sediment Interface." In: "Studies Regarding the Effect of the Reserve Mining Company Discharge in Lake Superior." U.S. EPA, Office of Enforcement and General Council, Washington, D.C. 1028-1121 (1973).

77. Fillos, J. "The Effect of Benthal Deposits on the Oxygen and Nutrient Economy of Natural Flowing Waters." Ph.D. Thesis, New York University, 201 p. (1970).

78. Fillos, J. and Molof, A.H. "Effect of Benthal Deposits on Oxygen and Nutrient Economy of Flowing Waters." J. Water Poll. Control Fed. 44: 644-662 (1972).

79. Mortimer, C.H. "The Exchange of Dissolved Substances Between Mud and Water in Lakes." J. Ecology 29: 280-329 (1941).

80. Mortimer, C.H. "The Exchange of Dissolved Substances Between Mud and Water in Lakes." J. Ecology 30: 147-201 (1942).

81. Stein, J.E. and Denison, J.G. "In Situ Benthal Oxygen Demand of Cellulose Fibers." Adv. in Water Poll. Res. 3: 181-193 (1966).

82. McKeown, J.J., Benedict, A.H. and Locke, G.M. "Studies on the Behavior of Benthal Deposits of Wood Origin." J. Water Poll. Control Fed. 40: R333-R354 (1968).

83. Fair, G.M., Moore, E.W. and Thomas, Jr., A.A. "The Natural Purification of River Muds and Pollutional Sediments." Sewage Works J. 13: 270-307 (1941) 13: 756-779 (1941) and 13: 1209-1228 (1941).

84. Mueller, J.H. and Su, W.J. "Benthal Oxygen Demands and Leaching Rates of Treated Sludges." J. Water Poll. Control Fed. 44: 2303-2315 (1972).

85. Conway, C. "Oxygen Depletion in the Hypolimnion" M.S. Thesis, University of Wisconsin (1973).

86. Gorham, E. and Swaine, D.J. "The Influence of Oxidizing and Reducing Conditions Upon the Distribution of Some Elements in Lake Sediments." Limn. and Oceano. 10: 268-279 (1965).

87. Oldaker, W.H., Burgum, A.A. and Pahren, H.R. "Pilot-Plant Study of Benthic Oxygen Demand of River Bottom Sediments." J. Water Poll. Control Fed. 40: 1688-1701 (1968).

88. Pamatmat, M.M. "Oxygen Consumption by the Seabed. IV. Shipboard and Laboratory Experiments." Limn. and Oceano. 16: 536-550 (1971).

89. Pamatmat, M.M. and Banse, K. "Oxygen Consumption by the Seabed. II. In Situ Measurements to a Depth of 180 m." Limn. and Oceano. 14: 250-259 (1969).

90. Pomeroy, L.R., Smith, E.E. and Grant, C.M. "The Exchange of Phosphate between Estuarine Water and Sediments." Limn. and Oceano. 10: 167-172 (1965).

91. Spear, R.D. "The Release of Phosphorus from Lake Sediments" Ph.D. Thesis, University of Wisconsin (1970).

92. Sridharan, N. "Aqueous Environmental Chemistry of Phosphorus in Lower Green Bay." Ph.D. Thesis, University of Wisconsin (1970).

93. Bortleson, G.C. "Use of Lake Sediments Cores to Estimate Eutrophication." Ph.D. Thesis, University of Wisconsin (1970).

94. Gessner, F. "Untersuchungen Über Den Phosphathaushalt Des Amazonas" Internatl. Rez. ges. Hydrobiol. Vol. 45, 339-345.

95. Olsen, S. "Phosphate Adsorption and Isotopic Exchange in Lake Muds." Verd. Internatl. Ver. Theor. Angew. Limn. 13: 915-922 (1958).

96. Hynes, H.B.N. and Greib, B.J. "Movement of Phosphate and Other Ions from and Through Lake Muds." J. Fish Res. Bd. Can. 27: 653-668 (1970).

97. Carritt, D.E. and Goodgal, S. "Sorption Reactions and Some Ecological Implications." Deep-Sea Res. 1: 224-243 (1954).

98. Jitts, H.R. "The Adsorption of Phosphate by Estuarine Bottom Deposits" Austral. J. Mar. Freshwater Res. 10: 7-21 (1959).

99. Gahler, A.R. "Field Studies on Sediment - Water Algal Nutrient Interchange Processes and Water Quality of Upper Klamath and Agency Lakes." U.S.D.A. Fed.Water Poll. Control Agency Northwest Region, Corvallis, Working paper 66 (1969).

100. Gahler, A.R. "Sediment-Water Nutrient Interchange." Proceedings Eutrophication-Biostimulation Assessment Workshop, University of California, 243-257 (1969).

101. MacPherson, L.B., Sinclair, N.R. and Hayes, F.R. "Lake
        Water and Sediment. III. The Effect of pH on the
        Partition of Inorganic Phosphate Between Water and
        Oxidized Mud or its Ash." Limn. and Oceano. 3: 318-
        326 (1958).

102. Golterman, H.L. "Natural Phosphate Sources in Relation to
        Phosphate Budgets: A Contribution to the Understanding
        of Eutrophication." Water Res. 7: 3-17 (1973).

103. McKee, G.D., Parish, L.P., Hirth, C.R., MacKenthun, K.M.
        and Keup, L.E. "Sediment-Water Nutrient Relationships-
        Part 2." Water and Sewage Works 117: 246-249 (1970).

104. Zicker, E.L., Berger, K.C. and Hasler, A.D. "Phosphorus
        Release from Bog Lake Muds." Limn. and Oceano. 1:
        296-303 (1956).

105. Correll, D.L., Faust, M.A. and Severn, D.J. "Phosphorus
        Flux and Cycling in Estuaries." Presentation at
        the Second Internatl. Estuarine Conference,
        Myrtle Beach, S.C., 50 p., October 1973.

106. Shapiro, J., Edmondson, W.T. and Allison, D.E. "Changes in
        the Chemical Composition of Sediments of Lake Washington,
        1958-1970." Limn. and Oceano. 16: 437-452 (1971).

107. Cowen, W. "Available Phosphorus in Urban Runoff and Lake
        Ontario Tributary Waters" Ph.D. Thesis, University of
        Wisconsin (1974).

108. Sirisinha, K. "Available Nitrogen in Madison Urban Storm-
        water Drainage and Selected Tributaries of Lake Ontario."
        M.S. Thesis, University of Wisconsin (1973).

109. Bentley, E.M. "The Effect of Marshes on Water Quality, Ph.D.
        Thesis, University of Wisconsin--Madison (1969).

110. Amundson, R.W. "Nutrient Availability of a Marsh Soil." M.S.
        Thesis, University of Wisconsin--Madison (1968).

111. Lee, G.F., Bentley, E. and Amundson, R. "Effect of Marshes on
        Water Quality." Presented at Internatl. Ecological Assoc.,
        Leningrad, Russia (in press) 46 p. (1971).

112. Kemp, A.L.W. and Mudrochova, A. "Distribution and Forms of
        Nitrogen in a Lake Ontario Sediment Core." Limn. and
        Oceano. 17: 855-867 (1972).

113. Byrnes, B.H., Keeney, D.R. and Graetz, D.A. "Release of Ammonium-N from Sediments to Waters." Proceedings 15th Conference Great Lakes Res. 15: 249-259 (1972).

114. Austin, E.R. and Lee, G.F. "Nitrogen Release from Lake Sediments." J. Water Poll. Control Fed. 45: 870-879 (1973).

115. Shepard, T. "Deep Water Channel Hits a Snag." San Diego Union, B 1; B 12, December 10, 1971.

116. Oliver, B.G. "Heavy Metals Levels of Ottawa and Rideau River Sediments." Environ. Science and Tech. 7: 135-137 (1973).

117. Hutchinson, E.G. A Treatise on Limnology, Vol I, John Wiley and Sons, New York, 1015 p. (1957).

118. Curtis, C.D. "Trace Element Distribution in Some British Carboniferous Sediments." Geochim. et Cosmochim. Acta 33: 519-523 (1969).

119. Duchart, P., Calvert, S.E. and Price, N.B. "Distribution of Trace Metals in the Pore Waters of Shallow Water Marine Sediments." Limn. and Oceano. 18: 605-610 (1973).

120. Jenne, E.A. "Controls on Mn, Fe, Co, Ni, Cu and Zn Concentrations in Soils and Water: The Significant Role of Hydrous Mn and Fe Oxides." In: Trace Inorganics in Water, Am. Chem. Society Advances in Chemistry Series 73, Washington, D.C., 337-387 (1968).

121. Bonatti, E., Fisher, D.E., Joensuu, O. and Rydell, H.S. "Post Depositional Mobility of Some Transitional Elements, Phosphorus, Uranium and Thorium in Deep Sea Sediments." Geochim. et Cosmochim. Acta 35: 189-201 (1971).

122. Lopez, J.M. "Aqueous Environmental Chemistry of Copper and other Heavy Metals in Torch Lake and Selected Waters of the Keweenaw Peninsula Area of Lake Superior." M.S. Thesis, University of Wisconsin-Madison (1973).

123. Fetterolf, C.M., Michigan Water Resources Comm., Personal Communication to G. Fred Lee (1972).

124. Wright, T.D., Leddy, D.G., Brandt, D.J. and Virnig, T.T. "Water Quality Alteration of Torch Lake, Michigan, by Cultural Factors." Proceedings 16th Conference Great Lakes Res., Internatl. Assoc. Great Lakes Res. (in press) (1973).

125. Jernelöv, A. and B. Asell "Feasibility of Restoration of Mercury-Contaminated Bodies of Water." Proceedings Conference on Heavy Metals in the Aquatic Environment, Nashville, Tenn. (1973).

126. Keup, L.E., McKee, G.D., Raabe, E.W. and Warner, R.W. "Water Quality Effects of Leaching from Submerged Soils." J. Am. Water Works Assoc. 62: 391-396 (1970).

127. Laubenberger, G. and Hartman, L. "Storage of Heavy Metal Salts in Bottom Deposits of Rivers and Their Effect on the Biocense of Mud." Wasserwirtschaft 60: 372-75 (1970).

128. Gregor, C.D. "Solubilization of Lead in Lake and Reservoir Sediments by NTA." Environ. Science and Tech. 6: 278-279 (1972).

129. Sillen, L.G. "The Physical Chemistry of Sea Water." Oceano. AAAS Publication, 549-582 (1961).

130. Seger, D. "Trace Metal Cycling in Sub-Tropical Estuaries." Presented at Conference on Recent Advances in Estuarine Research, Myrtle Beach, S.C., October, 1973.

131. Hepher, B. "On the Dynamics of Phosphorus Added to Fishponds in Israel." Limn. and Oceano. 3: 84-100 (1958).

132. Cross, F.A., Duke, T.W. and Willis, J.N. "Biogeochemistry of Trace Elements in a Coastal Plain Estuary: Distribution of Manganese, Iron, and Zinc in Sediments, Water and Polychaetous Worms." Chesapeake Science 11: 221-234 (1970).

133. Chipman, W., Schommers, E. and Boyer, M. "Uptake, Accumulation and Retention of Radioactive Manganese by the Marine Annelid Worm, Hermione hystrix." In: Radioactivity in the Sea, IAEA Pub. No. 25, 16 p. (1968).

134. Duke, T.W., Willis, J.N., and Price, T.J. "Cycling of Trace Elements in the Estuarine Environment. I. Movement and Distribution of Zinc 65 and Stable Zinc in Experimental Ponds." Chesapeake Science 7: 1-10 (1966).

135. Brungs, W.A., Jr. "The Relative Distribution of Multiple Radionuclides in a Fresh Water Pond." Ph.D. Thesis, Ohio State University, 90 p. (1963).

136. Wentink, G.R. and Etzel, J.E. "Removal of Metal Ions by Soil." J. Water Poll. Control Fed. 44: 1561-1574 (1972).

137. Collins, B.I. "The Concentration Control of Soluble Copper in a Mine Tailings Stream." Geochim. et Cosmochim. Acta 37: 69-75 (1973).

138. Kudo, A. and Gloyna, E.F. "Transport of ^{137}Cs-II. Inter-
     action with Bed Sediments." Water Res. 5: 71-79 (1971).

139. Peterson, J.O. "A study of Lead in Lake Sediments." Ph.D.
     Thesis, University of Wisconsin-Madison (1973).

140. de Groot, A.J. and Allersma, E. "Field Observations on the
     Transport of Heavy Metals in Sediments." Proceedings
     Conference on Heavy Metals in the Aquatic Environment,
     Nashville, Tenn. (1973).

141. Gibbs, R.J. "Mechanisms of Trace Metal Transport in Rivers."
     Science 180: 71-73 (1973).

142. Sanchez, I. "Aqueous Environmental Chemistry of Copper."
     Ph.D. Thesis, University of Wisconsin-Madison (1971).

143. Sanchez, I. and Lee, G.F. "Sorption of Copper on Lake Monona
     Sediments-Effect of NTA on Copper release from the
     Sediments." Water Res. 7: 587-593 (1973).

144. Hughes, R.A. and Lee, G.F. Toxaphene Accumulation in Fish in
     Lakes Treated for Rough Fish Control." Environ. Science
     and Tech. 7: 934-938 (1973).

145. Veith, G.D. and Lee, G.F. "Water Chemistry of Toxaphene-
     Role of Lake Sediments." Environ. Science and Tech.
     5: 230-234 (1971).

146. Olney, C.E. "Transfer of Pesticides through Water, Sediments
     and Aquatic Life." Rhode Island Water Resources Center
     8: 26-32 (1972).

147. Dixon, J.B., Moore, D.E., Agnihotri, N.P. and Lewis, Jr., D.E.
     "Exchange of Diquat $^{2+}$ in Soil Clays, Vermiculite, and
     Smectite." Proceedings Soil Science Soc. Amer. 34:
     805-808 (1970).

148. Leshniowsky, W.O., Dugan, P.R., Pfister, R.M., Frea, J.I. and
     Randles, C.I. "Adsorption of Chlorinated Hydrocarbon
     Pesticides by Microbial Floc and Lake Sediment and Its
     Ecological Implications." Proceedings 13th Great Lakes
     Conference 13: 611-618 (1970).

149. Scarrett, D.J. and Zitko, V. "Bunker C Oil in Sediments and
     Benthic Animals from Shallow Depths in Chedabucto Bay,
     N.S." J. Fish Res. Bd. Can. 29: 1347-1350 (1970).

150. Maehler, C.Z. and Greenberg, A.E. "Identification of Petroleum in Estuarine Waters." J. Am. Society Civil Eng. 94: 969-978 (1968).

151. Cochran, L.G., Gay, J.P. and Hill, H.N. "Detection and Identification. Key to Water Pollution Control in a Petrochemical Plant." Ind. Proceedings Des. Poll. Control, Proceedings Am. Inst. Chem. Eng. Workshop 4: 97-105 (1972).

152. Bengtsson, L. and Berggren, H. "The Bottom Fauna in an Oil-Contaminated Lake." Ambio 1: 141-144 (1972).

153. Hall, K.J. "Natural Organic Matter in the Aquatic Environment." Ph.D. Thesis, University of Wisconsin-Madison, 312 p. (1970).

154. Faure, J. "Effect of Organic Matter in a Water Course On radioactive Pollution. Methods of Extracting, Fractionating and Identifying the Organic Constituents and Their Radionuclide Affinities." National Tech. Information Service, Report CEA-R-4335, 63 p. (1972).

155. Plumb, Jr., R.H. and Lee, G.F. "A Note on Iron - Organic Relationship in Natural Waters." Water Res. 7: 581-585 (1973).

156. Sever, J. and Parker, P.L. "Fatty Alcohol (Normal and Isoprenoid) in Sediments." Science 164: 1052-1054 (1969).

157. Welte, D.H. and Ebhardt, G. "Distribution of Long Chain n-Paraffins and n-fatty acids in Sediments from the Persian Gulf." Geochem. et Cosmochim. Acta 32: 465-466 (1968).

158. Hites, R.A. and Biemann, K. "Water Pollution: Organic Compounds in the Charles River, Boston." Science 178: 158-160 (1972).

159. Environmental Protection Agency "Interaction of Nitrotriacetic Acid with Suspended and Bottom Material." Water Poll. Control Res. Ser. 16020 SFR, 31 p. (1971).

160. Wagner, K. and Siddigi, I. "Toxic Materials in Soil Amendments." Naturwissenschaften 66: 160-161 (1973).

161. Doyle, R.W. "Isolation of Enzymes and other Organic Anions from Freshwater Sediments." Limn. and Oceano. 13: 518-522 (1968).

162. Boyd, C.E. "Influence of Organic Matter on Some Characteristics of Aquatic Soils." Hydrobiologia 36: 17-21 (1970).

163. Bader, R.G. "Some Experimental Studies with Organic Compounds and Minerals." Symposium on the Environmental Chemistry of Marine Sediments, University of Rhode Island, Occasional Publication No. 1: 42-57 (1962).

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13. ABSTRACT

An extensive literature review was made as a part of an effort to establish relationships between the presence of various contaminants within sediments and the effects of sediment dredging and disposal on water quality and aquatic organisms. The review revealed that there is little or no evidence that a relation exists between bulk-sediment composition and pollutional tendencies of dredged sediment. It is technically unsound to base disposal criteria on bulk-sediment composition because to do so assumes that all forms of each chemical have an equal impact on the environment. Use of criteria for dredged material disposal that are based on parameters normally used in evaluating environmental impact of domestic and industrial wastewaters is unrealistic because it is considered unlikely that there is a relation between environmental impact of a particular dredged sediment and a particular numerical value for any of these parameters in sediment. There is a need to develop simple analytical tests to evaluate the potential of sediment contamination on water quality. The use of a standard Elutriate Test (developed by EPA and the Corps for PL 92-532) to determine pollution potential of dredged material is superior to bulk analysis because the test recognizes that all chemicals in sediment are not equally available to aquatic organisms. The Elutriate Test is considered practical since it can be performed in a reasonable period of time and because it provides a better estimate of chemical availablilty in sediment than the bulk analysis. Several factors may affect the validity of Elutriate Test results and evaluation of the factors is recommended as a subject of further study. Also, a factor should be developed to relate results of the empirical Elutriate Test with actual environmental impacts. From the literature review and investigation of criteria based on bulk-sediment analysis and water-quality criteria, it is concluded that dredged material disposal criteria should be based on a time-concentration-toxicity relationship for each chemical constituent, which could be developed from short-term bioassays with selected organisms.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Aquatic ecosystems						
Disposal						
Dredged materials						
Sediment						
Water quality						