Desorption of Pollutants from Mississippi River Sediments in the GREAT II Study Reach
Lab Simulation Study

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Environmental Action Team

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CHAPTER I

INTRODUCTION

Each year approximately 300 million cubic yards of material are dredged from our nation's waterways. The major purpose of dredging is to provide safe depths for navigation usage ranging from small recreational boats on inland rivers to huge ore carriers on the Great Lakes.

Several million cubic yards of material are dredged each year on the Mississippi River to establish and maintain a nine foot channel for the hundreds of barges using the river. Erosion and siltation would close many parts of the Mississippi to barge traffic if it were not dredged. The loss of navigation would significantly impact energy costs, commodity transport, and national defense.

Disposing of the dredge material has become a major environmental concern. The Federal Water Pollution Control Act Ammendment of 1972 (Public Law 92-500), require evaluation of material to be dredged in order to predict any adverse environmental impact. A major concern of this evaluation is the potential of pollutants that are present in the dredge material to desorb and violate water quality standards. Different methods of dredging and dredge material disposal have different environmental and economic impacts. The final choice of dredging method therefore, must consider these costs and be made on a case by case basis.

It is the responsibility of the Army Corps of Engineers to maintain and control much of our nation's navigable waters. Congress allocated 30 million dollars to the Army Corps of Engineers to study the issues of dredge material disposal, including environmental impacts, and economic factors. To accomplish this goal the Corps initiated the Dredge Material Research Program in 1973. Although much of the research has been completed many questions remain unanswered.

In 1976 the Great River Environmental Action Team I (GREAT I) was created through authorization by Congress. Under the coordination of the Army Corps of Engineers and the U.S. Fish and Wildlife Service, GREAT I was directed to develop a management strategy for the Upper Mississippi River, from lock and dam 10 at Guttenberg, Iowa, to Saint Paul, Minnesota. The formation of GREAT II followed in 1977. GREAT II responsibility was for that stretch of river from Guttenberg to Saverton, Missouri. Both GREAT I and GREAT II received funding to study the effects of river dredging. In Jan of 1979 a contract was awarded by the GREAT II to the University of Iowa to conduct a laboratory investigation of the desorption of pollutants by Mississippi River muds. This study attempted to simulate the effects of river dredging and/or dredge disposal. The objectives of the proposal were:

1) To collect sediment and water samples from ten locations of the GREAT II study reach of the Mississippi River and perform elutriate tests for eight heavy metals, three organics, and six other parameters.
2) To perform kinetic experiments to evaluate desorption rate constants.
3) To calculate the dilution factor at the edge of the mixing zone under various dredge disposal conditions to predict water quality impact.

5mg/l in [illegible],
Ill.
Wisc.
Iowa 4. mg/l

Potentially one of the most severe impacts during dredge material discharge is the depletion of dissolved oxygen in the receiving water column. Water quality standards have established minimum acceptable dissolved oxygen levels at 4 mg/l. Dissolved oxygen levels below 4 mg/l for sustained periods of time can have a severe ecological impact upon many aquatic organisms. The Dredge Material Research Program has studied oxygen depletion resulting from open water "batch" dumping of dredge material. Very little research however, has been done on oxygen depletion resulting from various other dredge disposal alternatives. Little information is available on methods for measuring the oxygen uptake of a disposed dredged material or on methods for predicting this uptake by in-situ measurement of a conventional bulk sediment parameter, for example, total solids. The development of such a predictive technique would greatly facilitate the environmental assessment of a proposed dredging operation.

The additional objectives of this research were:

1) Develop and evaluate a reliable laboratory method for measuring the oxygen demand exerted by a sediment after dredging and disposal.
2) Identify and evaluate a possible correlation of the measured sediment oxygen uptake with a readily measured bulk sediment characteristics; for example, total solids.
3) Propose a kinetic model for the standard elutriate test and for the discharge of dredge materials into navigable waters of the GREAT II study reach.

CHAPTER II

LITERATURE REVIEW

Discharge of Dredged or Fill Material - Rules and Regulations

Before any dredging operations take place a permit must be obtained from the Secretary of Army through the Army Corps of Engineers. In compliance with Section 404(b) of Public Law 92-500, the Environmental Protection Agency (EPA) promulgated final guidelines (Federal Register 40, 173, pp 41292-41298, September 5, 1975) for the evaluation of the effects of proposed discharge of dredge material into navigable waters. Permit application and evaluation is required to assure that discharge of dredge material will have no adverse effect on municipal water supplies, shellfish beds, fishery areas, or recreational areas. The Regional Administrator of EPA may require further evaluation if assurance is not obtained.

There are two major considerations which the permit evaluations must address, water quality effects and physical-chemical-biological effects. Major physical effects are the covering of benthic communities and degradation or destruction of wetlands. The principle concern of chemical-biological interactive effects is that dredge material may contain chemical contaminants that have potential adverse effects on benthic communities. These effects are difficult to predict and case by case studies may be required. Dredge material that provides reasonable assurance that no contamination exists and that are predominantly sand and sediment larger than silt and material that is discharged for beach restoration may be excluded from these evaluations.

Violation of water quality standards is the second major consideration addressed by the pre-dredging evaluations. Duration of turbidity, release of nutrients, levels of pathogenic organisms, oil and grease, and toxic chemicals must be evaluated. The recommended method for predicting many of these water quality effects is the standard elutriate test, Lee (1977). This test attempts to simulate open water disposal of dredged material. The exclusive use of the test for predicting such a variety of water quality effects on a nationwide basis have been criticized because of variations in the methodology, sample collection and handling, and dredge material.

Costs

Many new regulations for environmental protection present increased financial costs. An example in dredging and dredge discharge comes from the Saint Paul District of the Mississippi River (GREAT I). This district covers 250 miles of river. Estimated costs for actual dredging operations in 1975 were 2.5 million dollars by Cable and Pearson (1976). Over 600,000 dollars was spent for environmental considerations, laboratory analysis, and using alternative discharge sites. Costs increased 31 percent over the previous year while the actual amount of material dredged was 28 percent less. Dredging had been going as deep as 13 feet to provide a 9 foot channel. The over-dredging was performed in the past to give channel stability since dredging to only 10 feet silted in, in a matter of days. Dredge depths have since been decreased to 12 and 11 feet in attempt to save money. If more frequent dredging will be required costs will significantly rise again. It is essential therefore that environmental evaluations concerning dredging operations be accurate and that the resulting regulations and alternatives chosen be both economically and environmentally acceptable.

Sediment and Release of Contaminants

The Symposium on the Interaction Between Sediment and Freshwater, Golterman et al. (1977), concluded that one of the principle problems in researching sediment chemistry by laboratory study is the complete simulation of the conditions that occur in natural systems. It is virtually impossible to physically simulate the degree of mixing within the sediments and between the sediments and water. It has frequently been recommended that the degree of mixing or dilution that occurs during dredge operations be modeled in order to more accurately predict resultant chemical concentrations.

The rate of release of contaminants from dredged sediment is also an important environmental concern. The Symposium stated that, "It is rare that information is available on rates of release from sediments as well as rates of dilution that occur in natural waters." Kinetic experiments on desorption rates as well as modeling the dilution at the mixing zones are thus a justified and necessary part of studies on dredging effects.

When evaluating dredge material impact on water quality, it is important to determine those chemical contaminants that are available to the organisms in the water and not just bulk chemical composition of the sediments. The earliest criteria for dredge material discharge were based on bulk chemical composition of the sediment. It was later shown by Lee (1977) however that there was no relationship between bulk composition of sediments and the water pollution tendencies of the contaminants in the sediment. As a result most of the bulk chemical criteria have been eliminated. These have been or will be replaced by better "tools" for evaluating dredge material disposal. These include standard bioassay tests and the standard elutriate test. The standard elutriate test simulates the sediment water interaction during dredging and is affected by pH, oxidation-reduction potential, oxic/anoxic conditions, and the size fractions of sediment particles.

The pH of natural freshwater streams such as the Mississippi River, typically range from 7.0 - 8.3. If the pH in a laboratory simulation fell significantly below this range, it could result in changes in the release of contaminants to the water (23) according to Lee et al. (1977). At the unnatural, acidic test conditions scavengers such as iron oxides are not available to adsorb, chelate, and settle out the released contaminants. The results of such a study would be erroneously high concentrations of contaminants in the supernatant water.

A similar relationship has been observed with sediment oxidation-reduction potentials (ORP) by McCallister and Logan (1978). If a sediment has a low redox potential (approximately - 370mv), iron can be reduced resulting in partial decomposition of clay mineral and further release of contaminants. This can occur at acid or neutral pH. These results indicate that a potentially significant problem could occur if the contaminated sediment complexes are ever destabilized by changes in stream content, pH, or oxidation-reduction potential.

Golterman et al. (1977) have performed some related research on sediment particle fractions and sizes as related to their chemical contaminant compositions. A higher content of clay and silt in dredged material implies a higher concentration of surface area to adsorb contaminants than a dredged material that is predominantly coarse grain sand. O'Conner (1976) has determined in laboratory studies that small particle size and therefore increased surface area can overcome conditions such as low pH and/or ORP that favor desorption and release of contaminants. It is advisable, therefore, to assess particle size in order to determine what may happen during dredge material disposal. It has been proposed that coarse grained contaminated dredge material be mixed with finer material to increase the adsorption capacity of the overall discharge slurry. These studies recommended further research on sediment particle and size fractions in dredge material.

An understanding of the controls on the concentration of heavy metals in natural waters and sediments is fundamental in any systematic study of the aquatic chemistry of potential contaminant release during dredging and disposal operations. A review of the proposed controls on the concentrations of certain of the first transition series metals in soil solutions and natural waters, finds them inadequate to explain the existing data (Jenne, 1968). Principle control on the concentration is most probably adsorption by hydrous oxides of manganese and iron. Much of the recent experimental data was reviewed and shown to be highly consistent with the hydrous oxide model (Jenne, 1968). Hydrous metal oxides are of potential significance in the environmental chemistry of heavy metal contaminants (Cu, Cd, Pb, Zn, Ni, Hg, Fe, Mn) in natural water systems (Lee, 1975). The concentration of reduced iron in the interstitial water and exchangeable phases of sediments has a significant inhibitory effect on the amount of trace metals released into the Standard Elutriate (Brannon, 1976). It is anticipated that the same effect would occur in the water column during aquatic disposal.

The principal factors affecting the availability of hydrous oxide occluded heavy metals are Eh, pH, concentration of the metal of interest, concentration of competing metals, concentration of other ions capable of forming inorganic complexes and organic chelates. Of these factors, pH and Eh are probably the most significant (Jenne, 1968).

Eh and pH conditions in sediments usually result in the occurrence of higher metal concentrations in the interstitial water than occurs in the overlying water. The enrichment of trace metals in the interstitial water has been attributed to the burial of Fe and Mn oxides and hydroxides in sediments (Duchart, et al, 1973). Subsequent reduction of the Fe and Mn oxides releases adsorbed trace metals increasing their concentration in the interstitial water. Sediments high in interstitial water Fe could therefore be expected to release minimal amounts of heavy metals during dredging operations due to hydrous metal oxide formation of iron compounds and subsequent adsorption in the water column. Chemical exchange from sediments to overlying water is insignificant as long as oxygen concentration at the sediment interface remains above 1-2 mg/l (Mortimer, 1941, 1942).

The general mode of occurrence of the hydrous oxides in recent sediments as partial coatings on the silicate minerals rather than only as discrete, well-crystallized minerals allows the oxides to exert chemical activity far out of proportion to their concentrations (Jenne, 1968). Since these oxides occur as coatings, the sorption of heavy metals by clays may be because of hydrous oxides of manganese and iron in minor amounts.

The Elutriate Test

The standard elutriate test attempts to simulate open water disposal of hydraulicly dredged material. The elutriate test now specified by the Army Corps of Engineers and the EPA has undergone many revisions and is being continuously reevaluated. A detailed description of the test procedure is presented in Chapter IV and is summarized as follows; one part bottom sediment from the dredge site is shaken vigorously with 4 parts of site water for 30 minutes under oxic conditions. The sediment-water slurry is allowed to stand quiescently for 1 hour. The supernatant (elutriate) is withdrawn and can be differentiated into soluble and nonsoluble fractions by filtration through a 0.45 micron filter.

The 1 to 4 sediment to water ratio was chosen because it is thought to be the optimum pumping ratio for hydraulic dredging. This ratio is not applicable to mechanical dredging nor is it necessarily applicable to all hydraulic dredges as discharge slurries can vary from 10 percent to 90 percent solids (w/w). The one hour settling period provides additional time for possible contaminant release from the sediment and simulates a reasonable particle settling time in the water column at the disposal site. To complete the test the supernatant is filtered through a 0.45 micron filter to separate the soluble fraction of the elutriate water.

Since the development of the above procedure and its adoption by EPA many questions have been left unanswered. The following is a partial list of factors affecting the elutriate test procedures and/or test results.

1. Sediment to water ratio
2. Methods of agitating the sediment-water mixture
3. Agitation time of the sediment-water mixture
4. Settling time after the 30 minute agitation time before withdrawing supernatant
5. Sediment storage times prior to performing the elutriate test
6. Oxygen status of the sediment-water mixture (oxic or anoxic) throughout the test procedure
7. pH of the sediment-water mixture throughout the elutriate test procedure

One of the most rigorous studies of the factors influencing elutriate test results was done by Lee, Lopez, and Piwoni (1976). The following is a summary of their findings which apply to the authors' research.

The sediment to water volumetric ratio is inversely related to the release of orthophosphate and directly related to ammonia nitrogen (NH_3-N). In one particular elutriate analysis 2 mg/l of NH_3-N was present at a sediment to water ratio of 1:4 (20 percent sediment) and 0.4 mg/l NH_3-N was observed at a ratio of 1:19 (5 percent sediment). Conversely, orthophosphate went from 0.02 mg/l as P in a 5 percent sediment mixture to 0.01 mg/l as P in a 20 percent mixture.

The effect of sediment-water agitation time was studied for periods from 15 to 90 minutes. Agitation time was determined to have a negligible influence on the elutriate results although some minor differences were observed in release of orthophosphate. Mechanical agitation with compressed air was used in this study.

Different methods of agitation including stirring, mechanical shaking, compressed air, and compressed nitrogen were studied. Elutriate test results were not significantly different for the stirred and the mechanically shaken vessels under similar ORP conditions. Erratic ORP conditions encountered during stirring and shaking however required that compressed air agitation be utilized to control ORP and ensure higher levels of dissolved oxygen. Comparisons were made using compressed nitrogen agitation versus compressed air. Results showed that ammonia and phosphorous release were 50 percent greater under the anoxic conditions.

Settling times of 1 hour versus 24 hours were also studied. Little difference was observed in elutriate concentrations of orthophosphate, COD, and oil and grease, as with several other parameters. However, a significant ammonium release was observed with one sample having a 50 percent higher concentration after the 24 hour settling period. The study also concluded that a sediment storage time of 1 month at 4°C affected an increase in the release of ammonium (13%) and orthophosphate (40%). Except for ammonia, there was no statistically significant evidence that related bulk sediment composition to elutriate concentrations. The study stressed that the ammonia relationship was not consistent and that full support remains for keeping bulk chemical criteria out of government regulation of dredge material discharge.

The study also supported elimination of the "1.5" factor. Previous regulations stated that if the elutriate contained levels of contaminants 1.5 times the accepted levels of EPA Water Quality Standards, then the sediment was considered to be contaminated and alternative methods for disposal must be used. Dilution factors and mixing zones have subsequently been included in disposal evaluation and have resulted in elimination of the 1.5 factor.

The study recommended that the standard elutriate test be modified to include compressed air agitation to control ORP conditions and that water from the dredge disposal site be used in the elutriate mixture and not water from the dredge site. Recommendations were also made concerning further study of several areas including settling time, storage time, and analysis of sediment to water ratios at different dredge operations. It was suggested by O'Conner (1976) that on site monitoring of oxygen concentration and pH be conducted to substantiate elutriate test procedures. The report encouraged field study of operations that used onland and confined disposal practices especially where these were being used as alternatives to open water disposal. The Lee, Lopez, and Piwani (1976) study stressed that there was insufficient field data on these disposal practices and on the elutriate's validity for predicting impacts of these operations.

Dredging and Dredge Material Disposal

An important point to be considered in evaluating chemical contamination at a dredge disposal site is the impact of dilution. Lee (1976) stated, "dilution is an important mechanism, which can render excessive concentrations of contaminants in water and sediment harmless or environmentally insignificant." Elutriate tests have shown that certain contaminants are present in quantities that exceed EPA water quality criteria according to WES (1977). Lee (1976) however, states that there has not been a reliably documented case showing that current methods of open water disposal of dredged sediments have ever been adverse to water quality or aquatic ecosystems due to chemical contamination. There may be however, different impacts during the all day, open water discharge operations that occur on the Mississippi River. There is little data available on these types of operations.

Discharge Site Alternatives

When an open water dredge discharge operation has been determined to have adverse environmental impacts, an onland, onshore, or confined area is usually selected as the alternative discharge site. The use of these alternative sites could result in more severe impacts than those at the original open water discharge site. Impacts could include groundwater pollution from holding basins of dredge material or uptake of chemical contaminants by terrestial plants. Prolonged discharge times could be expected from the restricted overflow of the holding basins increasing the possible contaminant exposure to the receiving stream. These holding basins can be interpreted as point discharges under the National Pollutant Discharge Elimination System thus requiring discharge permits, treatment, and regular monitoring of the overflow from the basins. Widom (1972) and Lee and Jones (1977) have shown releases of contaminants from confined disposal sites greater than open water disposal operations. Water in confined disposal areas can be anoxic. Iron oxides normally present under oxic conditions can chelate contaminants available in the water. The iron oxides would not do so under anoxic conditions. When near shore or onshore discharges take place, much of the silts and clays are washed back to the open water. Much of the chemical contaminants in sediments are adsorbed to silt and clay according to Lee and Jones (1976). Alternative dredge discharge sites may be quite sensitive areas for wildlife habitat, fish spawning, and slow moving water resulting in slower dilution and less disperal of contaminants. Lee (1977) has recommended that confined dredge discharge sites be closely evaluated if they are being used in place of open water discharges.

Oxygen Uptake Studies of Dredge Material

Little research has been done on oxygen uptake by dredge material. Some laboratory and field investigations have been conducted by Lee et al. (1975) and Schubel et al. (1976) of the Dredge Material Research Program. These investigations considered only coastal or estuarine dredging operations and three of the four involved dredge material disposal by ocean dumping. In general all four studies found no significant impact upon the water column with respect to dissolved oxygen depletion during any dredging and disposal operations. The results, conclusions, and recommendations of these studies are summarized below.

A field investigation conducted by Brown and Clark (1968) of the United States Health Service monitored the impact of dredging on the dissolved oxygen concentration in the water column. Water quality monitoring stations were set up in the Arthur Kill and Kill Van Kill tidal straits between New York and New Jersey. Dissolved oxygen concentrations were monitored before, during, and after mechanical dredging and ocean dumping operations. During dredging dissolved oxygen levels were reduced from 16 to 83 percent below the pre-dredging concentrations. Two of the seven sites monitored dropped below 2 mg/l from background concentrations greater than 5 mg/l. All dissolved oxygen monitoring was at 5 feet below the surface.

A laboratory investigation of the oxygen demand of dredge material during the elutriate test was done by Lee et al. (1975) and the Dredge Material Research Program. The test apparatus consisted of a continuously stirred BOD bottle filled with site water containing a measured amount of dredge material. A potentiometric probe was used to continuously monitor the dissolved oxygen concentration. Materials analyzed were from estuarine areas where dredging operations conventionally take place. Results and conclusions of the study were:

1. Deionized water used in place of disposal site water resulted in similar measurement of oxygen uptake.
2. Temperature increases during 60 minute periods of oxygen uptake measurements showed increases in oxygen uptake rates.
3. Results of the analyses were reproducible.
4. Oxygen uptake rates were said to approach a "pseudo" first order relationship. The study cited Reynolds et al. (1973) as having found uptake rates to approach a two phase first order reaction.

5. Results of the oxygen uptakes measured ranged from 160-360 gO_2/m^3 of wet sediment for the first hour.

Oxygen uptake of the dredge material was thought to be caused by chemical oxidation of reduced species of iron and sulfide. The study recommended that chemical characteristics of sediments be studied to find correlations to predict oxygen uptake and that studies be performed on a variety of materials to be dredged. The foremost recommendation made by the study was that the elutriate test should be run under oxic conditions using compressed air to maintain a positive ORP because it did not appear that open water dredge disposal resulted in significant oxygen depletion.

In 1977 laboratory and field investigations were completed by Lee et al. (1977) on Galveston and Texas City Channel Turning Basin dredge materials. The laboratory procedures for measuring oxygen uptake were the same as used in the 1975 Dredge Material Research Program Study. Sediment characteristics measured were ORP, total sulfide, total solids, and total iron. In general oxygen uptakes were observed to increase as levels of total sulfide increased. No other conclusions were made on the other sediment parameters measured in correlating with oxygen uptake. Nine dredge disposal sites were monitored before, during, and after dredge material discharge by ocean dumping. Four of the 9 sites monitored had dissolved oxygen depletions in the water column during dumping. The greatest depletion was 1.7 mg/l which was measured at a depth of 14 meters. No site had an oxygen depletion that took the oxygen concentration of the water column below 4.0 mg/l. The highest oxygen uptake measured in the laboratory did not correspond with the greatest depletion observed at the dump site. It seemed that chemical oxidation took place in the hopper while en route 12 kilometers to the dump site and satisfied a great deal of demand prior to dumping. No predictions were made from the laboratory measurements as to how much oxygen uptake a particular sediment would have on the disposal site water column or if the dredged slurry in the hopper would be anoxic. In conclusion Lee et al. (1977) observed no long term effect on dissolved oxygen levels at the disposal sites and felt that the dredge material studied would not have a severe oxygen depletion effect on the water column.

A study completed by Lee and Jones (1977) was done for the New York Corps of Engineers on the environmental impact of dumping dredged material at the New York Bight disposal site. Dissolved oxygen concentrations were measured at the dump site before, during, and after disposal. Oxygen levels in the hypolimnion were around 1 mg/l before dredge disposals. It was thought that these low levels were due to algal decomposition. Oxygen uptake analysis on the material to be dredged showed a slurry of material to have "appreciable uptake." During disposal of these materials oxygen concentration actually rose in the hypolimnion. This was said to be the result of the entrainment of oxygen rich water present above the thermocline by the discharged dredged material. The rest of the water column monitored showed 2 to 3 mg/l depletions of oxygen with the passage of the turbidity plume. Measurements taken one hour later indicated that these depletions did not persist.

A laboratory and field investigation was completed by Schubel et al. (1976) of the Dredge Material Research Program. The study was on dredge material and hydraulic dredging operations in an estuary at Apalachicola Bay, Florida. The primary objectives of the study were to model the turbidity plume and assess release of metals and nutrients. A secondary objective was to predict short term oxygen demand of dredge material before discharge and verify these predictions by monitoring the dissolved oxygen in the water column during open water discharge of these materials from a pipeline. The oxygen depletion resulting from the discharge was found to be lower than that predicted by organic carbon content or total reducing capacity of the sediment. No data were presented on organic carbon content, iron, or COD. Total sulfide analyses were performed on the interstic.ial water of the material to be dredged. The dredge material studied was very fine grained and only about 20 percent total solids. The major oxygen consuming reactions of the sulfide system are:

$$2HS^- + 2O_2 \rightleftharpoons S_2O_3^{2-} + H_2O$$

$$HS^- + 2O_2 \rightleftharpoons SO_4^{2-} + H^+$$

The latter reaction was felt to be the major reaction to consider for the material being studied. Dissolved oxygen depletions in the water column were then predicted by levels of sulfide measured in intersticial water, volumes of dredge material to be discharged, estimating the dilution of the discharge, and measuring initial dissolved oxygen concentrations at the discharge site. Another method was also used to predict oxygen depletion at the discharge site. A modified Erlenmeyer flask was used for a respirometric device. Sediment slurry was injected with a syringe and dissolved oxygen was monitored for 10-15 minutes.

Results of these studies were:

1. Data showed the oxygen uptakes of duplicate samples to be reproducible.
2. Oxygen demand increased with the depth of samples below the sediment-water interface.
3. The "short-term" oxygen demand measured in the respriometer was satisfied within 10-15 minutes.
4. Oxygen demands measured by the respirometer were greater than those estimated by chemical analysis of intersticial water.
5. The greatest depletion monitored during discharge of the dredged material was 5.0 mg/l near the discharge pipe and the lowest depletion was 0.6 mg/l.

where is [illegible] [illegible]?

Oxygen depletions monitored during discharge were said to be lower than predicted by the respirometer and closer to that expected from sulfide analysis of the intersticial water. Neither method was reliable for accurately predicting the dissolved oxygen concentrations in the receiving water column. No predictions were made as to whether the discharge slurry would be oxic or anoxic.

CHAPTER III

SITE DESCRIPTION

Characteristics

Ten sites were sampled from along the GREAT II reach (Figure 1).

M.P. 320.0

Samples were collected from this site on 26 June 1979. This site is located in the main channel below Quincy, Illinois near the Northeast Power Company, across from Goose Island (Figure A-I). Physical parameters for this site are given in Table B-I.

M.P. 355.5

Samples were collected from two locations at this mile point on 10 July 1979. The first site is located in the main channel below Keokuk, Iowa off the shore of Fox Island (Figure A-II). Physical parameters for this site are given in Table B-II. The second site is located behind Fox Island in Grey's Chute (Figure A-II). Physical parameters for this site are given in Table B-III.

M.P. 424.0

Samples were collected from this site on 26 June 1979. This site is located in the main channel below Keithsburg, IL near Snipe

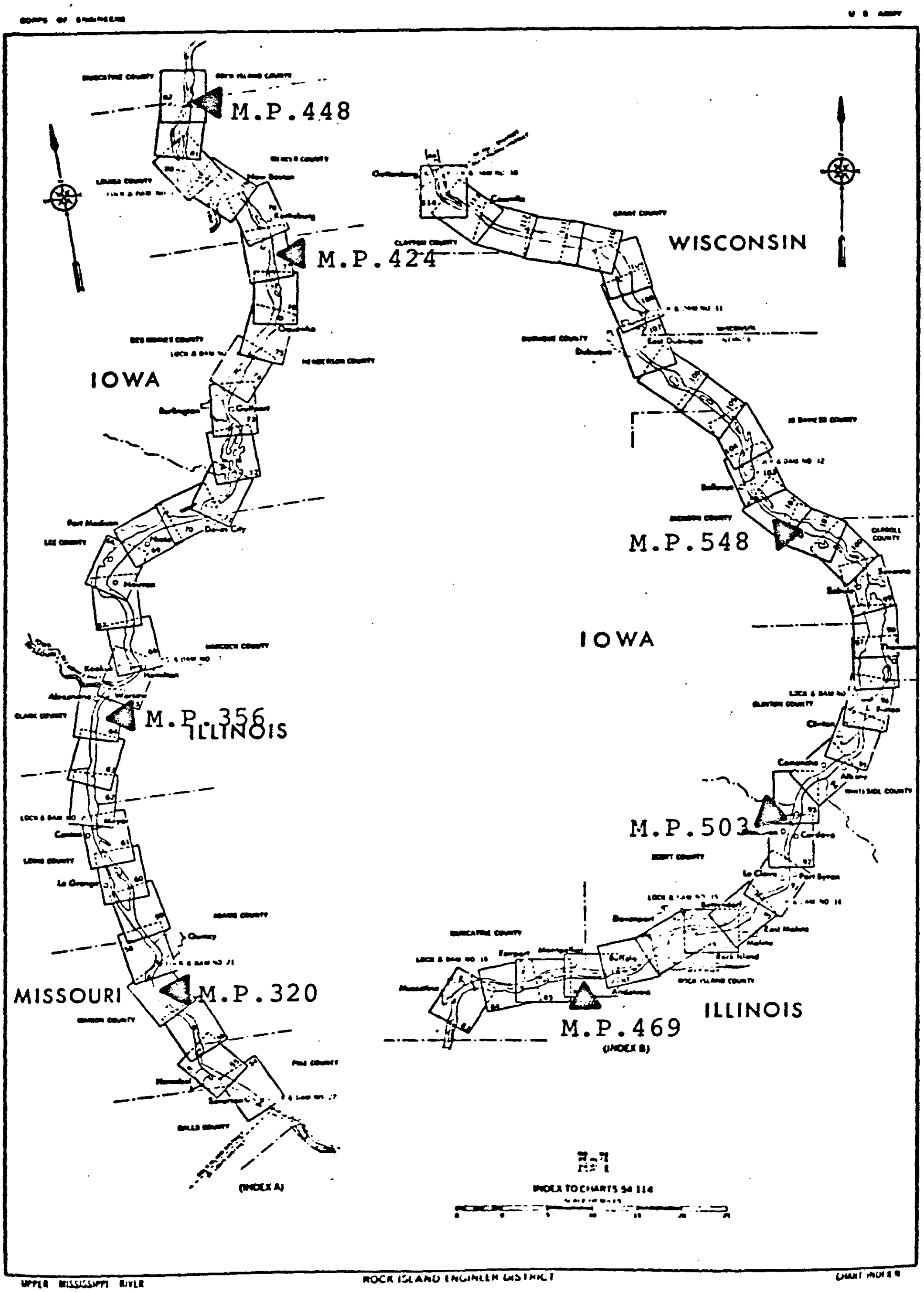


Figure 1. Great River Environmental Action Team Study Reach.

Island (Figure A-III). Physical parameters for this site are given in Table B-IV.

M.P. 448.0

Samples were collected from this site on 12 June 1979. This site is located in the main channel below Muscatine, Iowa near Bass Island (Figure A-IV). Physical parameters for this site are given in Table B-V.

M.P. 469.5

Samples were collected from this site on 12 June 1979. This site is located in the main channel above Montpelier, Iowa offshore Andalusia Island (Figure A-V). Physical parameters for this site are given in Table B-VI.

M.P. 503.5

Samples were collected from two locations at this mile point on 28 November 1978. The first site is located in the main channel above Princeton, Iowa directly north of Cordova, Illinois (Figure A-VI). The second site is located in Steamboat Slough (Figure A-VI).

M.P. 545.8

Samples were collected from this site on 29 May 1979. This site is located below Bellevue, Iowa at the confluence of Lainsville Slough and the Mississippi River called the Aspelmeier Ditch (Figure A-VII). Physical parameters for this site are given in Table B-VII.

M.P. 548.0

Samples were collected from this site on 29 May 1979. This site is located below Bellevue, Iowa just below the confluence of the Maquoketa River and the Mississippi River (Figure A-VII). Physical parameters for this site are given in Table B-VIII.

All samples with the exception of those collected 28 November 1979, were collected following an extended period of high water.

CHAPTER IV

MATERIALS AND METHODS

Sampling Procedures

Of the ten sites sampled seven were main channel sites. All main channel sediments were taken in or near the center of the channel. In some instances it was not possible to sample the center of the channel due to extreme depths and high current velocity. This occurred during high water conditions in May and early June. Aspel Meier Ditch and Greys Chute were not open channel sites. These sites were proposed for dredging to allow some channel flow into backwater areas and to remove extreme sediment deposits.

Sampling was done from an 18 foot flatbottom Jon boat with a 55 horsepower Mercury motor. The boat was equipped with a winch capable of handling over 100 pounds. The boat and motor were supplied by the University of Iowa Institute of Hydraulic Research.

Three sediment samples from each site were taken at approximately equal distances apart over the length of the dredge site. A Ponar Dredge sample was used to collect all sediments. The Ponar Dredge was capable of sampling to a maximum depth of about 5 inches and a maximum volume of about three liters. Sediment was carefully removed from the Ponar Dredge as a consolidated mass and placed directly into heavy plastic bags, sealed, and placed on ice for transport to the laboratory at Iowa City. At the laboratory the sediments in plastic bags were purged with nitrogen gas while being mixed with a glass stirring rod or by gloved hand. This procedure took less than a minute. Sample bags were fixed air tight and stored at 4°C. This procedure was also used by the Dredge Material Research Program and was felt to be the most practical and effective when collecting samples with a Ponar Dredge.

A core sample was attempted to be taken with a Wildco Corer Sampler, Model 2404. Attempts were made in channel and slough locations. No success was achieved in obtaining a core sample at either place. It was felt that the corer sampler was not properly designed for sampling in depths greater than six feet or in water with high current velocity. A core sample was taken by hand at Greys Chute. Chest waders were worn and the sample was taken in shallow water adjacent to the sample taken in deeper water by the Ponar Dredge. This core sample was taken for a study of the effect of sediment depth on oxygen uptake.

All dredge site water samples were collected approximately one foot below the surface. The water was placed in 5 gallon Nalgene containers. All containers had previously been acid washed and rinsed in deionized-distilled water. The samples were cooled during transit and stored in the laboratory at 4°C.

Sediment Analysis Procedures

Chemical oxygen demand was determined using a modification of Standard Methods (1975). Screwcap culture tubes and autoclave digestion were substituted for the recommended flasks and reflux apparatus. The modifications were selected on the basis of number of samples, availability of equipment, and economics. Jirka and Carter (1975), found no significant bias between COD values obtained from the procedures outlined in Standard Methods (1975) and those utilized in this study. Differences obtained between procedures are not significant as long as the period of digestion is two hours, temperatures are the same, and concentration of reagents are the same. Wet sediments were analyzed in duplicate or triplicate.

The total solids content of the sediment was determined in accordance with Standard Methods (1975). All analyses were done in duplicate or triplicate. Results were expressed as the percentage dry weight in the wet sediment. If intersticial water formed a supernatant over the sediment during storage the sample was completely mixed before the subsample was removed from the plastic container.

The volatile solids content of the sediment was determined in accordance with Standard Methods (1975). All analyses were done in duplicate or triplicate. Results were expressed as a percentage of the dry sediment weight.

Total sulfides were determined by the methylene blue method in accordance with Standard Methods (1975). Although there is not an EPA approved method for total sulfides in sediments the Region VII office of EPA suggested that this procedure be used. Wet samples were analyzed in duplicate or triplicate and results were expressed as mg S/kg dry sediment.

Total iron was determined using the atomic absorption spectrophotometric method as outlined in the EPA Manual, "Methods for Chemical Analysis of Water and Wastes" (1974). The sediment was dried at 103°C prior to analysis. Results were expressed as mg Fe/kg dry sediment. Analyses were all run in duplicate.

The oxidation-reduction potential of the sediments was determined at the time of sampling with an Orion 399A ORP Meter and Platinum Redox Electrode, Model 96-78. Readings were taken from the meter in millivolts and corrected to the normal hydrogen electrode.

Orthophosphate was determined by the single reagent method according to the EPA Manual (1974). The sediments were analyzed wet, and treated as though they were surface water samples. All samples were anlyzed in duplicate and results expressed as mg P/kg dry sediment.

Ammonia nitrogen was determined according to _Standard_ _Methods_. The sediment was analyzed wet as though it were surface water. Sample results were expressed as mg N/kg dry sediment.

Oil and grease content was determined using the separatory funnel method, EPA Manual (1974). Wet sediment was analyzed and results were expressed as mg of freon extractable matter/kg dry sediment.

Standard plate counts for the oxygen uptake bioactivity experiment were done in accordance with _Standard_ _Methods_ and results were expressed as numbers per gram of wet sediment.

The density of a sediment was determined by weighing a known volume of wet sediment. The weight per milliliter of the wet sediment sample was multiplied by its total solids content (percent expressed as a decimal). These values (grams dry sediment/wet volume of sediment) were used to convert various results of sediment analyses that were expressed as units per dry sediment to units per wet volume (i.e., mg/kg dry sed to g/m^3 wet sed). These new values were used in Phase 1 of the data analysis. Table 1 presents subsample sizes, limits of detectability, and coefficients of variation for the analyses.

When sediments were pre-weighed and analyzed wet, the test procedures were the same as for analysis of liquid samples. The equation below was used to convert a mg/l result from a particular analytical procedure to a mg/kg dry sediment value knowing the percent solids content.

$$\text{mg/kg} = \frac{(C)(V)}{(T.S.)(0.00001)(W)}$$

C = result in milligrams per liter from the analysis as though it were a water sample

V = volume of sample, water plus wet sediment, liters

T.S. = total solids, percent

W = weight of wet sediment used, grams

mg/kg = milligrams per kilogram dry sediment

Analytical procedures used for site water, intersticial water, and elutriate water, were the same as those used in the sediment analyses.

Preparation of the Elutriate

The procedure used to prepare elutriates is outlined in the Federal Register (1975) and was detailed by the Environmental Effects Laboratory, WES (1976). The following is a summary of the elutriate test procedure used during the study.

Step 1 One liter of wet sediment was placed in a 5 gallon Nalgene container. Four liters of unfiltered dredge

Table 1

SAMPLE SIZE, DETECTIBILITY, AND VARIATES OF SEDIMENT ANALYSIS

	Sample Size, Grams	Limit of Detectibility	Coefficient of Variation, %
Chemical Oxygen Demand, mg/kg	0.2-5.0	10	5.4
Total Solids, %	5-20	0.1	1.0
Volatile Solids, %	5-20	0.1	8.1
Total Sulfide, mg/kg	5-20	10	17.0
Total Iron, mg/kg	0.1-1.0	10	10.0
ORP, mv	1 liter	N.D.	5.0
Oil and Grease, mg/kg	3-10	16	N.D.
Ammonia Nitrogen, mg/kg	0.3-7.0	1	N.D.
Orthophosphate, mg/kg	0.3-7.0	1	N.D.

N.D. - not determined

site water was added to the container to give a final sediment to water volumetric ratio of 1:4. This mixture was then referred to as the elutriate slurry.

Step 2 A large coarse bubble stone diffuser was placed at the bottom of the container. Compressed air was passed through a deionized water trap before going to the diffusers. The air flow rate was sufficiently high to assure good mixing and oxic conditions.

Step 3 Every ten minutes the tanks were mechanically mixed by hand (vigorous swirling) to assure complete mixing.

Step 4 After 30 minutes the air flow was shut off and the elutriate slurry was allowed to settle for one hour.

Step 5 After settling the supernatant was decanted and centrifuged to reduce suspended solids and to reduce time needed for subsequent filtering.

Step 6 After centrifugation the sample centrate was filtered through an acid rinsed 0.45 micron filter using an all glass filter apparatus.

Step 7 The filtrate is the "standard elutriate". It was stored in a clean plastic container at 4°C in the dark. All parameters for which the standard elutriate was to be analyzed were completed within two weeks of sample collection.

Digestion Procedure

For the determination of total metals on raw river water the sample was acidified with 1:1 HNO_3 to a pH of 2 at the time of collection. The sample was not filtered before processing. A representative aliquot of 100 ml of the well mixed sample was transferred to a 250 ml beaker and 3 ml of conc. HNO_3 added. The beaker was placed on a hot plate and evaporated to dryness cautiously, making certain that the sample did not boil. The beaker was cooled and another 3 ml portion of concentrated HNO_3 added. The beaker was covered with a watch glass and returned to the hot plate. The temperature of the hot plate was increased so that a gentle reflex action occurred. Heating continued, with additional acid added as necessary, until the digestion was complete (generally indicated by a light colored residue). Sufficient 1:1 HCl was added and the beaker warmed again to dissolve the residue. Beaker walls and watch glass were washed down with distilled water and the sample filtered to remove silicates and other insoluble material that could clog the atomizer. The volume was adjusted to approximately 50 ml. Filtered and nonfiltered standard elutriate samples were digested in the same manner. Sediment samples were dried overnight at 105°C. The dried sample was ground with a mortar and pestle and a representative aliquot of 1 gram mixed with approximately 50 ml of distilled water. This sediment slurry was digested in the same manner described above.

Extraction Procedure

Digested samples were extracted prior to analysis. The pH of the samples was adjusted to pH 2.5 using 30% NH_4OH and 2.5% HCl with a pH meter. The samples were transferred to a 100 ml volumetric flask and 2.5 ml fresh APDC (ammonium pyrrolidine dithiocarbonate) solution added. The 10.0 ml MIBK (methyl isobutyl ketone) was added, and the samples were shaken vigorously for one minute. The layers were allowed to separate, and deionized distilled water was added until the MIBK layer was completely in the neck of the flask. Sample blanks, standard blanks and prepared standards were subjected to identical extraction procedures. The MIBK layer was sampled for analysis via atomic absorption spectroscopy.

Atomic Absorption

Extracted samples were analyzed on a Jarrell-Ash Atomic Absorption Unit Model No. 280 using a Fisher Micro Thermal Atomizer (Model 2). A 20 microliter sample was transferred to the tantulum ribbon of the MTA. Maximization of dry, ash, and atomize cycles was accomplished. Following wavelength maximization from suggested values (Table 2), 20 microliter samples were analyzed until reproducibility of 0.1 unit was achieved on at least two runs of the sample. Standards and blanks were also analyzed in this same manner.

Other Measured Parameters

Dissolved oxygen measurements of raw river water and sediment-water interface water were performed with a YSI Oxygen Meter Model No. 57 in the field or fixed in the field and titrated up on return to the laboratory.

Oxidation-reduction potential measurements were accomplished on raw river water and sediment samples in the field using an Orion Research Model 399 A/F analog pH meter. pH was determined using an Orion research grade pH electrode in the laboratory. ORP measurements were accomplished using a combination platinum thimble type electrode.

Element	Analytical Wavelength	Wavelength for Background Correction	Sensitivity	Approx. Atomization Setting	Effect of Hydrogen Addition*
Ag	3281A	Sn 3262A	$1 \times 10^{-13}g$	m 60%	none
Al	3093A	3070A	$5 \times 10^{-10}g$	100%	sens plus
As	1937A	1920A questionable	$10^{-9}g$	90%	little
Au	2428A	Sn 2421A	$2 \times 10^{-11}g$	100%	none
Ba	5536A		$2 \times 10^{-11}g$	90%	sens
Be	2349A	Sn 2354A	$2 \times 10^{-13}g$	90%	sens
Bi	2231A	Continuum	$5 \times 10^{-11}g$	55%	repro
Cd	2288A	2276A	2×10^{-13}	50%	sens
Cr	3579A	3520A	$2 \times 10^{-11}g$	85%	sens
Cu	3247A	3234A	$2 \times 10^{-12}g$	70%	repro
Mn	2795A	Pb 2820A	$2 \times 10^{-12}g$	80%	repro
Pb	2833A	2823A	$5 \times 10^{-11}g$	50%	none
Sb	2176A	2179A	$3 \times 10^{-10}g$	80%	none
Sn	2863A	2839A	$2 \chi 10^{-10}g$	70%	sens
Zn	2139A	2125A	$1 \times 10^{-11}g$	70%	repro

*sens - increase in sensitivity on addition of hydrogen
repro - increase in reproducibility on addition of hydrogen
sens plus - increase in both sensitivity and reproducibility on addition of hydrogen
none - no effect observed on addition of hydrogen

Table 2. Wavelength and Conditions for use with the MTA-2.

ORP and pH measurements of the elutriate samples were made using the same analog pH meter.

Differential Fractionation

A portion of unfiltered elutriate was filtered through an 8.0 µm membrane and analyzed for metals. Another portion was filtered through a 5.0 µm membrane and analyzed for metal content.

USGS performed Pipette Analysis on an unfiltered sample which was divided into five fractions:

a) 53 µm and above

b) 16 - 53 µm

c) 8 - 16 µm

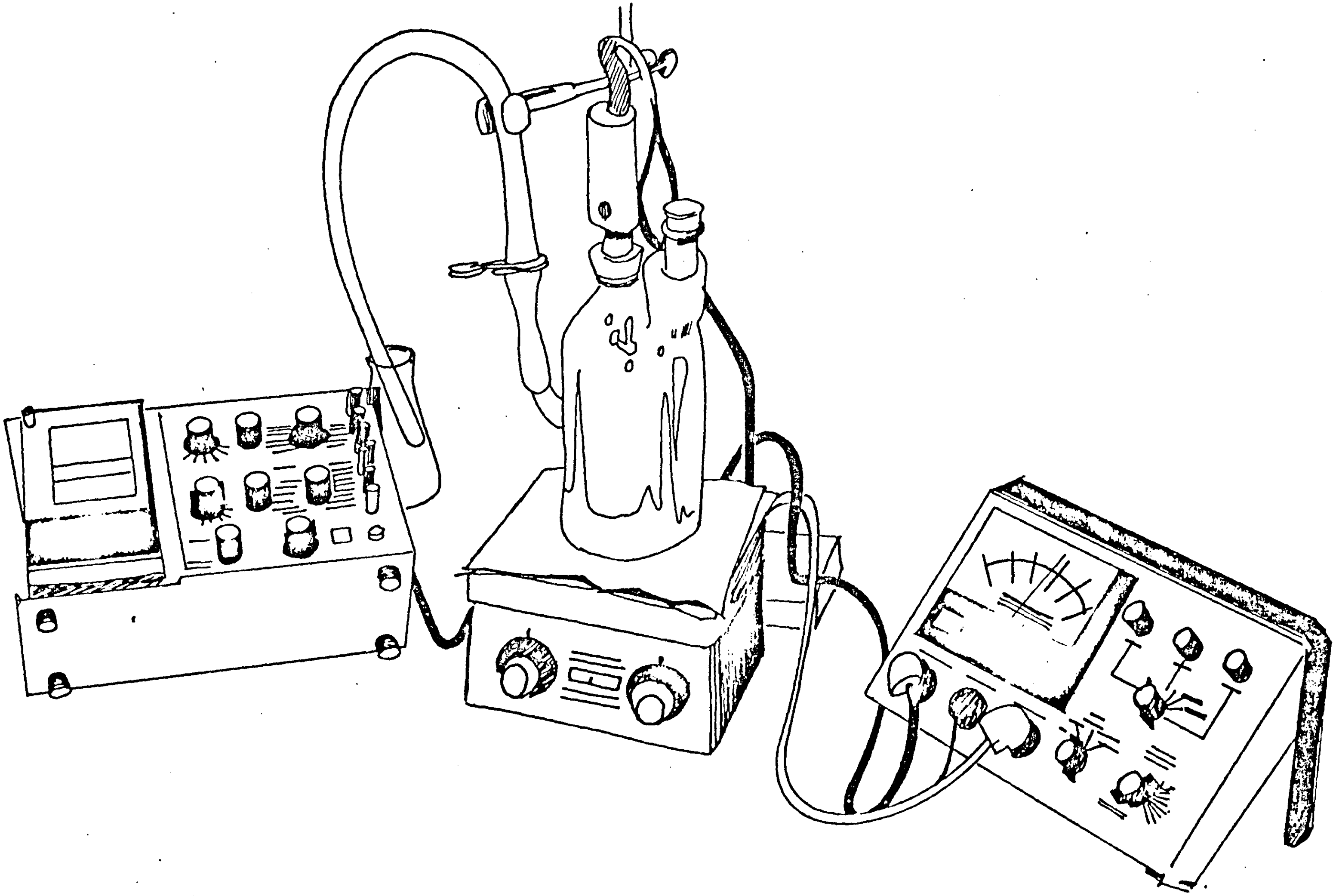
d) 4 - 8 µm

e) 2 - 4 µm

These fractions were analyzed for metal content associated with each of the size fractions.

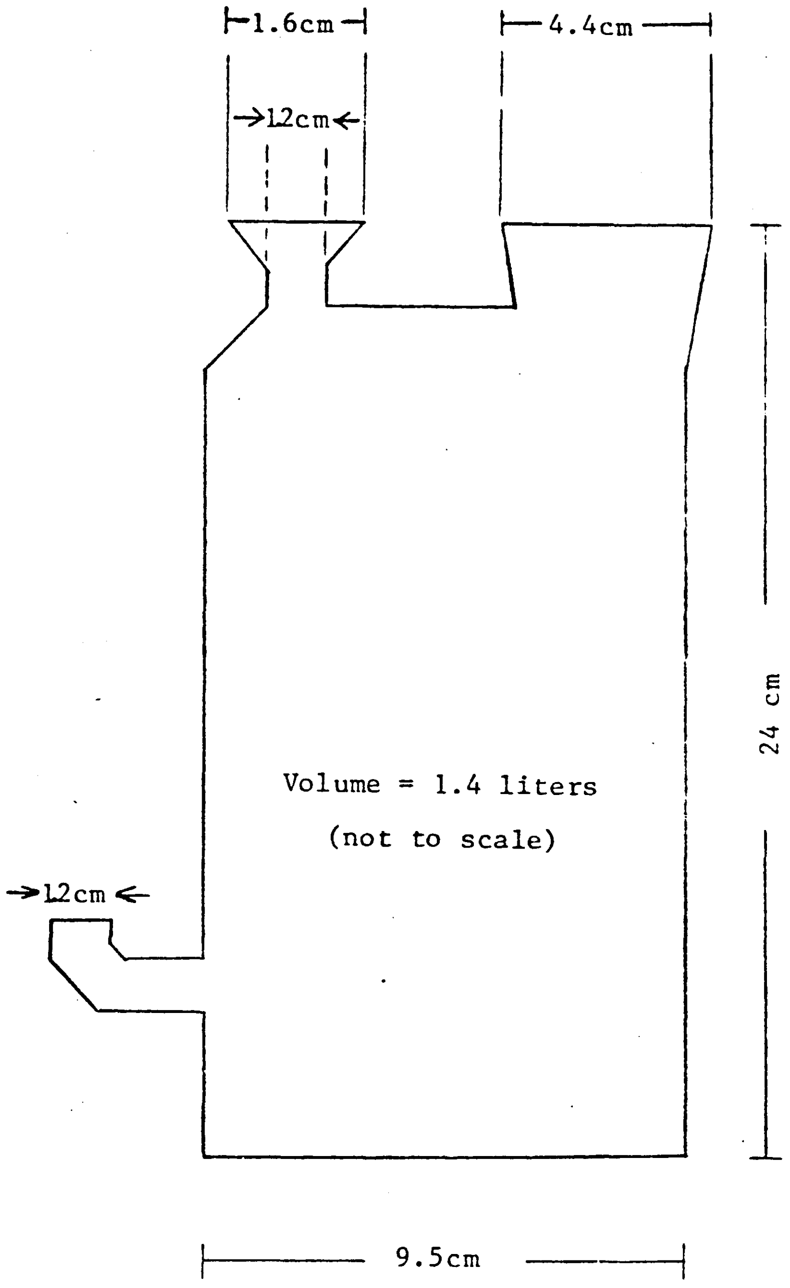
Oxygen Uptake Apparatus

A schematic diagram of the equipment used to measure oxygen uptake is shown in Figure 2. The dissolved oxygen meter was a Y.S.I. Model 57, the recorder was a Y.S.I. Model 81A, and the dissolved oxygen probe was a Y.S.I. Model 5720A. The glass reactor was placed on a Corning Automatic stirrer Model PC-351. Inside the glass reactor was a three inch teflon coated stir bar. Dimensions of the glass reactor are shown in Figure 3. A 20 milliliter syringe was used to inject the sediment. The opening at the end of the syringe was enlarged



A. RESPIROMETER AND APPARATUS

Figure 2. Oxygen Uptake Apparatus



B. GLASS RESPIROMETER

Figure 3.

to allow sediment discharge. A solid rubber stopper was bored out to fit tightly around the syringe and also to fit tightly into the glass injection port.

Procedure for Oxygen Uptake Analysis

The glass reactor was filled with site water and adjusted to either 25° ± 2°C or to 7° ± 2°C using an ice bath. Temperatures were checked using a thermocouple in the D.O. probe, before, during, and after all runs to assure that the samples remained within the desired range. The dissolved oxygen meter was calibrated using the azide modification of the Winkler Method prior to daily analysis. The injection port was plugged with a solid stopper to prevent oxygen exchange with the atmosphere and bubble formation from the vortex created by stirring. The displacement tube was clamped shut the stirrer turned on to enough speed to assure complete suspension of all sediment injected into the reactor. The dissolved oxygen meter and recorder were turned on and allowed to equilibrate three to five minutes. Sediment samples in plastic bags were purged with nitrogen and mixed. The syringe was filled by removing the plunger and running the empty barrel into the sediment and replacing the plunger before removal from the plastic bag and nitrogen atmosphere. To minimize exposure of the sediment to oxic conditions excess sediment was emitted just prior to injection into the reactor. The solid rubber stopper was replaced by the syringe with the rubber stopper around it. Injection took place with the displacement tube clamp released until all of the sediment in the syringe (5-20 ml) was injected. The tube clamp was then shut and the syringe with rubber stopper remained in place until the analysis was complete. Air bubbles introduced into the reactor from the interstices of coarser sediments were emitted by briefly releasing the displacement tube clamp to allow the head in the displacement tube to force bubbles up through the water seal surrounding the probe. A majority of material discharged to the water column during hydraulic dredging operation will have settled to the bottom after a period of 60 minutes. Thus 60 minutes was selected for the length of the runs. Three 60 munute runs were made on all sediments studied at both 7°C and 25°C. There were a total of 24 dredge material samples studied.

Calculating Oxygen Uptake

The dissolved oxygen concentration at any time of an analysis may be found from the strip chart recordings made during every 60 minute run. The cumulative oxygen uptake over the 1 hour test period was calculated from either equation 1 or 2.

$$O_w = \frac{(D.O._I - D.O._F)(V)(10^6)}{(1000)\ \text{sed}} \qquad (1)$$

O_w = grams of oxygen consumed per cubic mater of wet sediment

$D.O._I$ = initial dissolved oxygen concentration, mg/l

$D.O._F$ = final dissolved oxygen concentration, mg/l

V = volume of reactor, liters

sed = volume of wet sediment injected, ml

$$O_D = \frac{(D.O._I - D.O._F)(V)}{(\text{sed})\ (D)} \quad (1000) \qquad (2)$$

O_D = milligrams of oxygen consumed per kilogram of dry sediment

D = density of sediment, grams of dry sediment per millimèter of wet sediment

$D.O._I$, $D.O._F$, sed, and V = as defined in equation 1.

Quality Control on Oxygen Uptake Apparatus

A quality control check on the apparatus was made using distilled water to determine if oxygen could leak into or out of the reactor during a 60 minute run. Figure 4 illustrates the result for a high (8.0 mg/l) and a low (1.0 mg/l) initial dissolved oxygen concentration.

Reproducibility and Coefficient of Variation of Oxygen Uptake

The coefficient of variation of oxygen uptake was determined by running 6 duplicates of a sediment that had an average uptake of 406 g/m^3. The runs, made at 25°C using deionized-distilled water, had a coefficient of variation of 7.2%.

Figure 5 is a summary plot of the six runs. Data from the runs were adjacent to a common initial dissolved oxygen concentration. The figure illustrates the reproducibility of the oxygen uptake analyses.

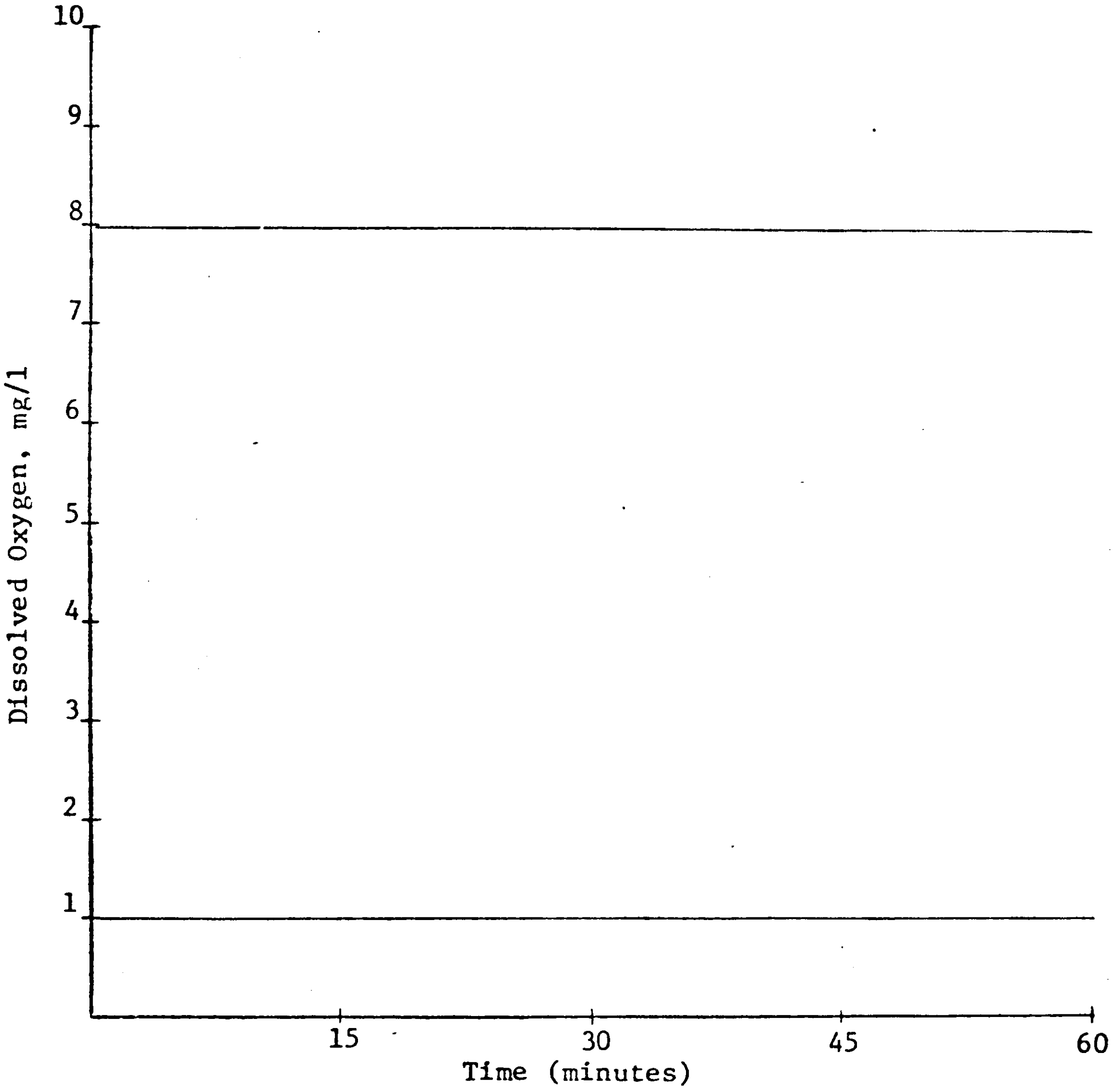


Figure 4. Quality control check of apparatus.

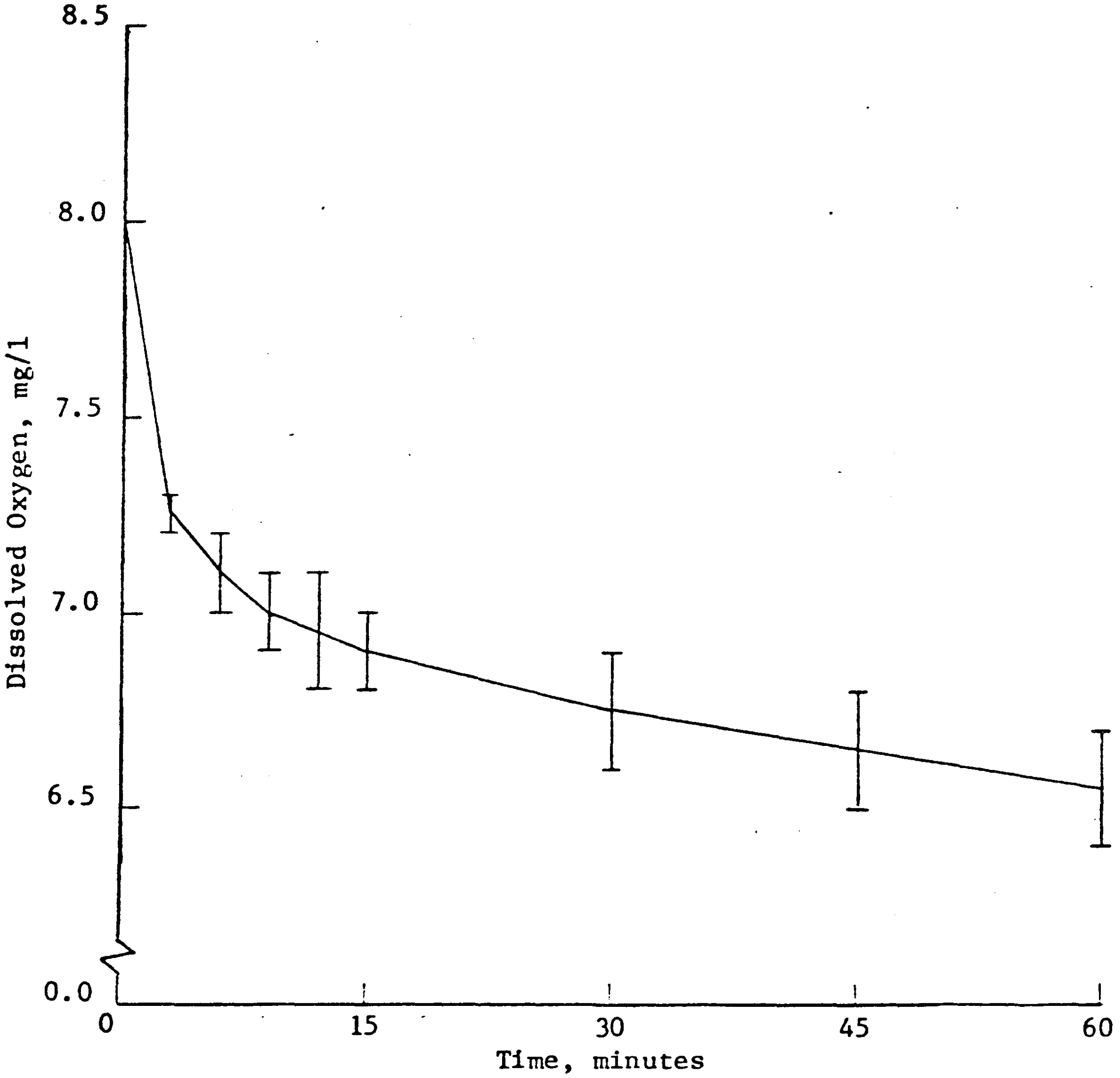


Figure 5. Reproducibility of oxygen uptake analysis.

CHAPTER V

HEAVY METALS: RESULTS AND DISCUSSION

Ten sites were sampled and analyzed from along the GREAT II reach (Figure 1). Of these ten sites, seven were main channel sites and three were slough areas. All analyses, except the main channel and slough analyses at Princeton, IA, were conducted on samples collected following an extended period of high water.

Correlations of Metal Concentrations with Sediment Parameters

Data was plotted for correlations of heavy metal desorption (filtered elutriates) with sediment parameters. Statistically significant correlations were not found for Mn, Pb, Cd or Zn with the sediment parameters (COD, TVS, PO_4-P). Iron concentrations showed an increasing tendency with increases in sediment Chemical Oxygen Demand (Figure 6). The correlation coefficient, $r = 0.94$, indicates a strong tendency for iron concentrations to increase as COD increases, possibly due to a sorption or chelation phenomena between iron and organic matter.

Data was plotted for correlations of heavy metal desorption (filtered elutriates) with elutriate concentrations of non-metal parameters. No significant correlations were found for Mn, Pb, Cd, Zn or Fe with elutriate concentrations of COD, TVS and PO_4-P.

Data was also analyzed for correlations of total suspended solids after one hour settling with total heavy metal concentrations

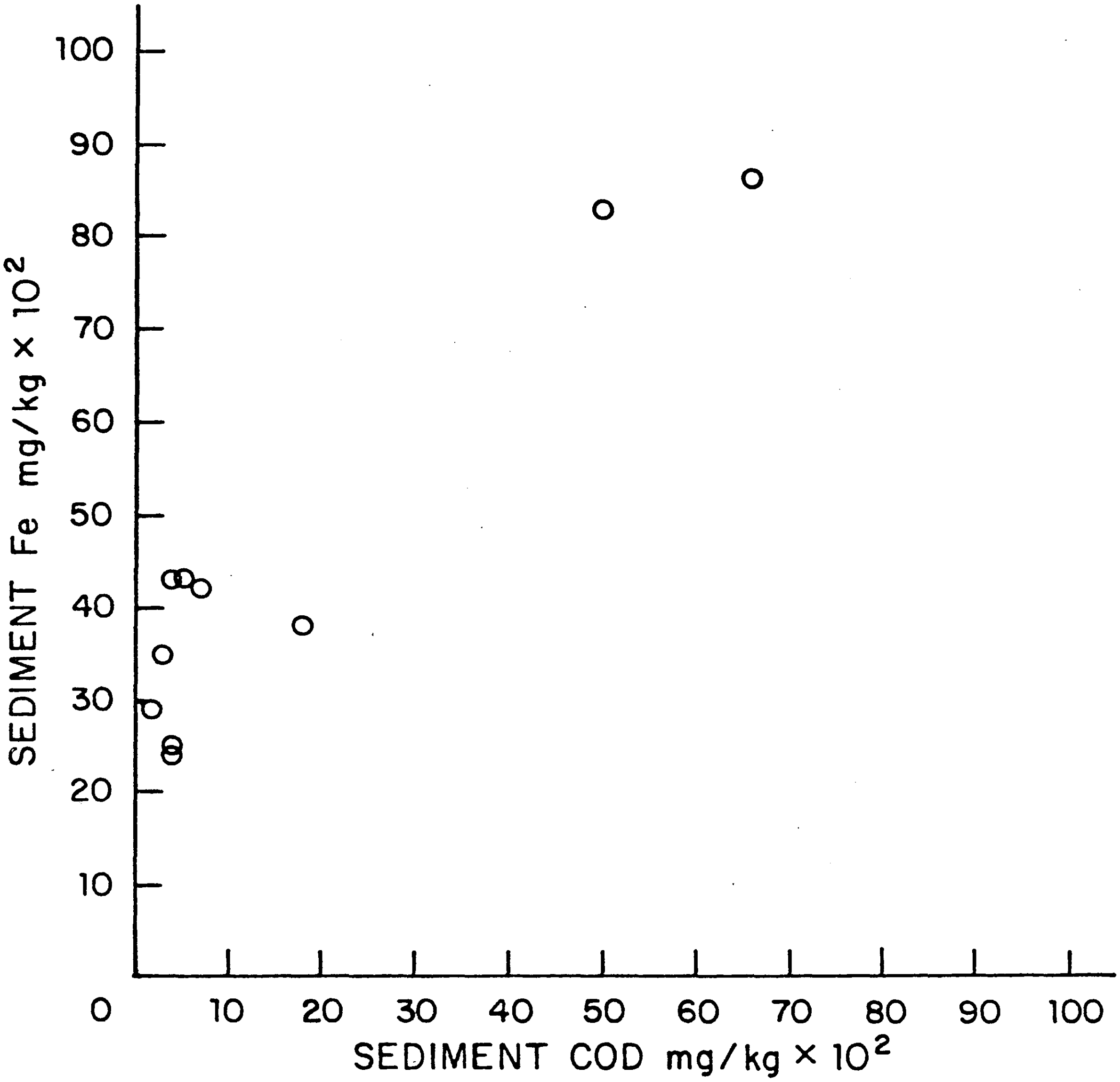


Figure 6. Sediment Iron Concentration vs. Chemical Oxygen Demand

of unfiltered elutriates. Total cadmium, copper, lead and zinc concentrations of settled, unfiltered elutriates showed no correlation with total suspended solids. Manganese concentrations of settled unfiltered elutriates showed a slight decreasing tendency with increasing total suspended solids (Figure 7). The correlation coefficient for this data, r = 0.37, indicates that only 14% of the variance in the data is accounted for in the statistical model. Iron concentrations of settled, unfiltered elutriates showed an increasing tendency with increases in settled total suspended solids concentrations (Figure 8). The high correlation coefficient, r = 0.88, indicates that iron is associated with the suspended solids.

Measures of Variation

Sediment heavy metal concentrations and a statistical analysis of sediment metal concentrations including mean, standard deviation and coefficient of variation are summarized in Table 3. The means for Cd, Cr, Cu, Mn, Pb, Zn and Fe are 0.46, 0.01, 2.4, 0.54, 2.4, 0.6 and 4505 mg/kg respectively. The coefficient variation shows a large variability between sites for Cr, Mn and Pb.

Table 4 illustrates the difficulty in predicting the elutriate concentration from bulk chemical measurements on the sediment. There is little correlation between the filtered elutriate iron concentration and the bulk sediment concentration. The nature of the sediment (organic vs. inorganic) and its source of contamination are highly variable and this results in variability of the elutriate from site to site.

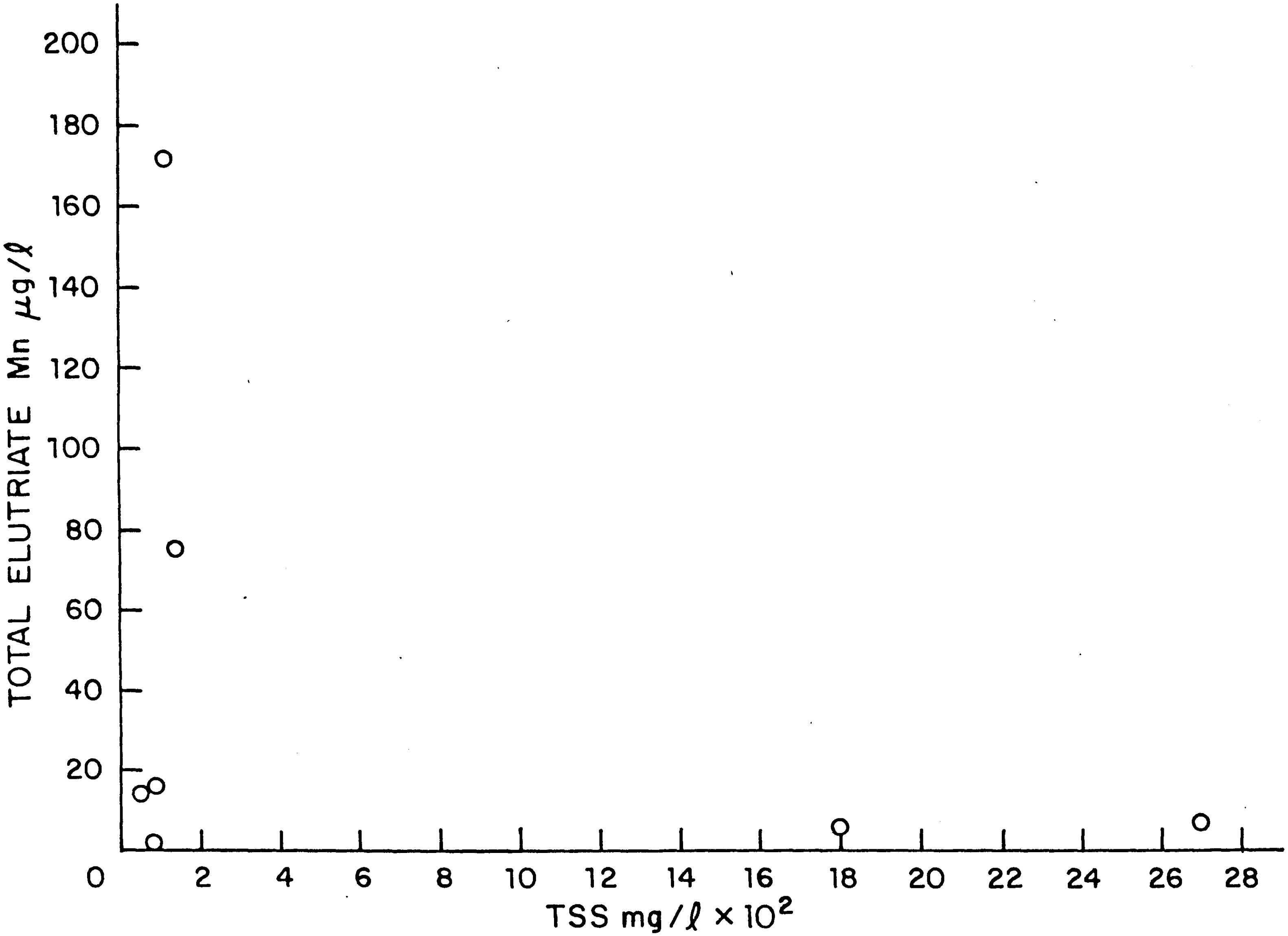


Figure 7. Unfiltered Elutriate Mn Concentrations vs. Total Suspended Solids

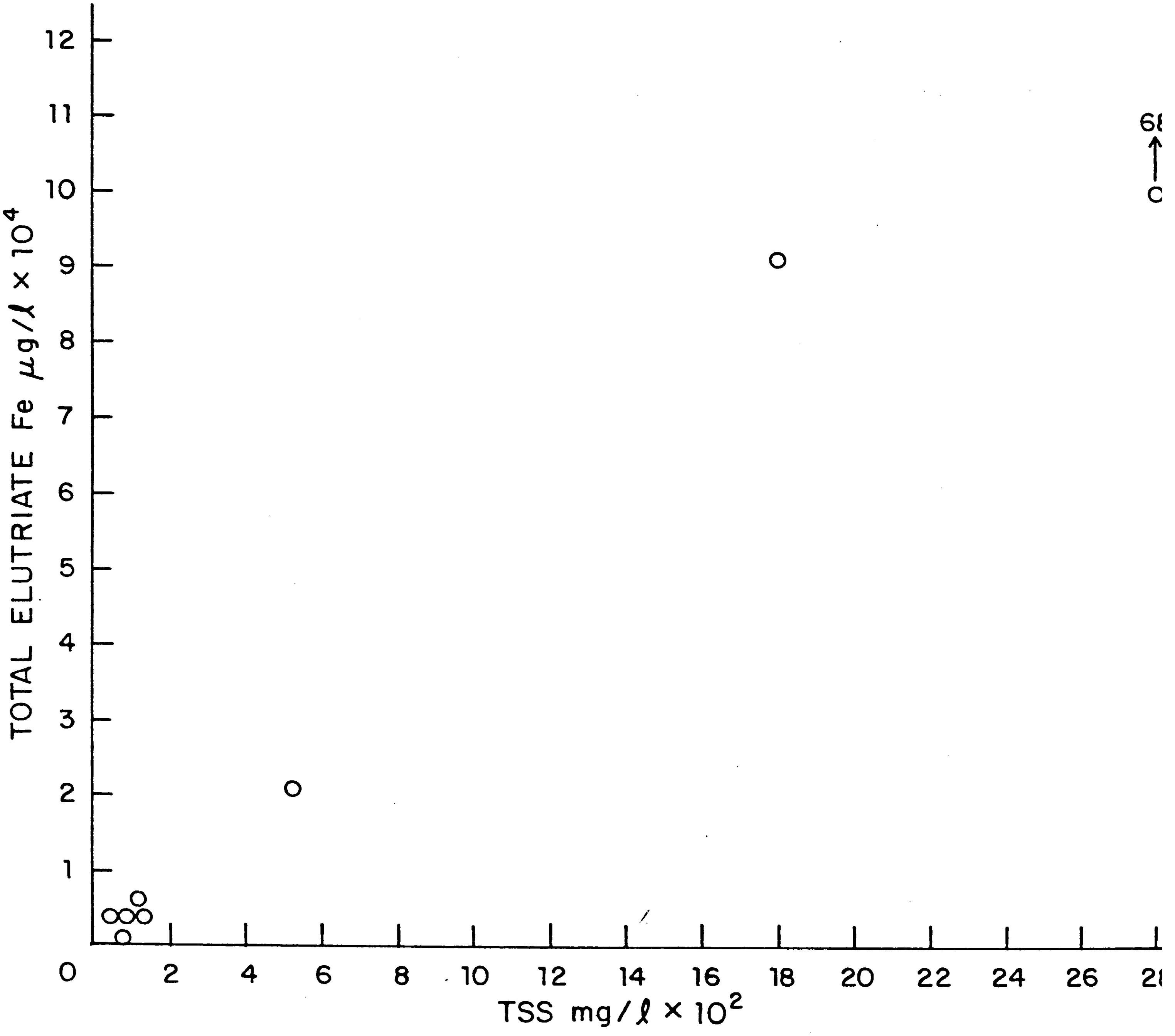


Figure 8. Unfiltered Elutriate Fe Concentrations vs. Total Suspended Solids

Table 3. Sediment Metal Concentrations*

M.P.	Cd	Cr	Cu	Mn	Pb	Zn	Fe
320.0	0.81	<0.01	1.7	2.1	<0.01	1.4	3500
356.0	0.80	0.02	1.5	0.08	3.1	×	2450
356.0	0.55	<0.01	3.4	0.07	4.1	×	3830
424.0	1.0	<0.01	4.6	1.3	<0.01	1.4	4371
448.0	0.61	<0.01	1.8	0.05	2.0	0.2	2908
469.5	0.57	<0.01	2.5	1.26	2.2	0.5	4350
503.5	0.03	0.01	0.4	0.03	0.2	0.4	2387
503.5	0.05	<0.01	0.6	0.07	0.1	0.1	4297
545.8	0.13	0.01	3.8	0.17	7.4	0.6	8660
548.0	0.07	0.07	3.5	0.28	5.0	0.3	8300
Grand Mean	0.46	0.01	2.4	0.54	2.4	0.6	4505
Std. Dev.	0.34	0.02	1.3	0.70	2.4	0.48	2109
Coeff. Var.	0.74	2.0	0.54	1.3	1	0.8	0.47

* all data in mg/kg
× no data

Table 4. Variations Among Sites for Iron Concentrations in Elutriates from the GREAT II Study Reach, Mississippi River

M.P.	Filtered Raw ug/l	Filtered Elutriate ug/l	Total (unfiltered) Elutriate ug/l	Total Sediment mg/kg
320.0	<20	<20	4530	3500
356.0	177	217	844	2455
356.0	<20	<20	20759	3828
424.0	<500	<500	3933	4371
448.0	<20	<20	3500	2908
469.5	<20	<20	6100	4350
503.5	286	47	x	2387
503.5	360	61	x	4297
545.8	<10	703	677000	8660
548.0	414	274	91000	8300
Mean	153	159	100958	4506
Min	~5	~10	844	2387
Max	414	703	677000	8660

x no data

Predominance Diagrams

In addition to metal concentration analyses, pH and oxidation-reduction potential (ORP) measurements were obtained on raw water samples, sediment samples and during the elutriate test. The pH and ORP data is summarized in Table 5. pH values for sediment were lower than those of raw water. The resultant pH of the elutriate generally was higher at the end of the elutriate test than that of the initial raw water. ORP values for sediments were all in the oxidized range, as were raw water and resultant elutriate values. ORP of the water was lower following the mixing period of the elutriate test. Measures of variation on the parameters of pH and ORP indicate relatively stable conditions from one site to another of similar substrate. Dirty, muddy samples were lower in pH and ORP than clean, sandy samples.

Iron and manganese chemistry often controls the release of other water quality constituents. To better interpret the significance of iron, manganese, pH and ORP data collected, Eh - pH Predominance Diagrams were prepared. In all cases the mean value was utilized in determining boundaries of iron and manganese species. Substitution of either the minimum or maximum values for Fe, Mn, pH and ORP shifts the boundary lines insignificantly. Carbonate and sulfur species were present in such small quantities that their regions of influence were inconsequential for the environmental conditions encountered in this study.

Eh-pH Predominance Diagram for Iron

The areas of predominance for the various iron species are indicated in Figure 9. The hash marked area of the diagram indicates

Table 5. Measures of variation for pH and ORP

	pH			ORP*		
M.P.	Raw	Elut	Sed	Raw	Elut	Sed
320.0	7.6	8.0	6.5	411	368	361
356.0	7.8	8.1	7.4	346	373	338
356.0	7.9	7.9	7.3	356	316	221
424.0	8.1	8.1	5.9	391	388	366
448.0	6.9	7.4	×	394	394	344
469.5	7.2	7.7	×	394	334	361
503.5	×	×	×	×	×	×
503.5	×	×	×	×	×	×
545.8	×	×	×	644	317	144
548.0	×	×	×	544	444	77
Mean	7.6	7.9	6.8	435	367	277
Std. Dev.	0.41	0.25	0.61	97	41	107
Coeff. Var.	.05	0.03	.09	0.22	0.11	0.39

× no data
* millivolts corrected to normal hydrogen electrode

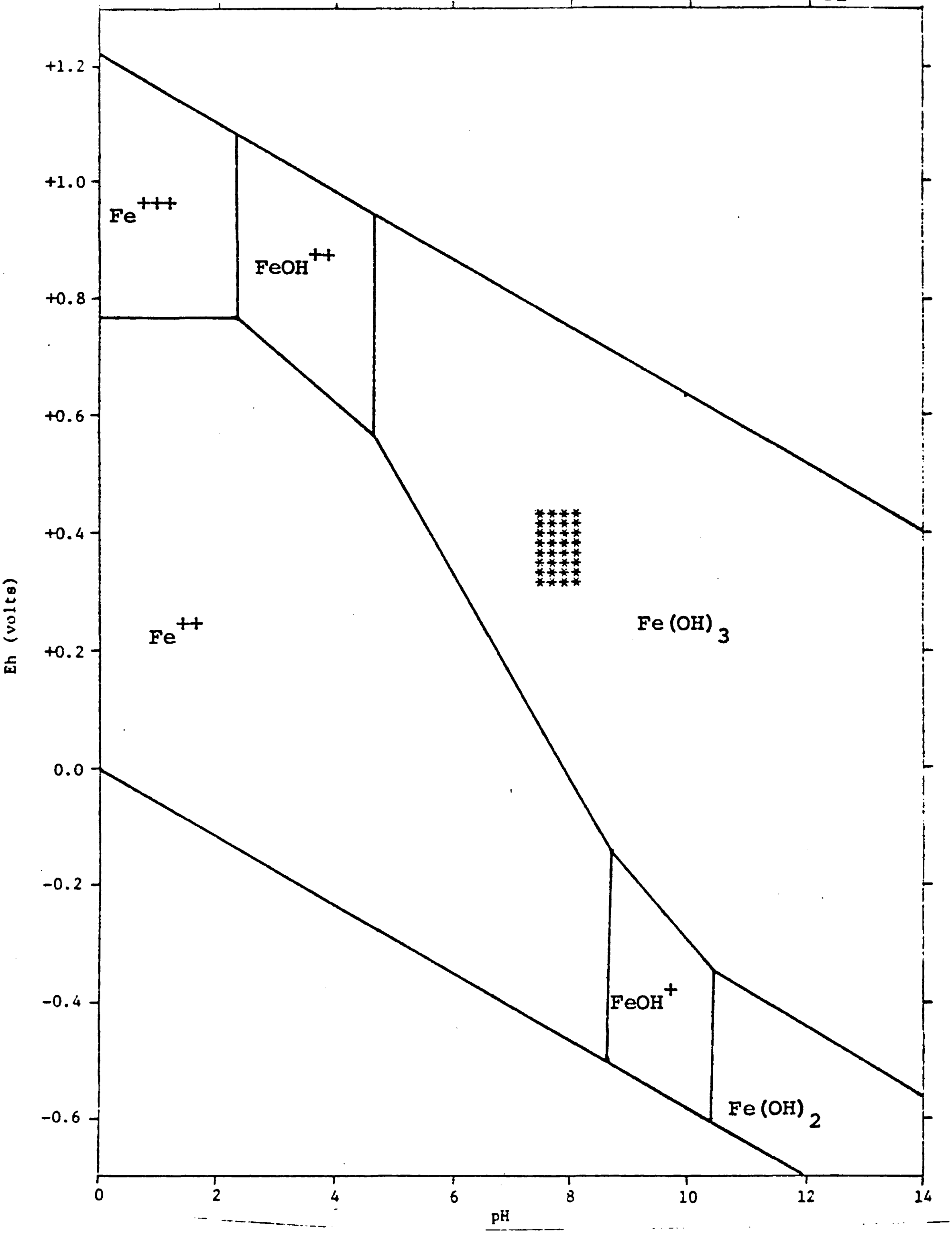


Figure 9. Eh - pH Diagram for the Iron-Water System: Iron = 2.8×10^{-6} M.

the area bounded by the minimum and maximum pH and ORP values encountered in this research during all thirty elutriate tests. This region indicates the predominating iron species under these environmental conditions. As indicated, in Figure 9, the predominant species in all cases in this study was ferric hydroxide, $Fe(OH)_3$. It can be inferred that this would be the predominant species during open water disposal of dredged materials from this river reach if conditions of chemical equilibrium prevail.

Eh-pH Predominance Diagrams for Manganese

The areas of predominance for the various manganese species are indicated in Figure 10. The hash marked area of the diagram indicates the area bounded by the minimum and maximum pH and ORP values encountered in this research. This region indicates the predominating manganese species under these environmental conditions. As indicated by Figure 10, the predominant species in this study was the divalent manganese ion, Mn^{++}. It can be inferred that this would be the predominant species of manganese during open water disposal of dredged materials from this river reach. Had the pH or ORP values been greater, the predominant species would have become one of the many oxides of manganese. Under anaerobic conditions, the electrode potential Eh would become negative and Mn^{+2} would clearly predominate. However, under high pH and Eh conditions (large dissolved oxygen concentrations) such as might occur during an algal bloom, manganese would precipitate and settle out of the water column. The use of predominance diagrams assumes chemical equilibrium and should only be interpreted to indicate general trends in data.

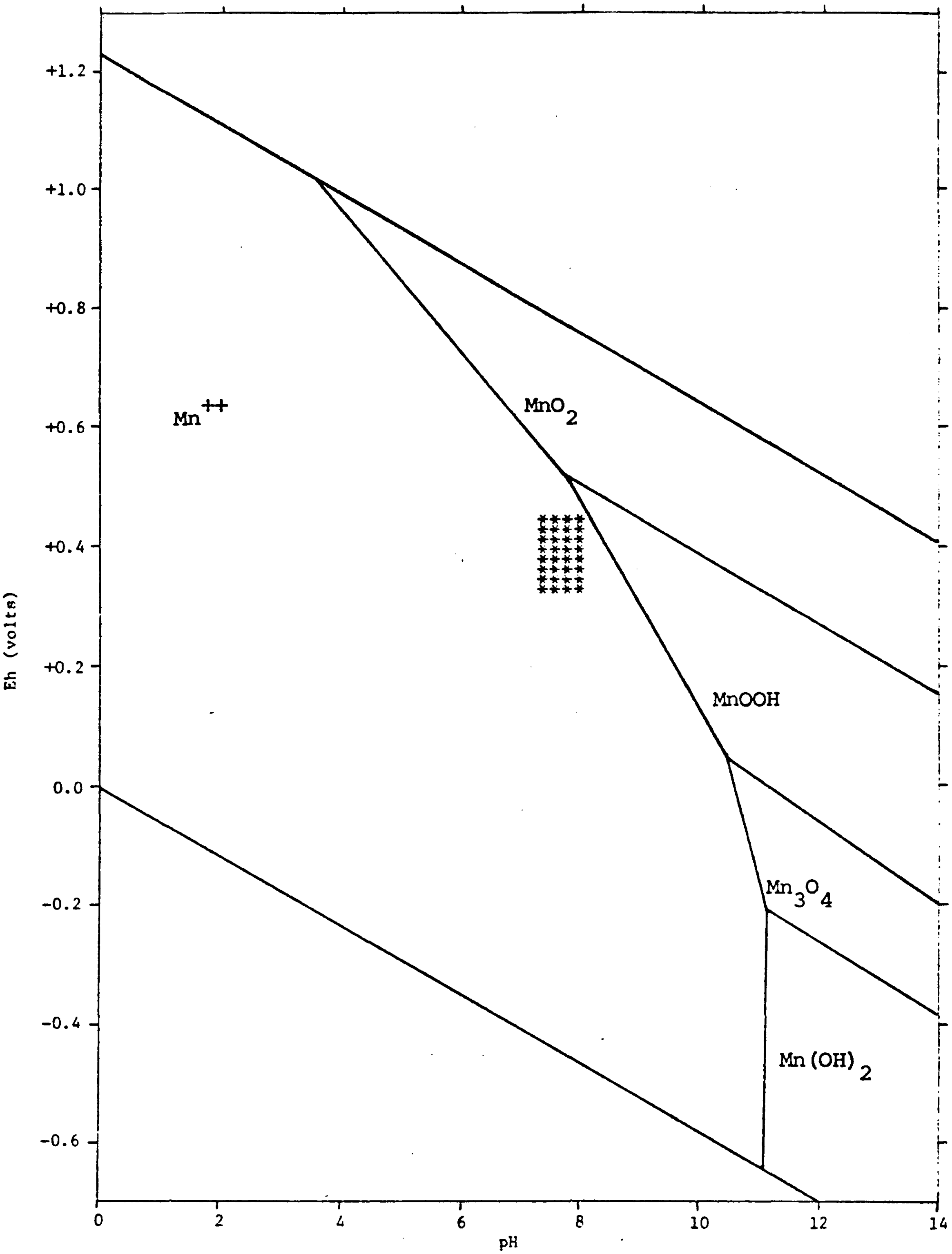


Figure 10. Eh-pH Diagram for the Manganese-Water System: Manganese = 8.2×10^{-8} M.

Filtered vs. Unfiltered Data

One of the major objectives of this research was to determine the effect of filter mesh on the elutriate. Analyses were conducted on settled, unfiltered samples; 8.0 μ filtered samples; 5.0 μ filtered samples and 0.45 μ filtered samples. Analysis of this data indicates a relatively small percentage of the total heavy metal concentration is in the dissolved state (Table 6). Apparently most of the heavy metals, especially iron, are associated with particulate matter which is removed by 0.45 μ filtration.

Alteration of Water Column Metal Concentration during the Elutriate Test

Chemical analyses indicate significant differences between the filtered and unfiltered elutriate concentrations. Research was undertaken to determine the metal concentrations as a function of particle size.

Table 7 presents the raw water vs. filtered elutriate metal concentration data for all ten sites analyzed. Overall, heavy metals were adsorbed during the elutriate test. However, some individual sediments exhibited a desorbing tendency. Elutriate iron concentrations were greater than raw water concentrations, on the average, due to large desorptions from sediment at M.P. 356.0 (C) and 545.8.

Table 8 presents the raw unfiltered metal concentrations compared with unfiltered samples. Heavy metal concentrations in unfiltered elutriate samples were generally greater than the raw water concentrations. This is due to the higher concentration of suspended solids in the elutriate sample than in the raw water. As mentioned previously,

Table 6. Percent of Elutriate Metals in the Dissolved State (0.45 μ filtered samples)

M.P.	Cd	Cr	Cu	Mn	Pb	Zn	Fe
320.0	58	×	27	30	×	33	0.2
356.0 (C)	23	×	16	0.7	16	×	×
356.0 (S)	43	×	0.5	30	39	×	0.05
424.0	35	×	14	0.02	×	10	6.4
448.0	×	×	×	5.7	×	×	0.3
469.5	×	×	×	10	×	×	0.2
503.5	×	×	×	×	×	×	×
503.5	×	×	×	×	×	×	×
545.8	×	×	×	23	×	×	0.1
548.0	×	×	×	×	×	×	0.3
Grand Mean	40	×	14	14	28	22	1.1
Std. Dev.	13	×	89	12	12	12	2.2
Coeff. Var.	.32	×	6.3	0.88	0.41	0.52	2.0

× no data

Table 7. Filtered Raw Water vs. Filtered Elutriate Metal Concentrations*

M.P.	Cd		Cr		Cu		Mn		Pb		Zn		Fe	
	R	E	R	E	R	E	R	E	R	E	R	E	R	E
320.0	5.3	5.3	<0.05	<0.05	7.8	4.6	4.5	4.2	<0.05	<0.05	26	14	<20	<20
356.0 (C)	0.3	0.07	<0.05	<0.05	3.3	1.2	<0.05	0.07	5.5	0.75	×	×	177	844
356.0 (S)	0.11	1.3	<0.05	<0.05	0.3	0.08	0.1	0.6	11	6.6	×	×	<20	<20
424.0	15	2.2	<0.05	<0.05	4.7	1.9	0.76	<0.05	<0.05	<0.05	50	1.9	<500	<500
448.0	<0.05	<0.05	<0.05	<0.05	5.3	1.1	71	4.3	<0.05	<0.05	<0.05	3.0	<20	<20
469.5	0.91	3.4	<0.05	<0.05	8.0	9.0	4.8	18	4.0	<0.05	1.8	9.5	<20	<20
503.5	0.5	0.9	0.3	0.1	×	7.3	0.1	2.0	5.9	2.4	×	×	286	47
503.5	0.4	0.6	<0.1	<0.1	6.8	0.2	1.5	0.9	0.08	<0.1	10	11	360	61
545.8	0.1	1.5	0.06	0.34	×	×	<0.05	0.80	×	×	×	×	<10	703
548.0	0.06	0.30	<0.05	<0.05	×	×	0.21	13	×	×	×	×	414	274
Grand Mean	2.3	1.4	0.04	0.05	5.2	3.2	8.3	4.4	3.3	1.2	18	7.9	153	222
Std. Dev.	4.5	1.2	0.09	0.10	2.5	3.2	21	5.9	3.8	2.2	19	4.7	156	293
Coeff. Var.	1.9	0.85	2.2	2.0	0.49	1.0	2.5	1.3	1.1	1.8	1.1	0.59	1.0	1.3

* all data in μg/l

× no data

R RAW

E ELUTRIATE

Table 8. Unfiltered Raw Water vs. Unfiltered Elutriate Metal Concentrations*

M.P.	Cd		Cr		Cu		Mn		Pb		Zn		Fe	
	R	E	R	E	R	E	R	E	R	E	R	E	R	E
320.0	11	5.7	<0.05	<0.05	23	17	9.0	14	×	×	25	43	3410	4530
356.0 (C)	0.80	1.3	<0.05	<0.05	11	7.5	0.45	9.7	6.9	4.8	×	×	4326	844
356.0 (S)	0.80	3.0	<0.05	<0.05	11	17	1.1	2.0	7.9	17	×	×	1538	20759
424.0	4.5	6.2	<0.05	<0.05	7.8	14	16	17	×	×	23	19	5150	3933
448.0	×	×	×	×	×	×	72	75	×	×	×	×	8500	3500
469.5	×	×	×	×	×	×	174	172	×	×	×	×	3742	6100
503.5	×	×	×	×	×	×	×	×	×	×	×	×	×	×
503.5	×	×	×	×	×	×	×	×	×	×	×	×	×	×
545.8	×	×	×	×	×	×	2.0	3.5	×	×	×	×	1930	677000
548.0	×	×	×	×	×	×	1.0	2.8	×	×	×	×	942	91000
Grand Mean	4.3	4.1	<0.05	<0.05	13	14	34	37	7.4	11	24	31	3692	100958
Std. Dev.	4.2	2.0	0	0	5.8	3.9	57	56	0.5	6.1	1.0	12	2265	219541
Coeff. Var.	0.97	0.49	0	0	0.45	0.28	1.7	1.5	0.068 7	0.55	0.042	0.39	0.61	2.2

* all data in µg/l

× no data

usually a large percentage of the total heavy metal is associated with the solids. Iron concentrations show the greatest alteration of raw water quality during the elutriate test.

Further research was undertaken to determine the size fraction of suspended material which contains the suspended heavy metals.

Analyses were performed on four sites: three main channel samples and one slough. Heavy metal concentrations of unfiltered, 8.0 μ filtered and 0.45 μ filtered samples were analyzed. The data for channel sites at M.P. 320, 424, and 356 are contained in Tables 9 and 10. Analysis of this data indicates 8.0 μ filtration removes approximately 90% of the total iron, 93% of the total lead, 75% of the total copper, 93% of the total manganese, and 16% of the total zinc. Zinc was the most soluble of the metals investigated with 46% of the total zinc passing a 0.45 μ cellulose-acetate membrane filter. For the other metals, 8.0 μ filtration removes a substantial portion of suspended metals with 5.0 μ filtration removing much of the remaining. Approximately 98% of the total suspended solids and 90% of the total volatile solids are removed by 8.0 μ filtration. Following one hour settling of the elutriate, the predominant particle sizes remaining suspended would be expected to be quite small, specifically the clay and silt fractions. It would seem that the mesh size of the filter employed is not very important since the difference between 8.0 and 0.45 μ filtration was not large. Evidently even fine clay particles (<4 μ) are filtered by an 8.0 μ filter due to cake formation and entrainment.

Table 9. Differential Filtration Analysis

M.P. 320.0 Elutriate	Fe	Cd	Cu	Mn	Zn
Unfiltered	4400	7.7	17	16	43
8.0 µ filtered	500	5.4	5.3	2.0	34
0.45 µ filtered	<20	4.4	5.0	<0.05	19

M.P. 424.0 Elutriate	Fe	Cd	Cu	Mn	Zn
Unfiltered	3225	7.9	14	17	19
8.0 µ filtered	500	4.8	5.3	0.8	16
0.45 µ filtered	<20	3.4	1.4	<0.05	8.5

* all data in µg/l

Table 9. Differential Filtration Analysis

M.P. 320.0 Elutriate	Fe	Cd	Cu	Mn	Zn
Unfiltered	4400	7.7	17	16	43
8.0 μ filtered	500	5.4	5.3	2.0	34
0.45 μ filtered	<20	4.4	5.0	<0.05	19

M.P. 424.0 Elutriate	Fe	Cd	Cu	Mn	Zn
Unfiltered	3225	7.9	14	17	19
8.0 μ filtered	500	4.8	5.3	0.8	16
0.45 μ filtered	<20	3.4	1.4	<0.05	8.5

* all data in μg/l

Table 10. Differential Filtration Analysis

M.P. 356.0 channel	Fe	Cd	Cu	Pb	TSS	TVS
Unfiltered	20750	0.8	25	26	94	14
8.0 µ filtered	290	0.06	5.0	1.8	2	1.6
5.0 µ filtered	130	<0.05	1.0	0.75	0.7	0.7
0.45 µ filtered	65	<0.05	<0.05	<0.05	0	0

M.P. 356.0 slough	Fe	Cd	Cu	Pb	TSS	TVS
Unfiltered	120000	8.4	46	58	3260	260
8.0 µ filtered	14000	0.6	4.3	3.3	10	2
5.0 µ filtered	345	<0.05	2.3	<0.05	0	0
0.45 µ filtered	145	<0.05	<0.05	<0.05	0	0

* all data in µg/l

Particle Size Analysis

To correct the problems encountered with cellulose-acetate membrane filtration for the purpose of differential fractionation analysis, the Sieve-Pipet Method used by the United States Geological Survey was employed. This method consists of removing a portion of partially settled unfiltered elutriate following a designated settling time from a prescribed depth. Sand has been previously removed from the sample by passing it through a 53 micron sieve. A summary of particle size, fall distance, settling time and computed fall velocities is presented in Table 11.

The USGS Laboratory, Iowa City, IA, performed routine sieve-pipet analysis on an elutriate prepared from a slough sample at M.P. 356, sediment and water. Table 12 indicates the breakdown on particle size for two samples run by USGS. This data shows 40% of the particles to be larger than 8.0 μ. This validates or confirms that entrainment was occurring using cellular-acetate membrane filters. Sample A was analyzed for the heavy metals Cd, Cu, Mn, and Zn. Sample B was analyzed for Fe. It is important to note that in both samples, half the total suspended sediment was between the 0.45 μ and 2 μ size. Metal concentrations for the various particle size fractions are presented in Table 13. Computations reveal that much of the Cd, Cu, and Fe are associated with the size fraction containing the largest percentage of suspended particles, the 0.45 μ - 2 μ fraction (clay and ferric hydroxide). Large percentages of the total metals are also associated with the sand fraction which is greater than 62 μ.

Table 13 presents the percentage of total suspended metal at each particle size fraction. This data reveals that 68.4% of the

Table 11. Particle Size Analysis, Pipet Method, Elutriated Sediment from the Slough at M.P. 356.

Particle Size	Fall Distance[a]	Settling Time[b]	Fall Velocity[c]
16 μ	10	366	2.7 × 10^{-2}
8 μ	10	1462	6.8 × 10^{-3}
4 μ	5	2922	1.7 × 10^{-3}
2 μ	3	7020	4.3 × 10^{-4}

a = cm
b = seconds
c = cm/second

Table 12. Particle Size Analysis, Sieve-Pipet, Elutriated Sediment from the Slough at M.P. 356

Sample A M.P. 356.0

	mg/l	%
>62µ	18.2	0.46
16-62µ	1003.8	25.50
8-16µ	537.2	13.65
4-8µ	92.4	2.35
2-4µ	215.7	5.47
<2µ	2069.3	52.57
TOTAL SUSPENDED SEDIMENT	3936.6	100.00

Sample B M.P. 356.0

	mg/l	%
>62µ	22.5	0.52
16-62µ	1184.3	27.39
8-16µ	700.0	16.19
4-8µ	70.5	1.63
2-4µ	206.9	4.78
<2µ	2139.7	49.49
TOTAL SUSPENDED SEDIMENT	4323.9	100.00

Table 13. Metal Concentrations vs. Particle Size Fraction, Elutriate from M.P. 356

	Cd		Cu		Mn		Zn		Fe	
Particle Size Fraction	μg/ℓ	%	μg/ℓ	%	μg/ℓ	%	μg/ℓ	%	μg/ℓ	%
>62μ	5.7	27.7	81.5	39.3	27.3	58.6	18.0	43.9	12000	10.9
16-62μ	1.0	4.9	8.0	3.9	-	-	10.0	23.4	10600	9.7
8-16μ	2.3	11.2	10.0	4.8	7.7	16.5	12.0	29.3	3000	2.7
4-8μ	0.4	1.9	1.0	0.5	6.6	14.2	1.0	2.4	2000	1.8
2-4μ	0.6	2.9	10.5	5.1	0.4	0.9	-	-	7000	6.4
0.45-2μ	10.6	51.2	96.4	46.4	4.0	8.6	-	1.0	74855	68.4
<0.45μ	<0.05	0.2	<0.05	-	0.6	1.2	-	-	145	0.1

suspended iron is in the 0.45 μ - 2 μ fraction. This is the size fraction containing ferric hydroxide (Shapiro, 1964; Hem, 1960; Langmeir and Whittemore, 1971). It is also important to note that 10.9% of the iron is associated with the sand fraction, presumably as a ferric hydroxide coating (Jenne, 1968). Therefore, 79.3% of the suspended iron may be considered in the form of ferric hydroxide, $Fe(OH)_3$. This is substantiated by the Eh-pH predominance diagram for the Iron:Water System (Figure 9).

Table 14 summarizes the important data from the particle size analysis. The sand and clay fraction together contain 53.03% of the total suspended solids, 79.4% of the suspended iron, 79.1% of the suspended cadmium, 85.7% of the suspended copper, 68.4% of the suspended manganese, 44.9% of the suspended zinc. This strongly indicates the role of hydrous metal oxides as heavy metal scavengers during the elutriate test.

What about clay minerals ??

Another important aspect of this data supporting hydrous oxide scavenging is that; while only 0.46% of the total suspended solids are in the sand fraction and have only 10.9% of the total suspended iron associated with them; 27.7% of the total suspended cadmium, 39.3% of the total suspended copper, 58.6% of the total suspended manganese and 43.9% of the total suspended zinc is adsorbed to the sand. This may be explained by the known ability of hydrous metal oxides to exert surface chemical activity far out of proportion to their total concentration (Jenne, 1968; Lee, 1975; Stumm and Morgan, 1970).

Table 14. Percent Total Metals vs. Percent Total Sediment

Particle Size Fraction	Sediment	Cd	Cu	Mn	Zn	Fe
>62μ	0.46	27.7	39.3	58.6	43.9	10.9
16-62μ	25.50	4.9	3.9	0	23.4	9.7
8-16μ	13.65	11.2	4.8	16.5	29.3	2.7
4-8μ	2.35	1.9	0.5	14.2	2.4	1.8
2-4μ	5.47	2.9	5.1	0.9	1.0	6.4
<2μ	52.57	51.4	46.4	9.8		68.5

CHAPTER VI

WATER QUALITY AND PESTICIDES: RESULTS AND DISCUSSION

Water quality samples of site water, sediments and elutriates were performed for ten sites in the GREAT II study reach. Water quality parameters included total suspended solids (TSS), volatile suspended solids (VSS), oil and grease, ammonia-nitrogen, ortho-phosphorus, and chemical oxygen demand (COD). Pesticide parameters were dieldrin, DDT, DDE, atrazine, Lasso (alachlor), and total PCB's (polychlorinated biphenyls).

Table 15 gives the average sediment concentrations for the water quality parameters at all ten sites. Correlations among these parameters are presented in Chapter VII. Generally the "dirty" samples were darker in color and contained finer-grained sediments. Slough samples were "dirtier" than main channel samples. Lower current velocities in backwater areas allow for finer-grained materials to settle. Note that the dirty sediments were obtained at mile points 545.8, 548 and 356. These sediments were characterized by high volatile solids content (>0.5%), low total solids (<83%), high COD (>1000 mg/l), and generally higher-than-average oil and grease, ammonia-nitrogen, and phosphate-phosphorus. It is the dirty sediments which are higher in organic matter and are therefore more likely to adsorb pesticides, chelated heavy metals, and hydrophobic trace organics. Most of the pesticide residues in the sediments were in less-than-detectable concentrations (see Table 16), except for DDE, a metabolite of DDT, which was slightly above the detectable limit in the two dirty sediments from mile points 545.8 and 548.

Table 15. Average Sediment Chemical Concentrations (3 samples at each station with duplicates)

Station M.P.	TS %	VS % of dry wt	oil & grease mg/kg	NH_3-N mg/kg	PO_4-P mg/kg	COD mg/kg
320	88.4	0.2	<16	12	4	290
356(S)	82.6	0.9	220	33	95	1800
356(MC)	88.7	0.2	67	15	6	360
424	90.0	0.3	216	14	4	370
448	87.8	0.2	172	11	0.1	205
469.5	84.5	0.4	15	12	1.5	475
503.5(S)	86.5	0.3	25	3.1	5.4	737
503.5(MC)	82.8	0.2	6	3.8	5.2	412
545.8(S)	81.0	1.2	730	9.7	11	6600
548(MC)	80.5	1.5	30	13	9	5000
Grand Mean	85.3	0.54	149	12.7	14.1	1620
Std. Dev.	3.4	0.50	222	8.2	28.6	2280
Coeff. Var.	4.0%	92.8%	149%	64.3%	203%	141%

Table 16. Average Sediment and Filtered Site Water Pesticide Concentrations*

M.P.	Date	Dieldrin		DDT		DDE		Atrazine	
		Sediment μg/kg††	Water ng/l†	Sediment μg/kg	Water ng/l	Sediment μg/kg	Water ng/l	Sediment μg/kg	Water ng/l
320(MC)**	6/26/79	<0.6	<3	<0.8	<6	<0.6	<5	<5	1050
356(S)	7/10/79		<6		<8		<6		1500
356(MC)	7/10/79		<6		<8		<6		1500
424(MC)	6/26/79	<0.6	<6	<0.8	<8	<0.6	<6	<5	770
448(MC	6/12/79	<0.5	<5	<0.8	<8	<0.5	<6	<5	1300
469.5(MC)	6/12/79	<0.5	<5	<0.8	<8	<0.5	<6	<5	1700
503.5(S)	11/28/78	<0.3	<3	<0.6	<6	<0.3	<5	<5	130
503.5(MC)	11/28/78	<0.3	<3	<0.6	<6	<0.3	<5	<5	160
545.8(S)	5/29/79	<0.3	<4	<0.6	29	0.8	20	<3	220
548(MC)	5/29/79	<0.3	<4	<0.6	11	0.6	13	<3	230

†† Sediment concentrations are μg/kg dry sediment

† Water concentrations are nanograms/l (parts per trillion) for filtered site water

** (MC) = main channel; (S) = slough

* Pesticide analyses were performed by University of Iowa Hygienic Laboratory under sub contract.

Table 16. Continued.

M.P.	Date	Lasso		PCB's	
		Sediment µg/kg	Water ng/l	Sediment µg/kg	Water ng/l
320(MC)	6/26/79	<2	515	<4	<100
356(S)	7/10/79		880		<100
356(MC)	7/10/79		490		<100
424(MC)	6/26/79	<2	260	<4	<100
448(MC)	6/12/79	<2	820	<5	<100
469.5(MC)	6/12/79	<2	1100	<5	<100
503.5(MC)	11/28/78			<5	<100
503.5(S)	11/28/78			<5	<100
545.8(S)	5/29/79			<3	
548(MC)	5/29/79			<3	<100

Pesticide concentrations for the herbicides Lasso (alachlor) and atrazine were on the order of 1 ppb in site water during June and July, 1979, following spring application. This is typical of the annual pattern for these herbicides in the Mississippi River according to recent analyses by Lauren Johnson, Chief Chemist, University of Iowa Hygienic Laboratory. Filtered and unfiltered analyses showed that atrazine and Lasso were 80-100% in the dissolved phase and were not increased during the standard elutriate test. Detecting DDT and DDE in site water from below the Maquoketa River (M.P.'s 545.8 and 548) was very unusual and indicated some illegal application, dumping of the insecticides, or possible flooding of disposal areas. The DDT and DDE concentrations at M.P.'s 545.8 and 548 exceeded the proposed 24-hr average allowable freshwater quality criteria of 0.23 nanograms/liter for DDT and its analogs (personal correspondence from Mr. John Eaton, Research Aquatic Biologist, USEPA Environmental Research Laboratory, Duluth, Minnesota). PCB's and dieldrin did not violate proposed freshwater criteria in site water or elutriate tests. The herbicides atrazine and Lasso are not presently included in any standards or criteria and are not thought to be toxic at these low levels.

Table 17 gives the site water and elutriate concentrations for the water quality parameters chemical oxygen demand, ortho-phosphorus (phosphate), ammonia-nitrogen, oil and grease, and total suspended solids in the elutriate test after a 30 minute elutriation and 1 hour of settling. There was considerable variation in these concentrations from site-to-site, especially for oil and grease. Note that the "dirtiest" sediments at M.P.'s 548, 545, and 356 Grey's Chute were not necessarily those which

TABLE 17

CHEMICAL CHARACTERISTICS OF SITE WATER AND ELUTRIATES

Location	COD,mg/l		Ortho-P,mg/l		NH_3-N,mg/l		O&G,mg/l		TSS,mg/l	
	S	E	S	E	S	E	S	E	S	E
M.P. 503		33				0.2		1		
Princeton	21	67	0.18	.05	0.16	0.15	4	<1		
		54		.05		0.15		<1		
M.P. 503		56		0.18		0.4		<1		
Princeton	27	46	0.21	0.12	0.18	0.5	<1	<1		
Slough		54		0.14		0.8		<1		
M.P. 548		14		<0.10		0.70		4		1750
Below Maq.	16	29	<0.01	0.02	0.15	0.45	<1	<1	43	2260
River		25		0.02		1.30		<1		1400
M.P. 545		19		<0.01		0.50		<1		960
Aspelmeier	21	13	<0.01	<0.01	0.10	0.50	4	<1	44	980
Ditch		17		0.02		1.25		31		6380
M.P. 469.5		39		0.03		1.80		2		176
Montpilier	19	22	0.04	0.04	0.60	0.80	<1	4	94	132
		6		0.04		0.40		46		64
M.P. 447		13		0.04		0.40		16		108
Below	31	15	0.03	0.04	0.60	0.40	<1	2	282	72
Mus.		9		0.05		0.40		10		232
M.P. 424		10		<0.01		0.20		1		63
Keithsburg	20	13	0.03	<0.01	<0.05	0.20	<1	<1	157	63
		8		<0.01		0.25		1		93
M.P. 320		27		0.07		0.10		5		64
Quincy	15	12	0.05	0.05	0.05	0.10	1	2	117	40
		10		0.07		0.10		<1		52
M.P. 356		24		0.08		0.3		<1		78
Keokuk	12	17	0.13	0.09	0.5	0.25	3	<1	88	118
Channel		8		0.10		0.25		<1		56
M.P. 356		12		0.08		0.35		<1		154
Greys	11	24	0.09	0.05	0.5	0.35	2	<1	56	314
Chute		27		0.02		1.70		<1		1130
Mean	19.7	24.7	0.08	0.05	0.30	0.50	1.6	4.4	110	697
Standard Deviation	6.5	16.5	0.07	0.05	0.24	0.44	1.64	10.1	77.6	1360
Coefficient of Variation	33%	67%	85.5%	90.6%	79.3%	88.7%	102.5%	230%	70.5%	195%

S = Site Water E = Elutriates

released the most COD, oil and grease, and ortho-P. This points out the difficulty in assessing dredge disposal desorption problems from bulk sediment characteristics alone. However, the dirty sediments did generally yield higher NH_3-N and were much more difficult to settle-out as measured by the large TSS concentrations in the standard elutriate tests for M.P.'s 548, 545, and 356. Ammonia desorption during the elutriate test occassionally exceeded water quality criteria, and required dilution factors are presented in Chapter VIII.

Tables 18 and 19 give the means and standard deviations for the pre-dredging samples and elutriates which were collected by the Corps of Engineers, Rock Island District, and analyzed by the United States Geological Survey (USGS), Denver Laboratory. In 1978 (Table 18), the USGS Lab performed the elutriate tests while in 1979 (Table 19), Mr. Brian Goodrum and colleagues performed the elutriates at the the Rock Island District Laboratory of the Corps of Engineers. COD, iron, manganese, and nickel were consistently desorbed (significant at the 95% confidence level in paired t-tests) in sixteen 1978 samples. COD, manganese, ammonia were significantly desorbed in sixteen samples from 1979 in the GREAT II reach. Zinc, copper, and iron showed some tendency for adsorption, while the herbicide atrazine was slightly adsorbed (possibly biodegradation). This statistical approach does not rule out that other chemicals may be significantly desorbed or adsorbed in any individual sample, but rather it represents the significant trends among all samples. For example, it was previously stated that the dirty samples consistently yielded high NH_3-N concentrations in standard elutriate tests.

Table 20 is the summary of elutriate testing for this study of 10 sites and 30 elutriates. There were no significant differences

Table 18. Mississippi River Pre-Dredging Samples, USGS 14-18 August, 1978; RM 320-548 Statistical Analyses

	$\bar{x}$, mean		std. dev. (n-1 wt.)		var. (n wt.)		Coeff. of Var. (%)†		t-test*
Parameter	S	E	S	E	S	E	S	E	
COD mg/l	24.44	70.75	5.59	65.29	29.25	3996.44	22.9	92.3	95%
NH_4-N mg/l	0.11	0.12	0.12	0.13	0.013	0.016	107.7	107.3	N.S.
PO_4-P mg/l	0.10	0.09	0.01	0.03	0.000	0.001	14.4	35.0	N.S.
Metals-μg/l									
Arsenic	2.13	1.13	0.34	0.34	0.109	0.109	16.1	30.4	N.S.
Beryllium	.00	1.25	.00	3.42	.000	10.94	-	273.3	N.S.
Cadmium	.00	.00	.000	.00	.000	.000	-	-	N.S.
Chromium	1.88	1.25	4.03	3.42	15.23	10.94	215.0	273.3	N.S.
Copper	4.63	3.44	1.26	0.96	1.48	0.87	27.2	28.0	N.S.
Iron	22.50	57.50	11.25	35.11	118.75	1156.25	50.0	61.1	95%
Lead	0.25	.00	0.58	.00	0.31	.000	230.9	-	N.S.
Manganese	2.50	99.38	4.47	207.92	18.75	40530.86	178.9	209.2	95%
Mercury	0.06	.00	0.06	.00	0.004	.000	99.1	-	N.S.
Nickel	0.75	4.00	1.00	1.15	0.94	1.25	133.3	28.9	95%
Selenium	0.13	0.31	0.34	0.48	0.109	0.214	273.3	153.2	N.S.
Zinc	3.75	10.00	10.25	7.30	98.44	50.00	273.3	73.0	N.S.
pH lab	8.43	8.33	0.13	0.12	0.016	0.014	1.5	1.4	N.S.
field	7.70		0.12		0.010		1.5		N.S.
Residue-dis.	220.75	216.38	10.57	14.50	104.813	197.11	4.8	6.7	N.S.
dis. vol.	59.75	62.63	14.24	10.58	109.19	104.98	23.8	16.9	N.S.
Spec. Cond.									
lab	359.19	364.75	26.17	25.06	642.15	588.56	7.3	6.9	N.S.
field	319.86	319.86	39.06	39.06	1307.84	1307.84	12.2	12.2	N.S.
Turbidity	0.32	0.69	0.08	0.23	0.007	0.050	26.2	33.5	N.S.
Water Temp, C°	25.23		0.34		0.087		1.3		
Depth, ft from surf.	11.3		1.41		1.714		12.5		

N.S. - no significant difference

* - t-test between the filtered site water and filtered elutriate waters reported at the 95% confidence level, n=16

† - coefficient of variation equals the standard deviation divided by the mean

Table 19. Mississippi River Pre-Dredging Samples, USGS
10-24 July, 1979; RM 323.5-489.4 Statistical Analyses

	$\bar{x}$, mean		std. dev. (n-1 wt.)		var. (n wt.)		Coeff. of Var. (%)†		t-test*
Parameter	S	E	S	E	S	E	S	E	
COD mg/l	27.1	55.9	5.12	22.19	24.46	457.21	19	40	99%
Iron, dis.µg/l	10.7	154.7	7.04	455.83	46.22	193931.5	66	295	N.S.
Mn, dis. µg/l	0.61	402.9	0.42	507.31	0.16	240205.4	69	126	99%
NH_4-N mg/l	0.011	0.33	0.012	0.428	0.00	0.17	110	131	99%
Arsenic dis µg/l	2.6	3.3	0.632	2.086	0.373	4.062	24	64	N.S.
Atrazine, T. µg/l	1.1	.87	0.219	0.233	0.044	0.051	18	27	98%
Copper, dis. µg/l	1.6	2.2	0.737	1.32	0.507	1.63	46	60	80%
Hg, dis. µg/l	0.22	0.23	0.068	0.080	0.004	0.006	31	35	N.S.
Ortho-PO_4-P mg/l	0.074	0.069	0.021	0.040	0.004	0.001	28	57	N.S.
Res. dis. 18° mg/l	239	235	29	29	791	803	12	12	N.S.
Res. Vol. dis. mg/l	77	75	18	19	312	323	24	25	N.S.
Zinc. dis. mg/l	8.9	19.0	14.4	27.7	193.7	715	161	146	N.S.

N.S. - no significant difference

* - t-test between the filtered site water and filtered elutriate reported at the highest confidence level, n=16

† - coefficient of variation equals the standard deviation divided by the mean

Table 20. Mississippi River GREAT II Samples
University of Iowa Statistical Analyses
November 1978-July 1979, RM 320-548

	$\bar{x}$, mean		std. dev. (n-1 wt.)		var. (n wt.)		Coeff. of Var. (%)†		n		t-test*
Parameter	S	E	S	E	S	E	S	E	S	E	
Chemical											
COD mg/l	19.7	24.7	6.5	16.5	27.76	264.0	33	67	10	30	N.S.
NH_3-N mg/l	.31	.51	.25	.45	.06	.19	81	88	8	30	N.S.
PO_4-P mg/l	.08	.05	.07	.05	.005	.003	85	91	10	30	N.S.
O & G mg/l	1.5	4.45	1.64	10.03	1.63	97.17	102	230	8	30	N.S.
Metals-µg/l											
Cadmium	2.27	1.39	4.75	2.17	20.67	4.54	210	156	10	30	N.S.
Chromium	.06	.08	.09	.13	.01	.02	147	165	10	30	N.S.
Copper	5.17	2.97	2.74	4.61	6.43	20.34	53	155	7	24	N.S.
Iron	153.2	138.47	164.1	249.01	29234.4	59937.18	107	180	10	30	N.S.
Mercury	.55	.27	1.22	.56	1.34	.30	220	208	10	30	N.S.
Manganese	8.23	6.21	22.13	17.86	440.87	308.43	269	288	10	30	N.S.
Nickel	11.06	18.37	17.68	24.31	293.4	566.40	160	132	8	24	N.S.
Lead	3.44	1.24	4.05	3.36	14.33	10.83	118	270	8	24	N.S.
Zinc	17.63	7.70	20.81	9.37	346.39	82.39	118	122	5	16	N.S.
Atrazine,											
ng/l	1300	1408	344.62	333.37	98966.67	92613.89	27	24	6	6	N.S.
raw-unfilt	1595		512.00		218458.33		32		6		N.S.
ORP (mv)											
unfilt	140	120	24.70	30.64	508.33	782.33	18	26	6	6	N.S.
Lasso, ng/l	657	612	325.37	249.17	88222.22	51739.8	50	41	6	6	N.S.
raw-unfilt	713		275.37		63188.89		39		6		N.S.

N.S. - no significant difference

* - t-test between the filtered site water and filtered elutriate water reported at the 95% confidence level

† - coefficient of variation equals the standard deviation divided by the mean

between the filtered site water and the filtered elutriates at the 95% confidence level over all sites. This is due to the marked variation from site to site. However, as shown in Table 17, there were pronounced differences between site water and elutriates for COD, NH_3-N, oil and grease, and total suspended solids with certain sediments (particularly sediments from M.P.'s 548, 545, 469.5, and 356 Grey's Chute). Phosphate and iron showed tendency for adsorption in the elutriate test.

A final summary of all desorbed chemicals at each station is presented in Table 21. Water quality criteria were seldom exceeded, but a discussion of the dilution factors that would be required is presented in Chapter VIII. Manganese, ammonia, COD, and oil and grease were the most frequently desorbed chemicals in the standard elutriate tests. Total iron and ortho-phosphorous were the most frequently "adsorbed" (the effect would include precipitation phenomena).

Table 21. Desorbed Chemicals in the Standard Elutriate Test

Date Sampled	Site Location	M.P.	Main Channel (MC) or Slough (S)	Desorbed Chemicals
11-28-78	Princeton, IA	503-504	MC	Mn, COD
11-28-78	Princeton, IA	503-504	S	COD, NH_3, PO_4
5-29-79	below Maguoketa R.	548	MC	COD, NH_3, Mn
5-29-79	Apple-Meier	545.4	S	NH_3, O & G, Fe, Mn
6-12-79	Montpellier	469.5	MC	Mn, O & G, Cd, Zn
6-12-79	below Muscatine	448	MC	Mn, O & G, Cd, Zn
6-26-79	Keithsburg	426	MC	NH_3
6-25-79	below Quincy	320	MC	
7-10-79	Keokuk	356	MC	Ni
7-10-79	Grey's Chute	356	S	COD, NH_3, Mn, Cd

Kinetic studies on the release of COD and NH_3-N as well as a proposed kinetic model are presented in Chapter VIII.

CHAPTER VII

RESULTS OF OXYGEN UPTAKE STUDIES

Oxygen Uptake and Bulk Sediment Parameters

Table 21 presents the oxygen uptake results of all samples from the eight proposed dredge sites on the Mississippi River. Each oxygen uptake result is the average of 3 one-hour analyses at each temperature. Results are expressed in grams of oxygen per unit volume of wet sediment and milligrams of oxygen per unit mass of dry sediment for each temperature. Table 22 presents the results of the chemical analyses of each sediment sample. Figure 11 through 15 are plots of each sediment characteristic versus its measured oxygen uptake at 25°C. Figures 16 through 25 illustrate bivariate relationships between all combinations of the sediment parameters. A summary of the least squares regression analyses of the data in Figures 11 through 25 is presented in Table 24. Abbreviations used in the data analysis and presentation are as follows:

TOD25W = oxygen uptake at 25°C, g/m^3 wet sed 1 hr
TOD7W = oxygen uptake at 7°C, g/m^3 wet sed 1 hr
TOD25D = oxygen uptake at 25°C, mg/kg dry sed 1 hr
TOD7D = oxygen uptake at 7°C, mg/kg dry sed 1 hr
TSS = T.S., percent
VSS = V.S., percent
TFE = Total Iron

TABLE 22

SEDIMENT OXYGEN UPTAKE*

Mile Point Location	Sample No.	Uptake g/m³ wet 25° C	Uptake mg/kg dry 25° C	Uptake g/m³ wet 7° C	Uptake mg/kg dry 7° C
M.P. 548	1	132	73	96	53
Below	2	272	200	208	153
Maq. R.	3	184	114	72	44
M.P. 545	4	75	50	29	21
Aspelmeier	5	128	71	104	58
Ditch	6	392	282	344	247
M.P. 769	7	96	68	32	23
Montpilier	8	28	17	11	7
	9	50	36	10	7
M.P. 447	10	44	29	8	5
Below	11	62	40	14	9
Muscatine	12	42	29	14	10
M.P. 424	13	14	9	14	9
Keithsburg	14	37	22	14	8
	15	8	5	12	8
M.P. 320	16	14	9	10	6
Quincy	17	22	14	12	8
	18	56	37	10	7
M.P. 356	19	112	72	27	17
Keokuk	20	149	97	37	24
Channel	21	107	73	23	16
M.P. 356	22	56	38	40	27
Greys	23	68	45	32	21
Chute	24	504	379	312	235

*Uptake results are the sediment oxygen demand exerted during the first hour after suspension in the dredge site water.

TABLE 23

SEDIMENT CHEMICAL CHARACTERISTICS

Mile Point Location	Sample No.	Total Solids %	Volatile Solids %	COD mg/kg dry	T.Iron mg/kg dry	ORP (mv)	Total Sulfide mg/kg dry
M.P. 548	1	86.3	1.5	4000	6000	144	-
Below	2	72.6	2.2	9700	13500	44	-
Maq. R.	3	82.6	0.9	1200	4200	44	-
M.P. 545	4	85.0	0.3	1100	3000	144	-
Aspelmeier	5	86.8	0.5	1500	11300	44	-
Ditch	6	70.9	2.8	16000	11800	44	-
M.P. 469	7	82.0	0.6	850	4100	344	-
Montipilier	8	88.0	0.4	380	5300	394	-
	9	83.5	0.2	200	3600	344	-
M.P. 477	10	89.0	0.2	200	2800	344	-
Below	11	87.2	0.3	200	3000	344	-
Muscatine	12	87.2	0.3	210	3000	344	-
M.P. 424	13	88.2	0.2	440	2500	366	-
Keithsburg	14	91.5	0.4	400	2900	381	-
	15	90.3	0.3	300	3700	361	-
M.P. 320	16	89.5	0.2	280	3500	361	-
Quincy	17	87.1	0.2	270	3400	361	-
	18	88.7	0.3	320	3700	361	-
M.P. 356	19	89.4	0.2	300	2200	321	-
Keokuk	20	87.7	0.3	550	2500	361	-
Channel	21	89.1	0.2	230	2600	331	-
M.P. 356	22	87.3	0.2	300	2800	281	-
Greys	23	88.7	0.2	370	3800	301	-
Chute	24	71.7	2.3	5000	5000	81	140

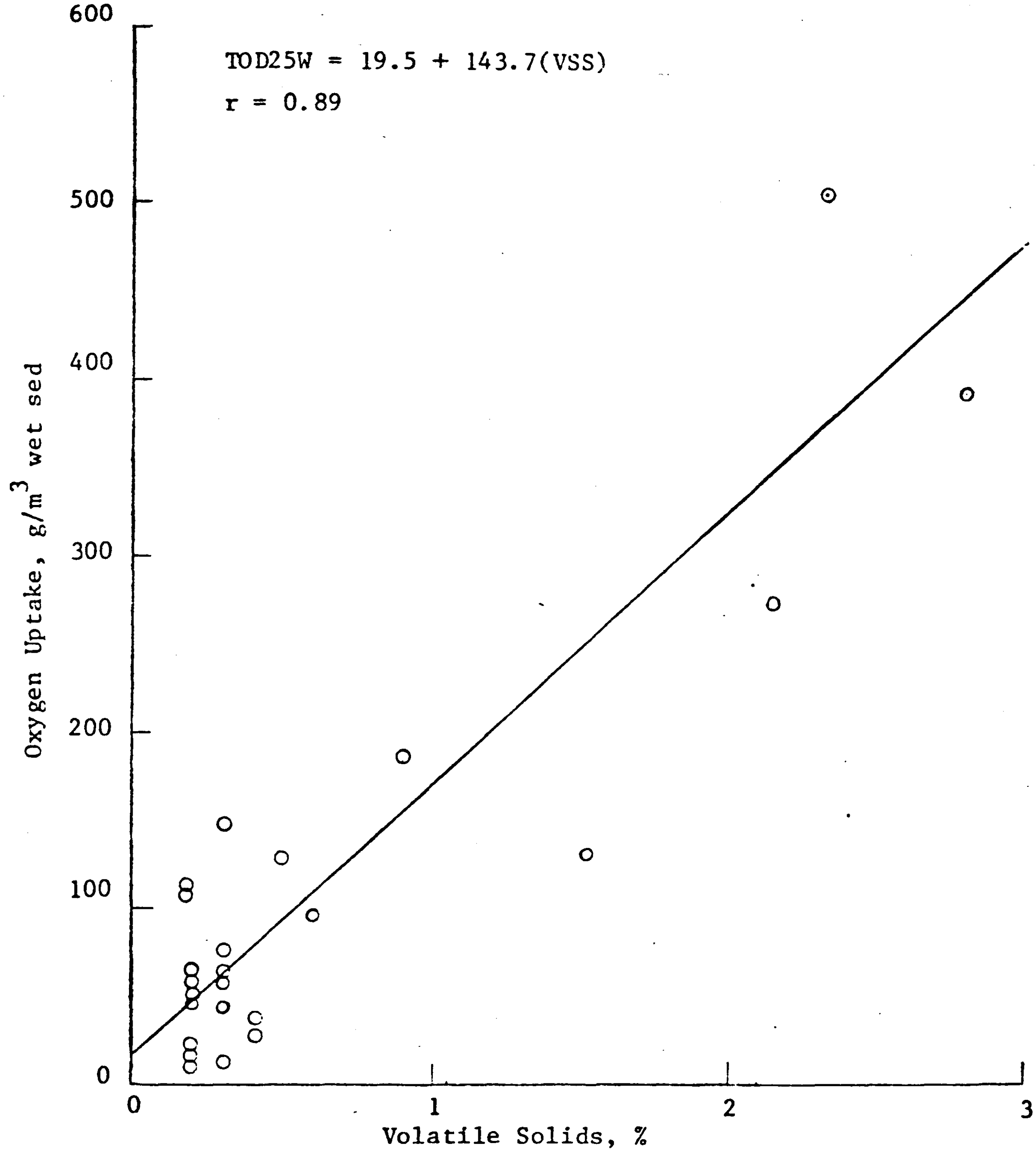


Figure 11. OXYGEN UPTAKE VERSUS SEDIMENT VOLATILE SOLIDS. TEMPERATURE = 25°C

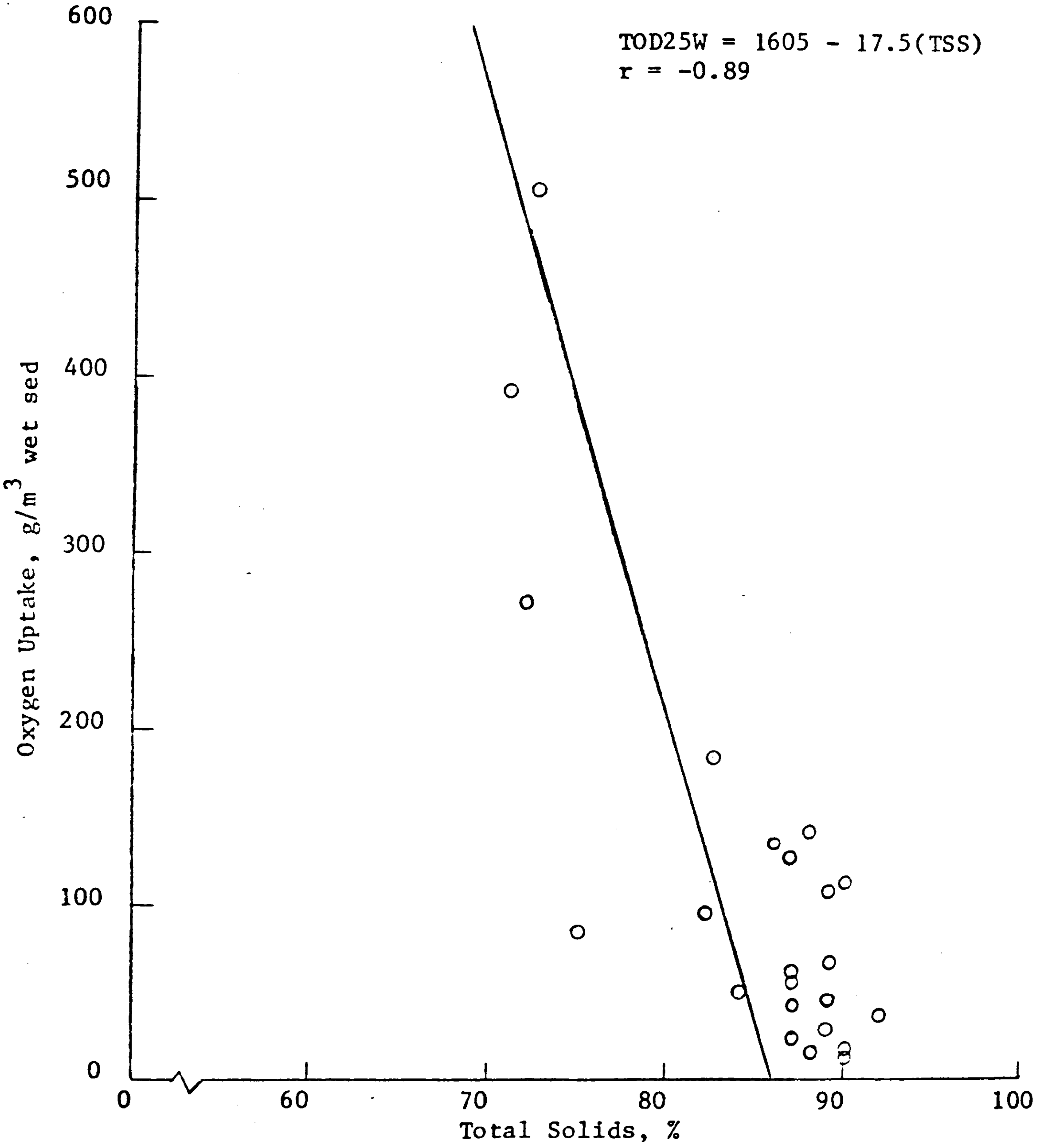


Figure 12. OXYGEN UPTAKE VERSUS SEDIMENT TOTAL SOLIDS.
TEMPERATURE = 25°C

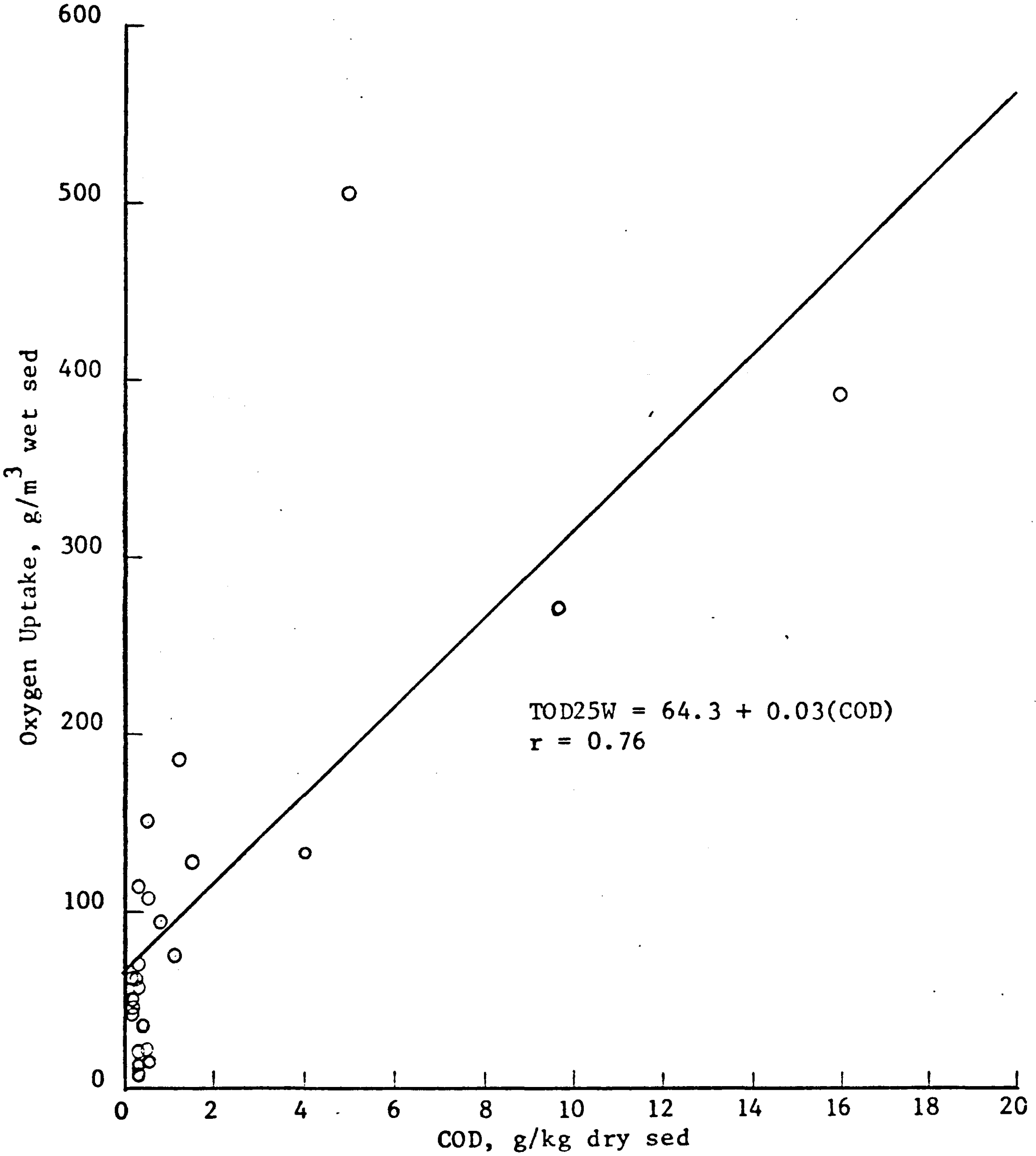


Figure 13. OXYGEN UPTAKE VERSUS SEDIMENT COD.
TEMPERATURE = 25°C

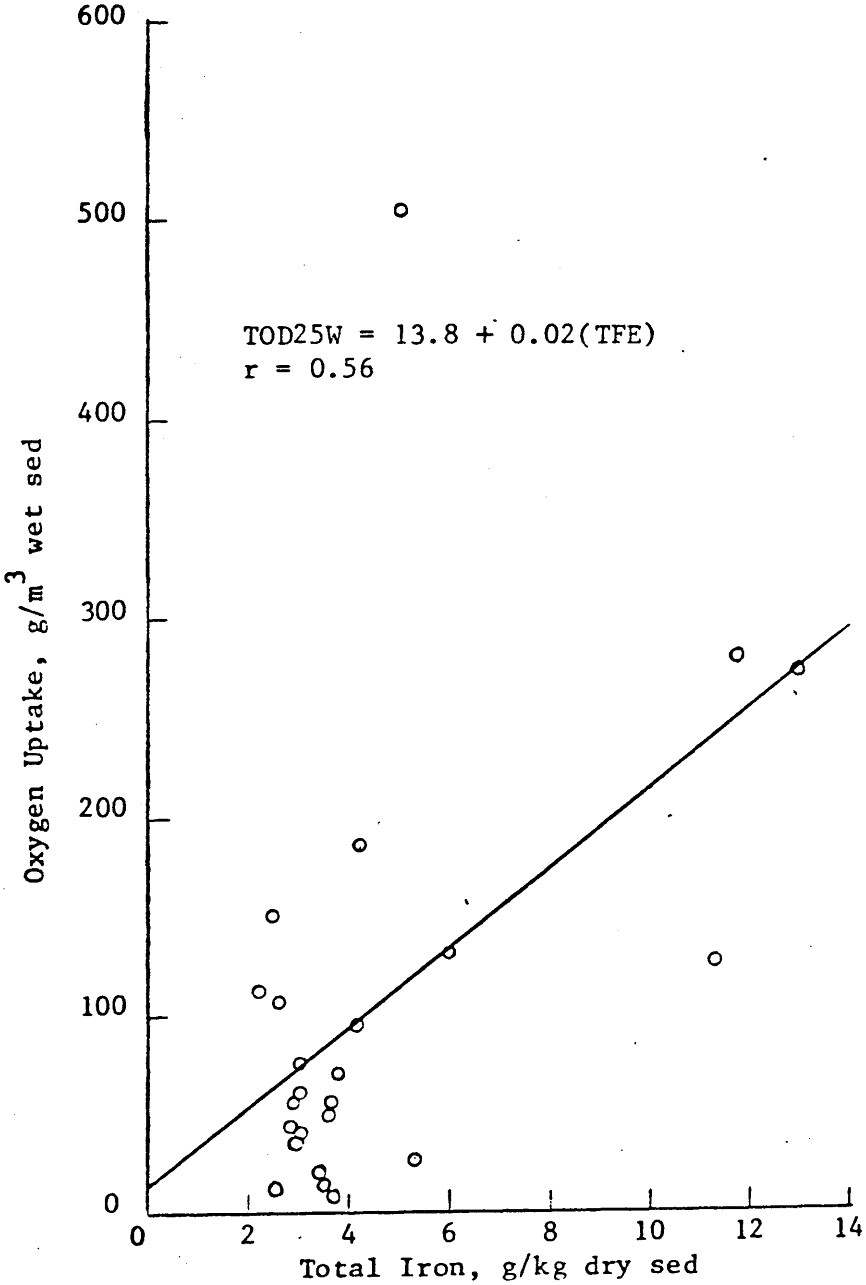


Figure 14. OXYGEN UPTAKE VERSUS SEDIMENT TOTAL IRON.
TEMPERATURE = 25°C

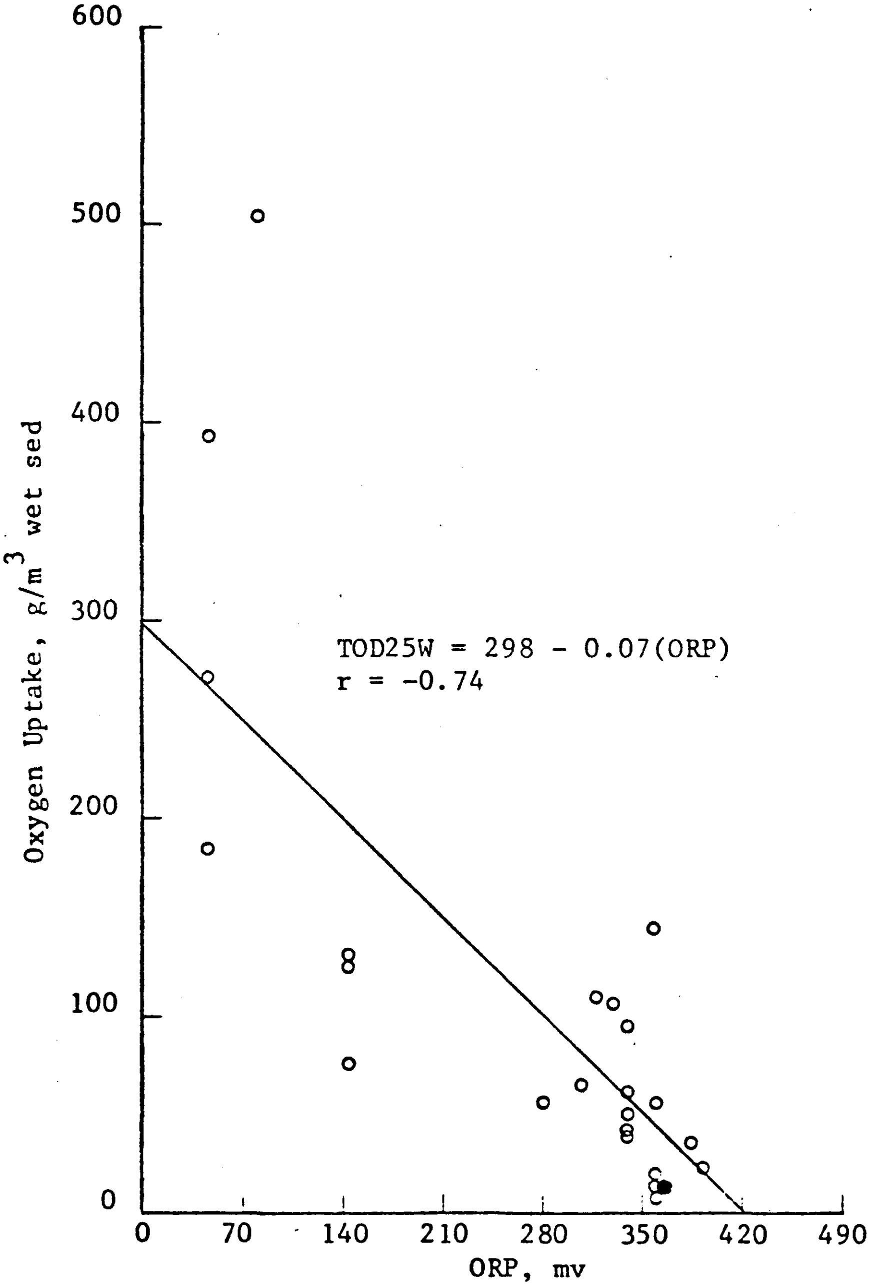


Figure 15. OXYGEN UPTAKE VERSUS SEDIMENT ORP.
TEMPERATURE = 25°C

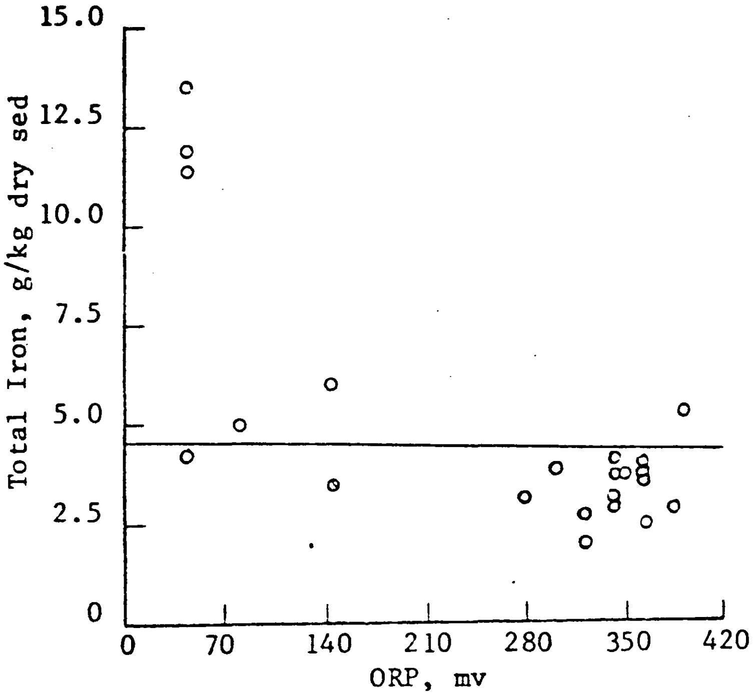


Figure 16. TOTAL IRON VERSUS ORP

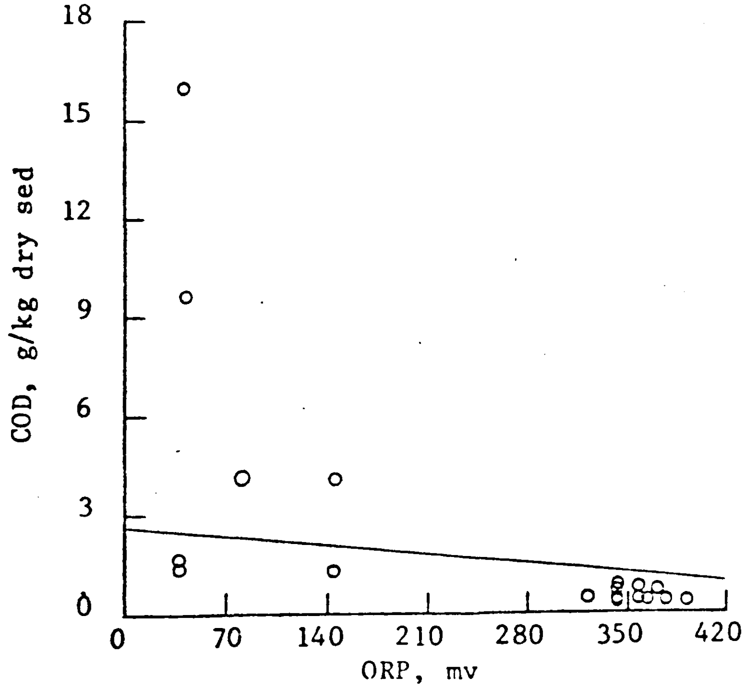


Figure 17. COD VERSUS ORP

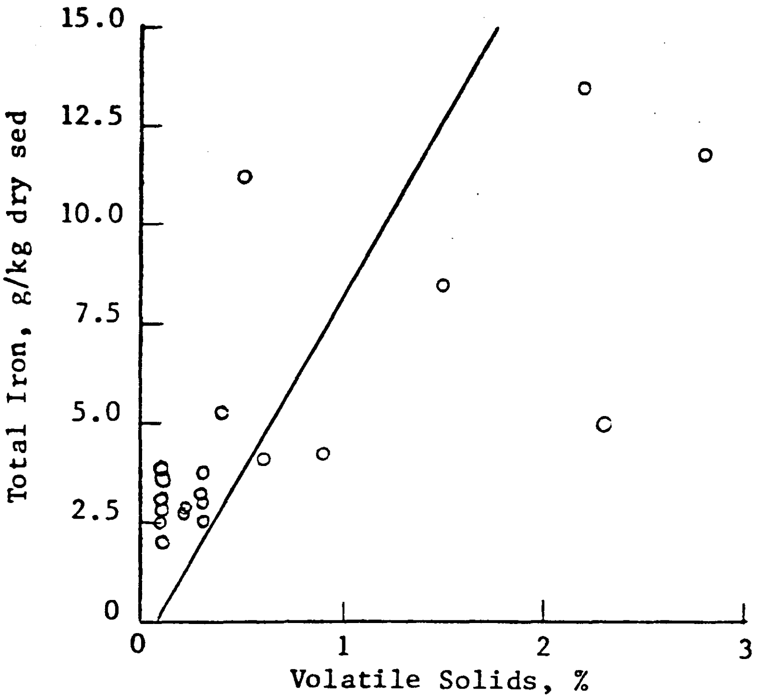


Figure 18. TOTAL IRON VERSUS VOLATILE SOLIDS

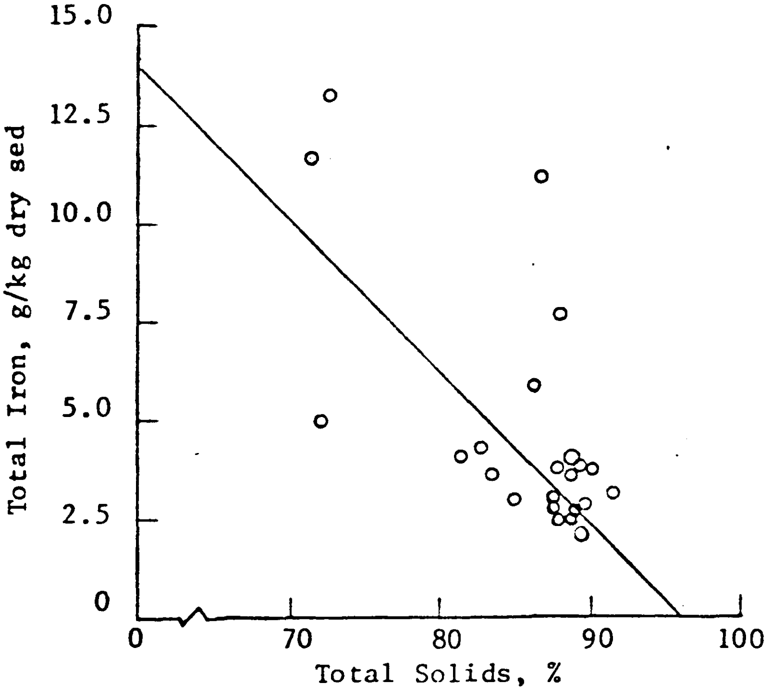


Figure 19. TOTAL IRON VERSUS TOTAL SOLIDS

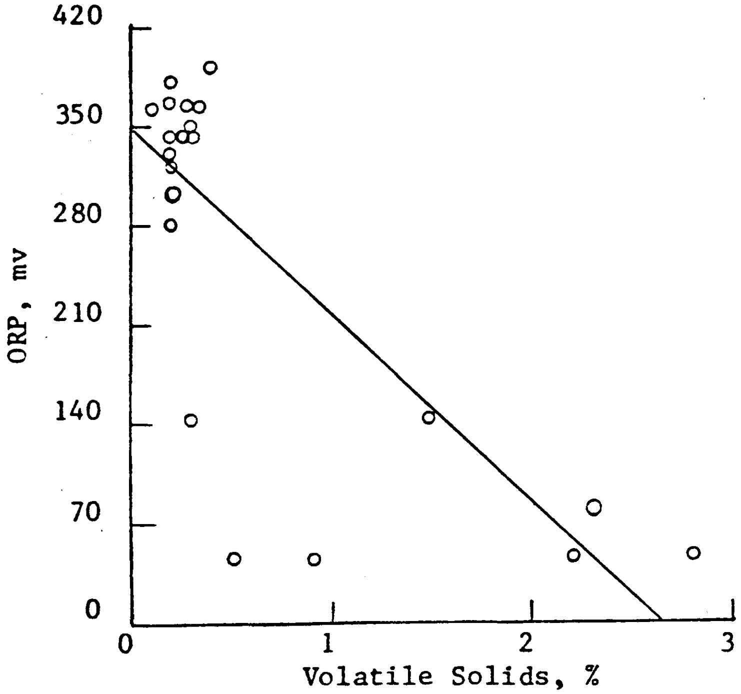


Figure 20. ORP VERSUS VOLATILE SOLIDS

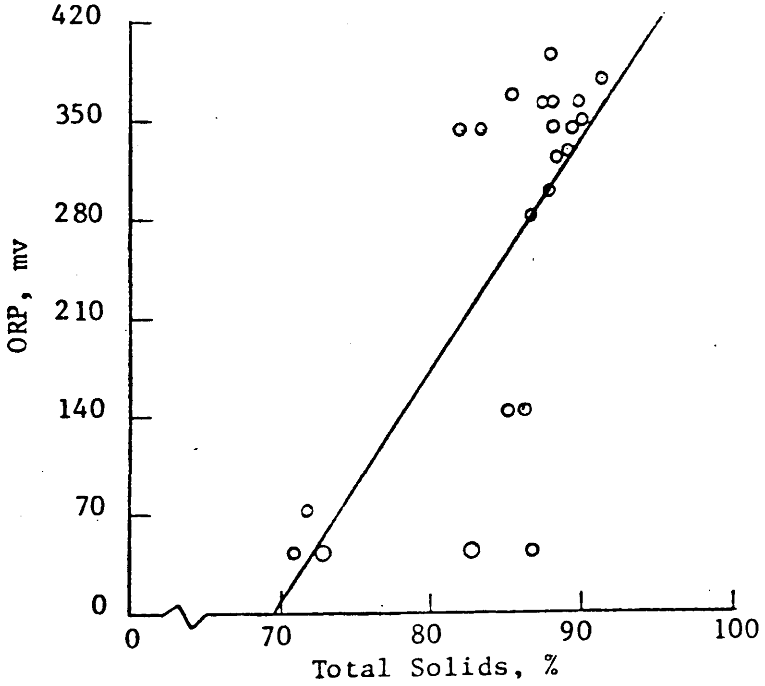


Figure 21. ORP VERSUS TOTAL SOLIDS

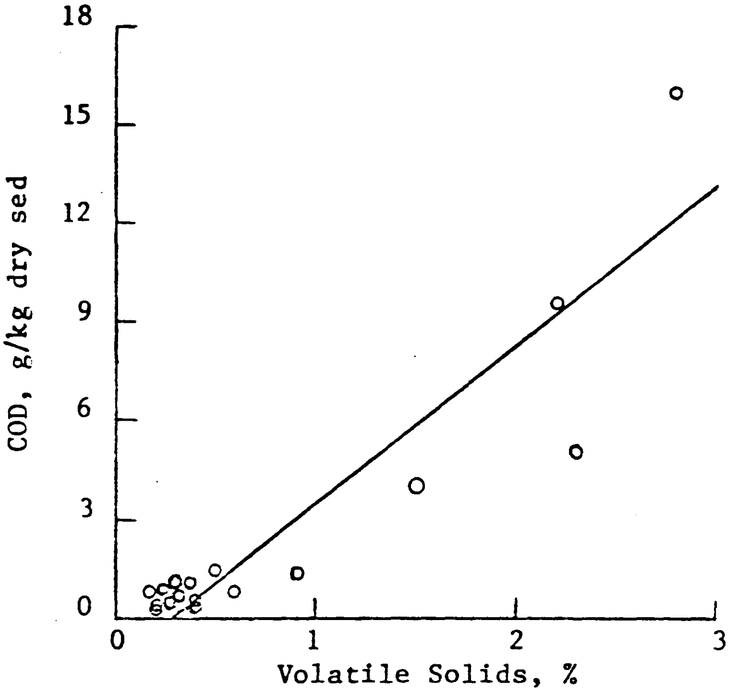


Figure 22. COD VERSUS VOLATILE SOLIDS

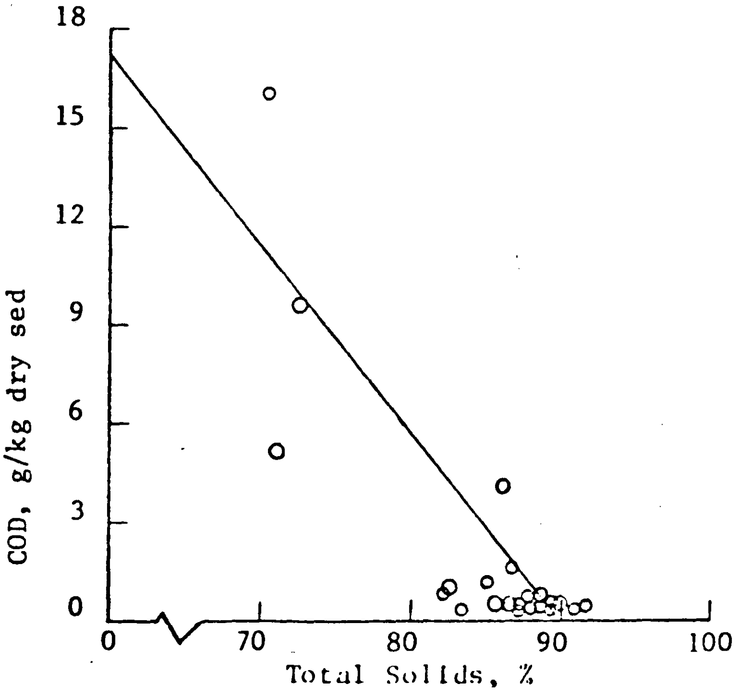


Figure 23. COD VERSUS TOTAL SOLIDS

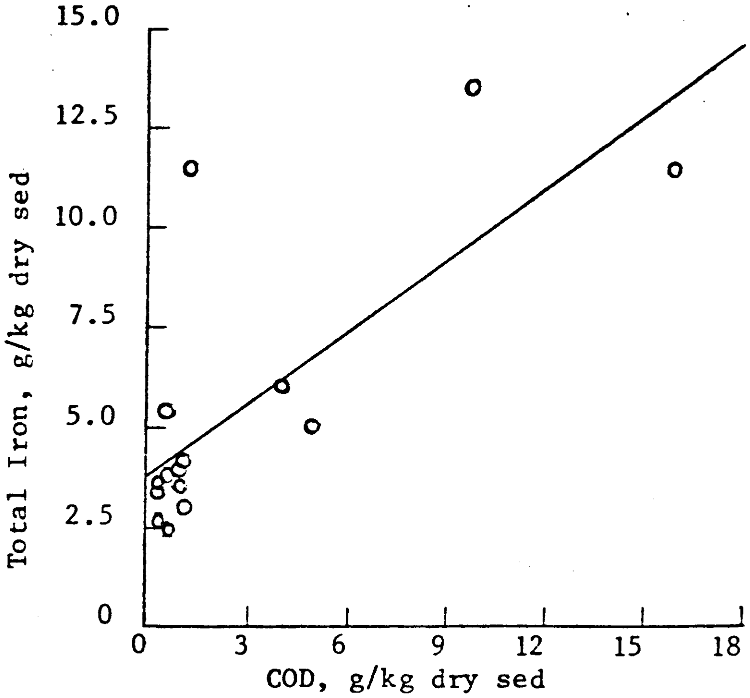


Figure 24. TOTAL IRON VERSUS COD

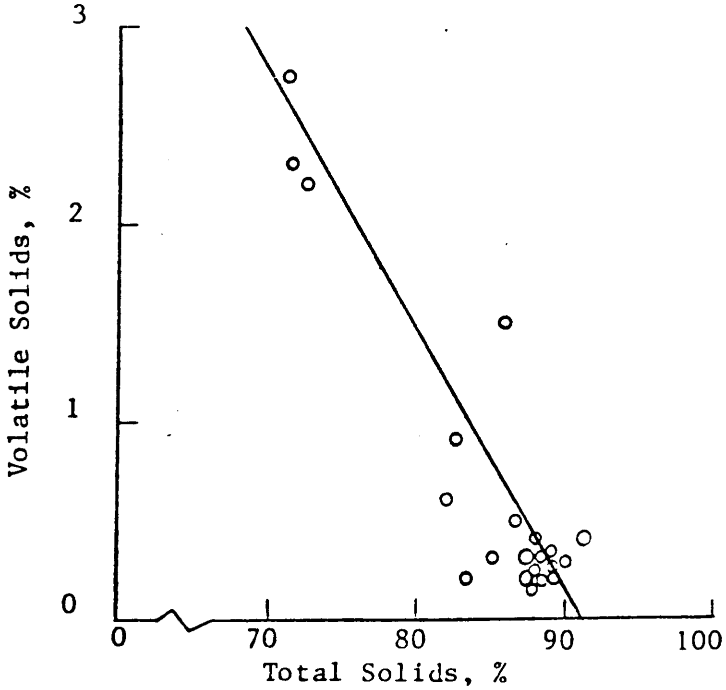


Figure 25. VOLATILE SOLIDS VERSUS TOTAL SOLIDS

TABLE 24

SUMMARY OF LEAST SQUARES LINEAR REGRESSION ANALYSIS OF SEDIMENT DATA

Figure	Equation	Correlation Coefficient
4. Oxygen Uptake-vs-Sediment V.S.	TOD25W = 19.5 + 143.7(VSS)	0.89 *
5. Oxygen Uptake-vs-Sediment T.S.	TOD25W = 1605 - 17.5(TSS)	-0.89 *
6. Oxygen Uptake-vs-Sediment COD	TOD25W = 64.3 + 0.03(COD)	0.76 *
7. Oxygen Uptake-vs-Sediment T.Iron	TOD25W = 13.8 + 0.02(TFE)	0.56 *
8. Oxygen Uptake-vs-Sediment ORP	TOD25W = 298 - 0.07(ORP)	-0.74 *
9. T.Iron-vs-ORP	TFE = 4558 - 0.03(ORP)	-0.73 *
10. COD-vs-ORP	COD = 2794 - 3.54(ORP)	-0.68 *
11. T.Iron-vs-V.S.	TFE = 8276 - 621(VSS)	0.74 *
12. T.Iron-vs-T.S.	TFE = 33440 - 338(TSS)	-0.67 *
13. ORP-vs-V.S.	ORP = 349 - 129(VSS)	-0.76 *
14. ORP-vs-T.S.	ORP = 1042 + 15.3(TSS)	0.73 *
15. COD-vs-V.S.	COD = -990 + 4500(VSS)	0.92 *
16. COD-vs-T.S.	COD = 44814 - 505(TSS)	-0.84 *
17. T.Iron-vs-COD	TFE = 3366+ 0.7(COD)	0.79 *
18. V.S.-vs-T.S.	VSS = 11 + 0.12(TSS)	-0.91 *

*indicates a significant correlation at 95% confidence.

Oxygen Uptake Measured With Distilled Water and Site Water

Oxygen uptake was measured in triplicate on a sediment from Aspelmeier Ditch (M.P. 545) using deionized-distilled water at 7°C and at 25°C. Oxygen uptake was then run on subsamples of the same sediment using site water at 7°C and at 25°C. Analysis of results showed that there was no significant difference between the mean values of oxygen uptake using deionized-distilled water and the mean values obtained using site water for each temperature. The variation in the oxygen uptake using disposal site water was slightly less, however, and was the method of choice for determining sediment oxygen demand.

Oxygen Uptake and Biological Activity

An experiment was performed on a sediment from Greys Chute (M.P. 356) to determine what portion of the total oxygen uptake during the 1-hour measurement was due to biological activity. The oxygen uptake of the sediment-distilled water slurry was determined by duplicate analysis to be 406 gO_2/m^3 of wet sediment at 25°C. Formaldehyde (formalin solution) was added to a separate sediment-water slurry to inhibit biological activity. The final formaldehyde concentration was 0.2% (v/v). The average oxygen uptake of duplicate analyses of the inhibited sediment was 392 gO_2/m^3 of wet sediment at 25°C. This was not a significant difference from the uninhibited sediment. Standard plate counts were made on the sediment before exposure to the formalin solution and were found to be $6x10^8$/gram of wet sediment. Standard plate counts were made on the inhibited sediment after oxygen uptake analysis and were found to be less than $1x10^6$/gram of wet sediment (>99% kill). Figure 26 illustrates the results of these oxygen uptake analyses.

Oxygen Uptake and Depth of Sediment Samples

A 14 inch core sample was taken near sample 24 at Greys Chute. Oxygen uptake was determined at 25°C on the core sample at different depths. Triplicate analyses were performed on subsamples withdrawn 0-2 inches (from top), 5-6 inches, and 12-14 inches. Mean values of the results were 224 $g0_2/m^3$, 709 $g0_2/m^3$, and 928 $g0_2/m^3$ of wet sediment, respectively. The oxygen uptake measured on a sample taken with the Ponar dredge at this site was 504 $g0_2/m^3$. Figure 27 illustrates these analyses.

Effect of Temperature on Oxygen Uptake

Figure 28 illustrates the oxygen uptake results at 7°C and 25°C for all 24 samples studied.

Oxygen Uptake and Initial Dissolved Oxygen Concentration

Oxygen uptake was determined for subsamples of a sediment from Keokuk (M.P. 356). Triplicate analyses were made using initial dissolved oxygen concentrations of 1.0 mg/l, 5.0 mg/l, and 8.0 mg/l. Analyses were for 30 minutes each. Initial dissolved oxygen concentrations in the respirometer were obtained by bubbling nitrogen gas through the water prior to sediment injection. The mean uptake values at 1.0 mg/l, 5.0 mg/l and 8.0 mg/l initial dissolved oxygen concentration were 232 g/m^3, 252 g/m^3, and 246 g/m^3 respectively. There was no significant difference between the means of the oxygen uptakes at the three different initial dissolved oxygen concentrations. Deionized-distilled water was used in these analyses.

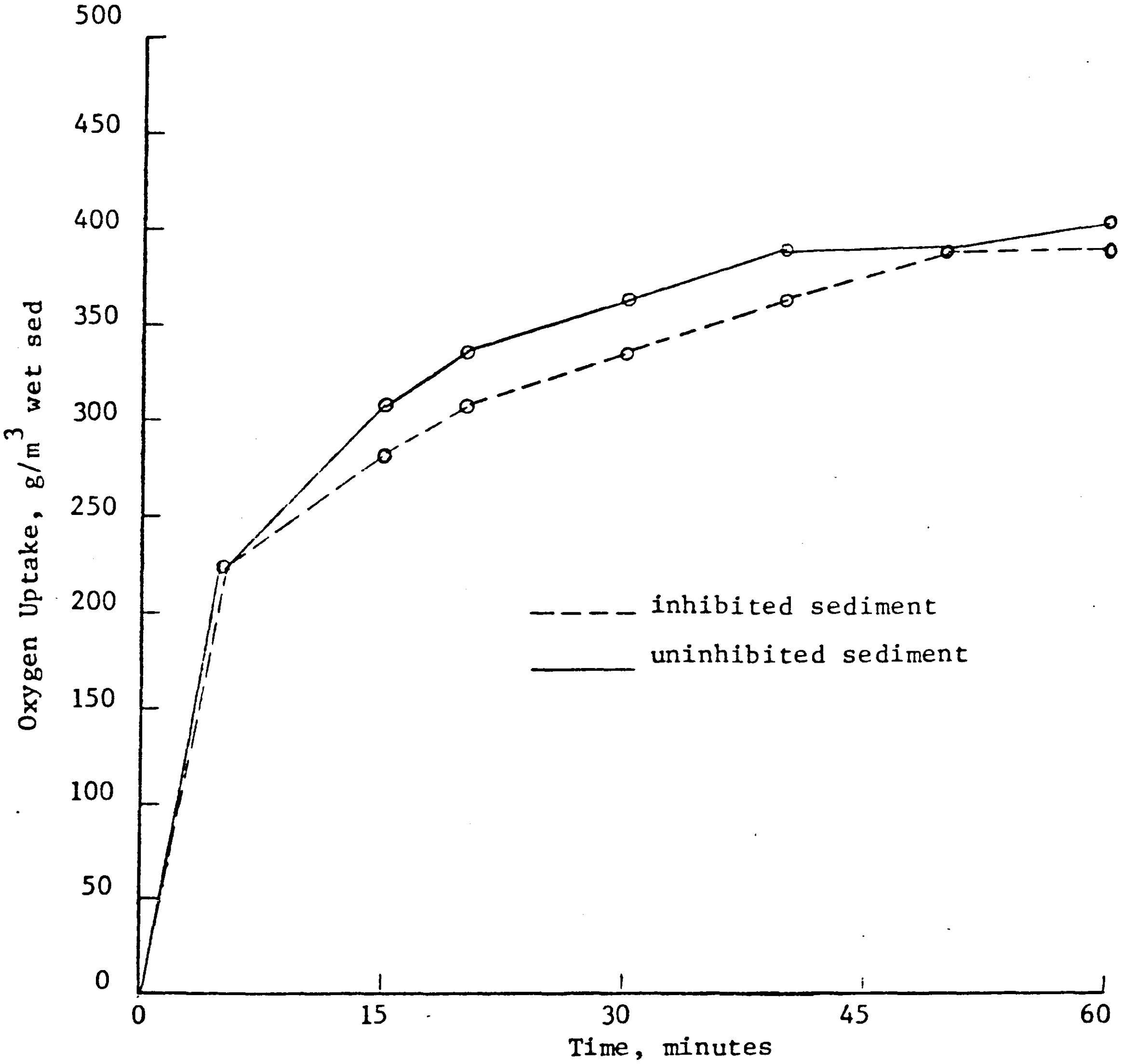


Figure 26. INFLUENCE OF BIOLOGICAL ACTIVITY ON OXYGEN UPTAKE

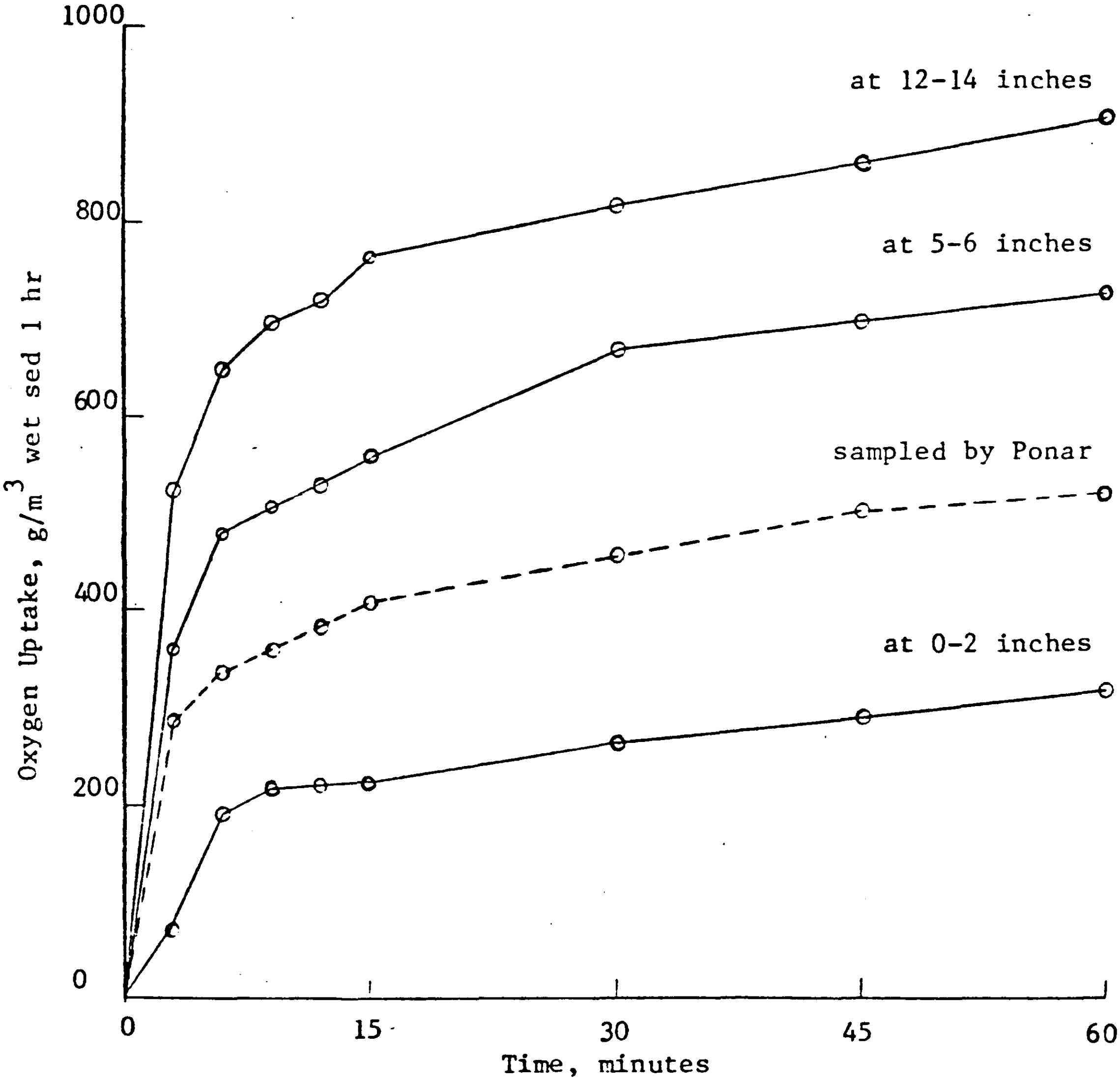


Figure 27. OXYGEN UPTAKE AT DIFFERENT DEPTHS

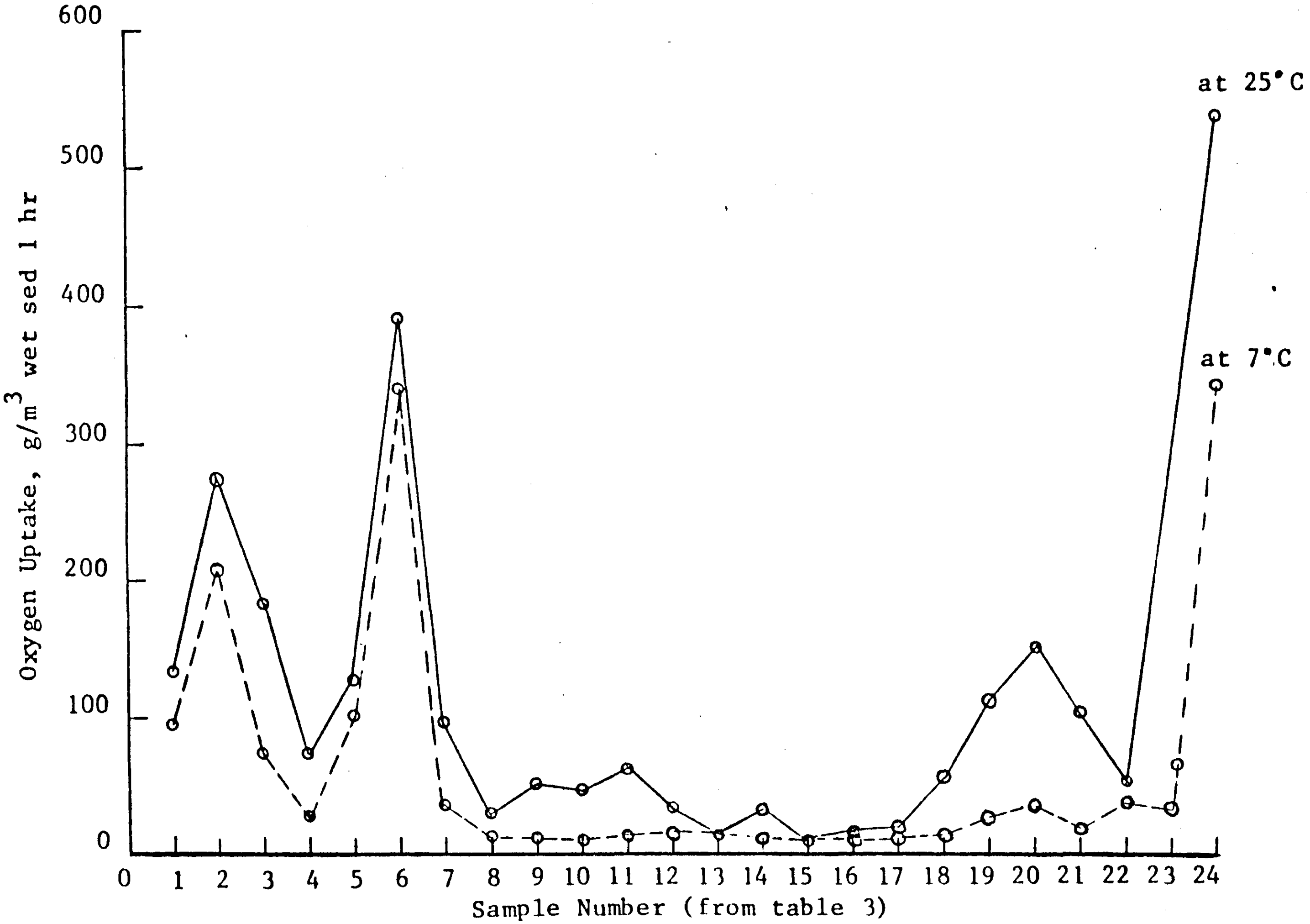


Figure 28. OXYGEN UPTAKE AT 7°C AND 25°C

Oxygen Uptake and Sample Storage

A sediment from the Iowa River was sampled with a Ponar dredge to study the effects of sample storage time on sediment oxygen uptake, COD, ORP, T.S., V.S., and T. Sulfide. The sample was taken approximately 300 feet upstream from the University Water Plant intake structure. The sample was collected and stored in accordance with the recommended procedure (Wes, 1976) as described in Chapter IV. The storage period was nine days. Table 25 and Figure 29 present these results.

Rates of Oxygen Uptake

Data resulting from 4 oxygen uptake experiments are plotted in Figures 30, 31, and 32 to illustrate the range of uptake rates encountered during this study. Figure 30 illustrates the rate of a sediment with high uptake at 25°C and 7°C (528 g/m^3 and 312 g/m^3). Figure 26 illustrates the rate of a sediment with low uptake at 25°C (42 g/m^3). The data appear to fit a first order reaction. Evaluation of the rate constants and additional analyses of these data follow.

Analysis of Oxygen Uptake Rates

A Thomas slope analysis was performed on the oxygen uptake data presented in Figures 30-32. Calculated values of the rate constant and the ultimate oxygen were substituted into the following first order rate equation to predict sediment oxygen uptake with time.

$$TOD_t = TOD_u \, (1 - e^{-kt}) \qquad (3)$$

TOD_t = oxygen uptake at time t, g/m^3 wet sediment

TOD_u = ultimate oxygen uptake, g/m^3 wet sediment

TABLE 25

EFFECT OF STORAGE TIME ON SEDIMENT CHARACTERISTICS

Day	O_2 Uptake g/m^3 wet 25°C	COD mg/kg dry	Total Solids %	Volatile Solids %	ORP (mv)	Total Sulfide mg/kg dry
0	616	11600	63.7	4.6	84	126
1	485*	12900	63.2	4.7	131	112
2	467*	12700	64.2	4.6	91	78*
3	504*	12800	65.7	4.2	81	62*
4	485*	13300	64.6	4.3	111	42*
5	448*	12800	63.9	4.1	131	36*
6	485*	13300	64.0	4.3	91	45*
7	420*	14800	64.9	4.0	101	51*
8	420*	14300	64.7	4.4	151	31*
9	400*	13900	64.8	4.5	161	48*

* significantly less than day 0 at 95% confidence using one-tailed 't' statistic

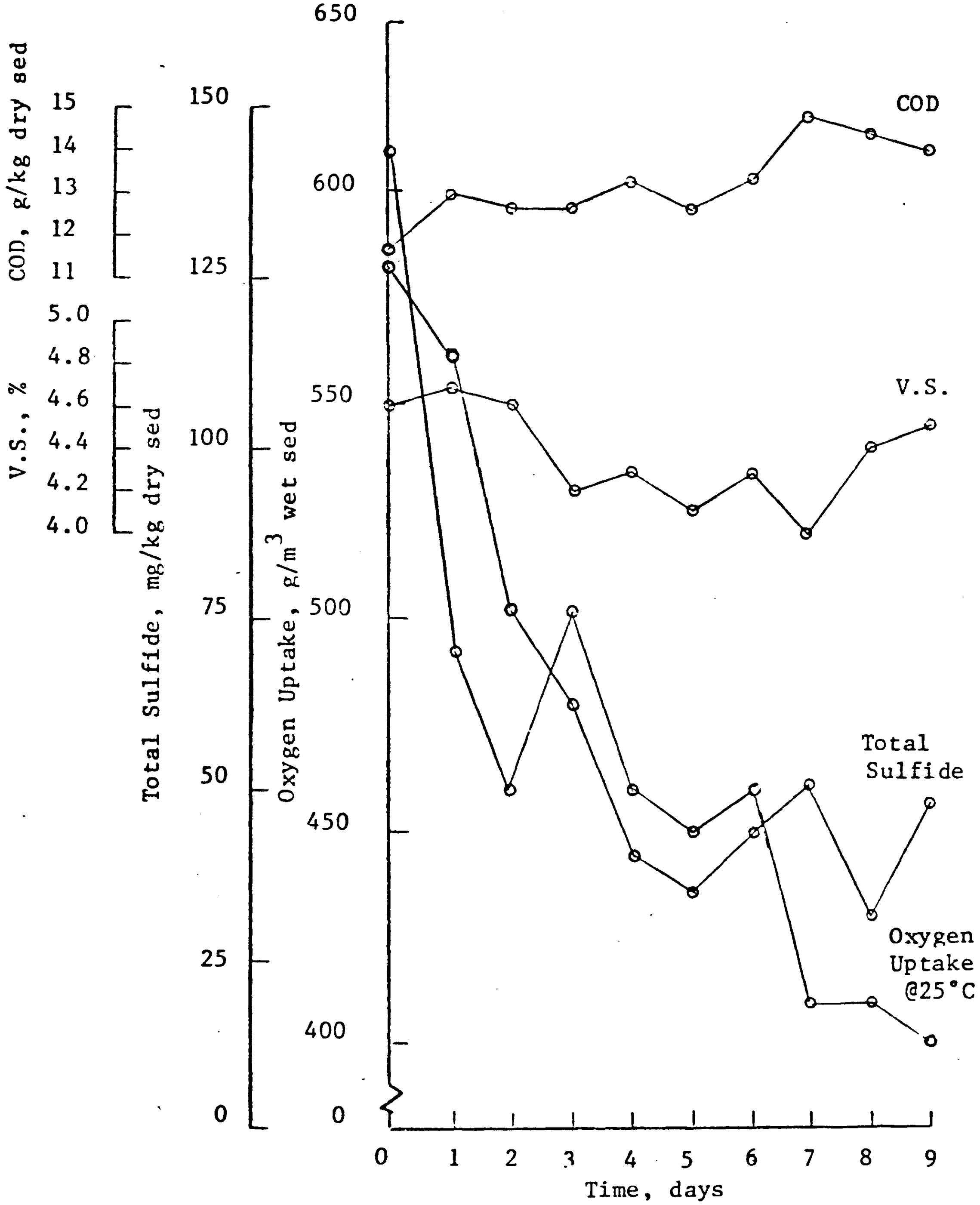


Figure 29. EFFECT OF STORAGE TIME ON SEDIMENT CHARACTERISTICS

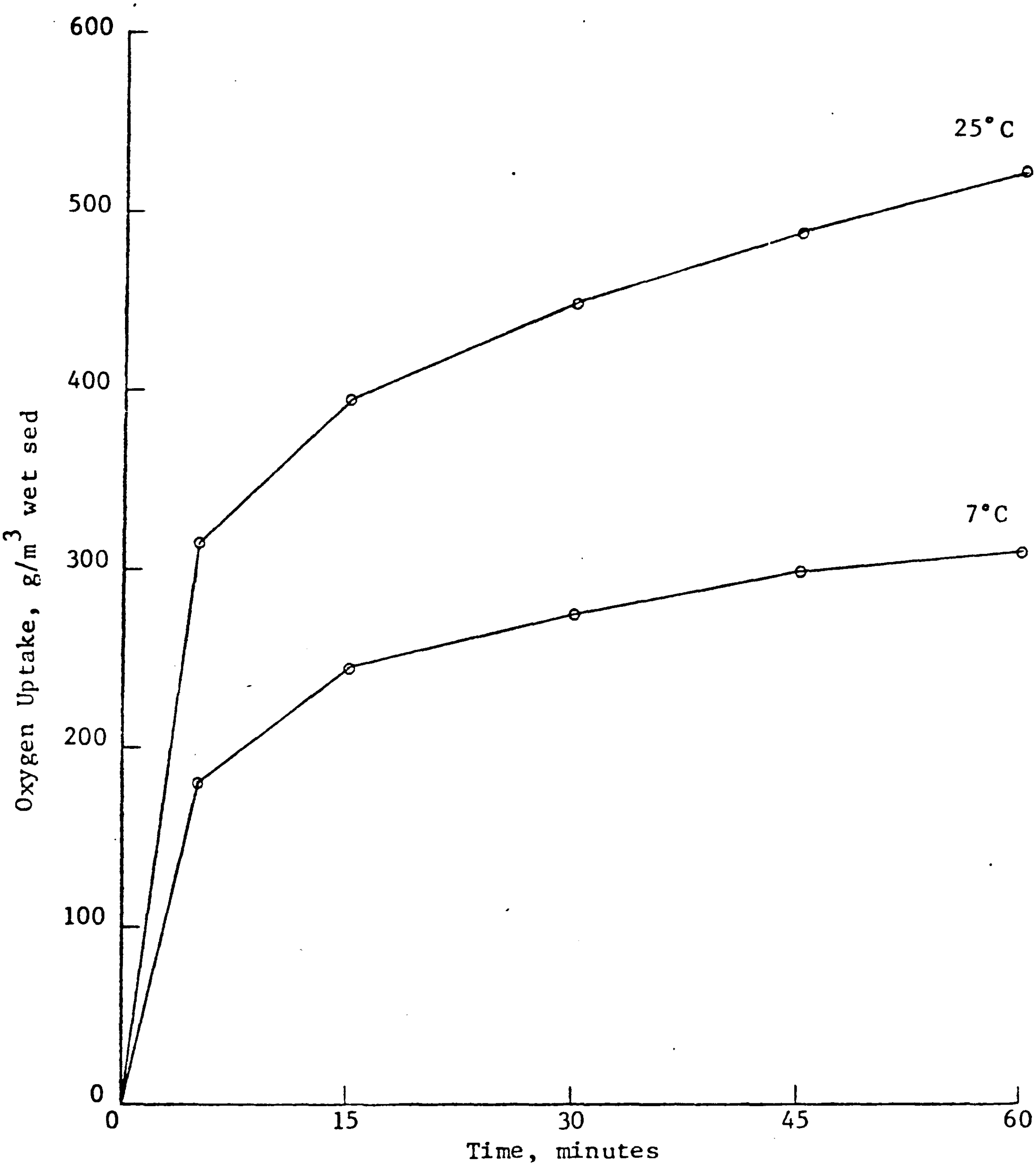


Figure 30. HIGH RATE OXYGEN UPTAKE AT 25°C AND 7°C
(GREYS CHUTE, M.P. 356)

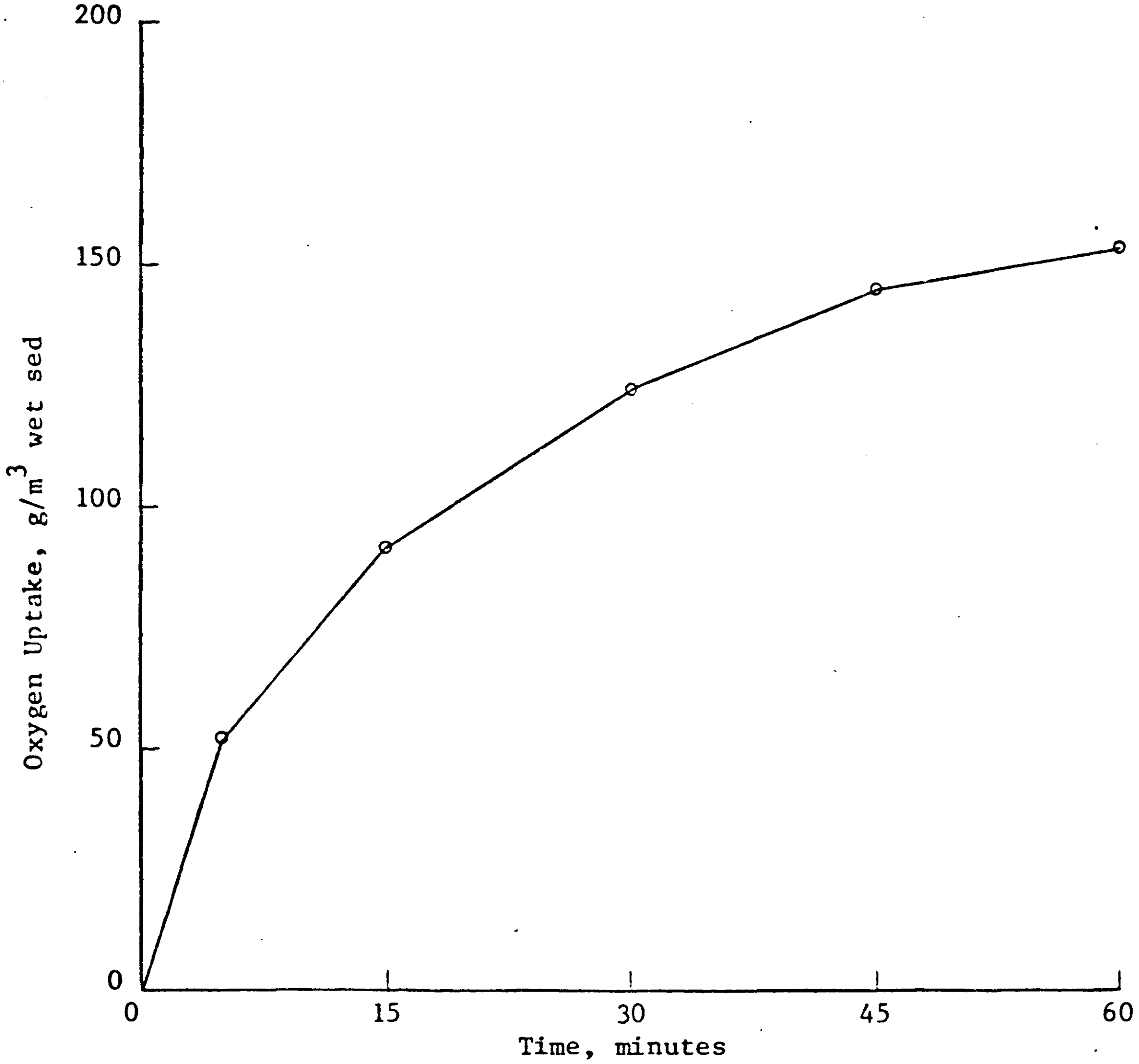


Figure 31. MEDIUM RATE OXYGEN UPTAKE RATE AT 25°C
(KEOKUK, M.P. 356)

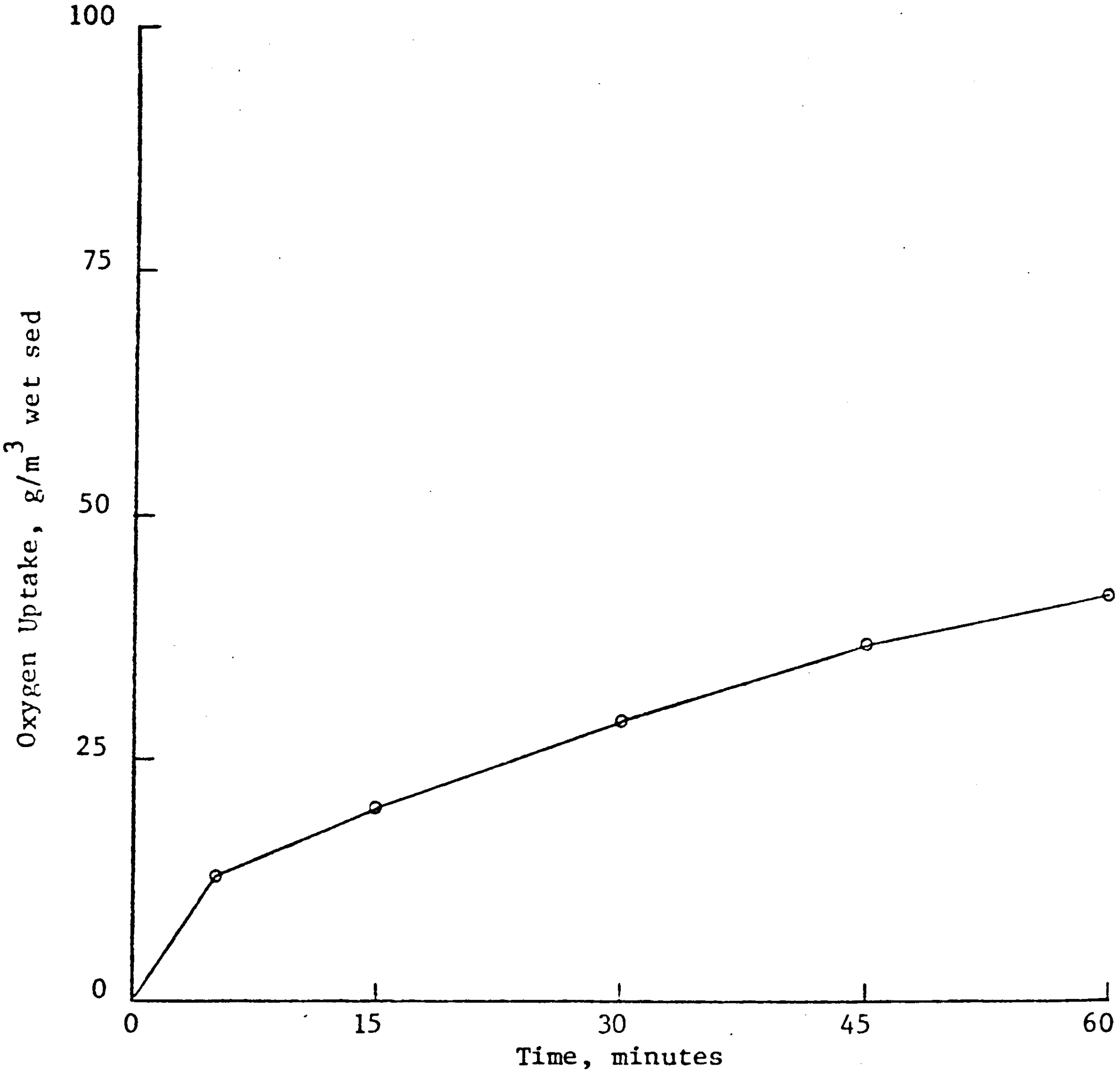


Figure 32.LOW RATE OXYGEN UPTAKE AT 25°C
(MUSCATINE, M.P. 447)

k = first order rate constant, min^{-1}

t = time, minutes

The values of TOD_t, predicted by the equation were plotted along with the observed oxygen uptake values. Figures 33 and 34 show the resulting relationships. Values for TOD_u and k for each of the figures are presented in Table 26 below.

Table 26

TOD_u AND k BY THOMAS SLOPE METHOD

	k, 1/min.	TOD_u g/m^3 wet sed	Sample Location
High Rate at 25°C	0.16	704	Greys Chute M.P. 356
High Rate at 7°C	0.15	402	Greys Chute M.P. 356
Medium Rate at 25°C	0.10	155	Keokuk M.P. 356
Low Rate at 25°C	0.07	41	Muscatine M.P. 447

Correlations of Oxygen Uptake With Sediment Analyses

The data analysis was performed to see if any readily measured bulk sediment characteristic would correlate with oxygen uptake. A significant correlation for predicting and modeling purposes would make determination of oxygen uptake much less time consuming and more economical. The data analyses showed some highly significant bivariate correlation between oxygen uptake and sediment COD, T.S. and V.S. The correlation coefficient between oxygen uptake and various combinations

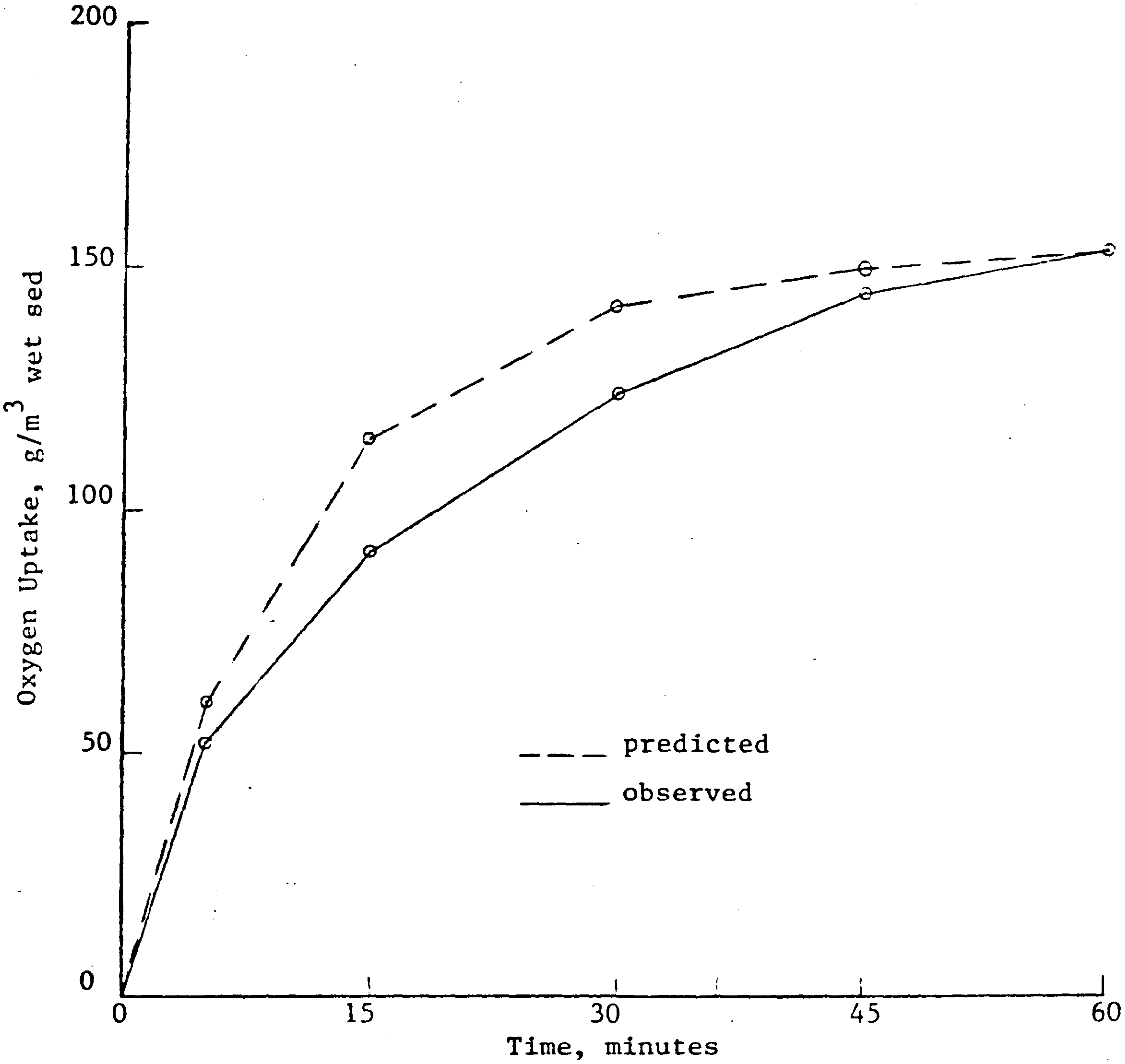


Figure 33. OBSERVED OXYGEN UPTAKE AT 25°C VERSUS OXYGEN UPTAKE PREDICTED BY $TOD_t = TOD_u (1-e^{-kt})$. KEOKUK, M.P. 356

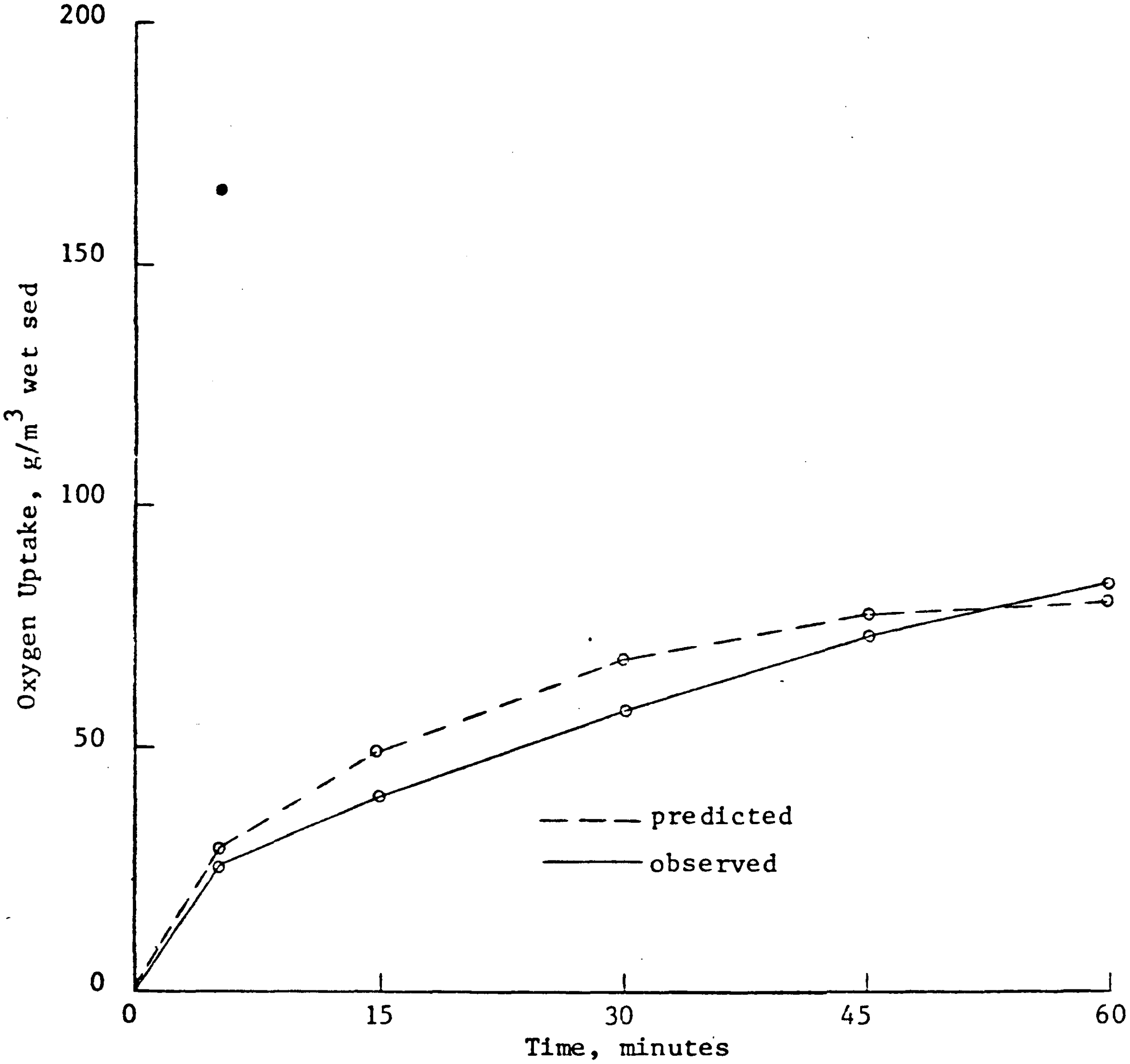


Figure 34. OBSERVED OXYGEN UPTAKE AT 25°C VERSUS OXYGEN UPTAKE PREDICTED BY $TOD_t = TOD_u (1-e^{-kt})$. MUSCATINE, M.P. 447

of additional predictor variables was not significantly improved over the highest bivariate correlation coefficient. The correlation of oxygen uptake with volatile solids had a significant correlation coefficient of 0.89 (Table 24). However, multiple linear regressions using 2, 3, and 4 predictor variable combinations did not improve upon the bivariate correlation coefficient of 0.96. Sediment volatile solids consistently had the highest bivariate correlation with oxygen uptake, ranging from 0.86 to 0.96 over the temperature range from 25°C - 7°C. The correlation between oxygen uptake and volatile solids support the benthic oxygen demand studies by Fair *et al* (1941) and Rolley and Owens (1967). These results also support the speculation by Schubel *et al* (1976) that the sediment's organic carbon content (V.S.) would be related to oxygen uptake.

Some high correlations between the various bulk sediment parameters were also observed. Sediment volatile solids with COD had a correlation coefficient greater than 0.90 as did sediment total solids with volatile solids (-0.91). The explanation for the high inverse correlation between total and volatile solids was not as obvious as that for the high correlations between volatile solids and COD. Most of the "dirty" sediments were very fine-grained (i.e. silts and clays). These sediments contained more volatile matter than the very coarse-grained "clean", sandy sediments. The fine-grained dirty sediment retained more water duing sample collection with the Ponar dredge than did the coarse-grained clean sediment. Thus when a total solids analysis was performed, the results consistently showed higher total solids on a clean coarse-grained sediment than on a fine-grained dirty sediment containing more volatile material.

Oxygen uptake measured at 7°C consistently had higher correlations with the bulk sediment parameters than did the oxygen uptake measured at 25°C. Oxygen uptake expressed as mass per unit volume of wet sediment (g/m^3) had higher correlations with the bulk sediment parameters than when it was expressed as mass per unit mass of dry sediment (g/kg). Expressing bulk sediment parameters in units per unit volume of wet sediment resulted in much poorer correlations than when they were expressed as units per unit mass of dry sediment.

These alternative units for expressing oxygen uptake and bulk sediment parameters were evaluated in order to optimize correlations and prediction of sediment oxygen demand. The recommended method of expression for sediment parameters is units of parameter (e.g. V.S.) per unit mass of dry sediment as calculated previously (Wes, 1977) This method assumes that the concentration of the parameter is zero in the intersticial water. This is reasonably correct for parameters such as V.S. and T.S. Parameters such as COD or total sulfide can have significant concentrations in the intersticial water depending on the sediment's ORP, its history, and its age. These concentrations can be significant even in samples that have a high sand and total solids content. A method of parameter expression that considers both the mass and nature of the solids and the volume and nature of the intersticial water should provide the best correlation with the sediment total oxygen demand. Parameter units of mass per unit volume of wet sediment (g/m^3) seemed to satisfy these criteria and were the first choice for analysis. Subsequent analyses, however, clearly indicated that for these data, the oxygen uptake could best be presented using the bulk sediment parameters expressed in the recommended units (mg/kg dry sed). It is believed that this occurred because the majority of the sediment samples were "clean" and the intersticial water approached the assumption of zero parametric concentration. Analysis of more "dirty" samples and their pore waters are needed to support the proposed rational method of expression and strengthen the correlation of oxygen demand with bulk sediment chemistry.

The Respirometric Method for Measuring Oxygen Uptake

The respirometric approach used in this study showed that reproducible measurements of oxygen uptake by suspended sediments could be obtained. It was felt that the apparatus used in this study was more precise and easier to use than the BOD bottle method used by Lee *et al* (1975, 1977). It also had the capability to monitor both the immediate oxygen demand exerted at the injection of sediment into the respirometer and the long term demand.

Two procedural steps in the respirometric method were studied to determine their influence on test results. These steps were the initial dissolved oxygen concentration in the respirometer and the use of site water or deionized-distilled water as the suspending medium. Triplicate evaluations of oxygen demand at three different initial concentrations of dissolved oxygen indicated that sediment oxygen uptake was not affected by oxygen concentrations between 1.0 mg/l and saturation. This supports benthic demand studies of Baity (1938) but conflicts with the results of Edwards and Rolley (1965) and Chiaro and Burke (1978) who found decreasing uptake and rate of uptake with decreasing oxygen concentration in the overlying water. Triplicate oxygen uptake analyses were used to determine that there was no significant difference between the mean oxygen demand using site water and the mean demand using deionized-distilled water. This indicates that the sediments, their intersticial water and the site water, were "clean" and low in oxygen demanding substances, e.g. reduced species of sulfur.

The source (chemical or biological) of the oxygen demand in these sediments was also determined. The demand exerted by a control sediment was not significantly different from the demand exerted by a sample tested with formaldehyde (0.2% v/v) to inhibit biological activity. This supports the results of Edwards and Rolley (1965) who found no correlations between benthic oxygen demand of scoured sediment and the sediment bacterial count. Therefore, oxidative chemical reactions are the source of the demand in these sediments.

Sampling Methods and Sample Storage

Figure 27 showed that oxygen uptake increased significantly with the depth of the sediment sample. This agrees with Reynolds *et al* (1973) as well as benthic oxygen demand studies by Ogunranbi and Dobbins (1970). It is speculated that as ORP becomes increasingly negative with the depths of the core sample, concentrations of reduced materials (sulfide and iron) also increase thus contributing to higher oxygen demands. Oxygen uptakes ranged from 224 g/m^3 to 928 g/m^3 in the 14 inch core sample taken at Greys Chute (M.P. 356). The depth of samples taken with the Ponar dredge sampler throughout the study was estimated to be 5 inches. The oxygen uptake of the Ponar sampled sediment was 504 g/m^3. These results indicate that the measured oxygen uptake of the sediments in this study were indicative of the depth sampled. They do not, however, indicate the much larger oxygen demand that may be exerted by sediments dredged from typical depths of 1 to 5 feet. The actual demand resulting from a deep dredging operation will vary with the dredge site's material and and its history. It is unlikely that this demand could be reliably estimated or predicted from a shallow (5 inch) sediment sample. The oxygen uptake of several subsamples taken from sediment cores to the expected dredged depth would provide a more reasonable estimate of the oxygen demand of the resuspended sediment. The use of a core sample would also eliminate interferences caused by exposure of the sediment to the variable water column and the atmosphere. The variation in oxygen uptake and bulk sediment chemistry with depth also indicates that the results of the standard elutriate test can be significantly influenced by the methodology of sediment collection, storage and preparation.

The sample storage experiment (Table 25 and Figure 29) indicated that significant decreases in oxygen uptake and total sulfide occurred during sample storage using recommended preservation conditions (Wes, 1977). The loss in oxygen uptake and total sulfide was significant after only 1 and 2 days of storage, respectively, probably due to oxygen transfer through the plastic storage bag. The stoichiometric amount of oxygen required to satisfy the complete oxidation of sulfide is 1.94 gO_2/gS. During the 9 days of storage the loss in total sulfide was 88.7 g/m^3 and the drop in oxygen demand was 217 g/m^3. Therefore, 172 g/m^3 or 80% of the loss of oxygen uptake could be attributed to sulfide conversion. Oxidation of reduced species of iron and manganese could readily account for the remaining 20%. The storage data indicate that there was no significant decrease in the sediment COD, T.S., or V.S. Although the sulfide oxidation should reduce the sediment COD, the theoretical reduction is only 1.3% which is well below the analytical variation of the COD test (5.4%).

These results clearly indicate that sediment oxygen demand should be determined immediately and that recommended protocol for sample preservation is not adequate to prevent significant changes in some bulk chemical parameters. All samples for the study were analyzed within 72 hours of collection. Although this is reasonably prompt, it resulted in a negative error of 15-20% in the oxygen demand. Collection of relatively undisturbed sediments using a core sampler rather than a Ponar dredge would improve the preservation of the physical and chemical properties of the in-situ materials.

Cumulative Oxygen Uptake and Uptake Rates at Different Temperatures

Figure 28 and Table 22 illustrate that the cumulative (1 hour) oxygen demand and the rate of oxygen demand were lower at 7°C than at 25°C. Linear regression analysis indicated that a significant relationship ($r = 0.95$) existed between the cumulative oxygen uptakes measured at the two temperatures.

$$\text{TOD25W} = 33.87 + 1.24\ (\text{TOD7W})$$

The reduction in oxygen demand at the lower temperatures was related to reduction in the kinetics of physio-chemical rather than biochemical reactions since the later oxygen demands were shown to be negligible in these sediments.

The sediment oxygen demand was modeled using a first order reaction rate expression. The magnitude of TODu was assumed to be independent of temperature. The variation in the first order rate constant (k) with temperature was formulated in terms of the von't Hoff-Arrhenius relationship for temperatures between 7° and 25°C.

$$(k)_T = (k)_{25}{}^{\theta(T-25)}$$

k_T = rate constant at temperature T, min.^{-1}

k_{25} = rate constant at 25°C, min.^{-1}

θ = temperature coefficient

Term θ was determined to be 1.004, 1.039 and 1.032 for high, medium and low oxygen demands respectively. The "goodness of fit" of the first order reaction varied inversely with the magnitude of the cumulative demand after 1 hour. The initial demand (0-10 minutes) followed closely to a first order rate. Thereafter, the observed demands were generally less than predicted. Samples having a large oxygen uptake could be best represented by two sequential zero order reactions. Similar diphasic uptake rates were observed by Reynolds *et al* (1973) in sediments from the Houston Ship Canal. Although the development of a complex kinetic relationship that more accurately represented the observed oxygen uptake rates would be of interest, it would have limited general use. Sediment-water chemistry and physical and biological characteristics vary with the site and within a particular site. This prohibits the use of a single kinetic expression that would consistently and accurately simulate all of the geo-chemical reactions that cumulatively produce an oxygen demand. The first order expression developed for this study provides a simple, and reasonable estimate of the oxygen status of the suspended sediments. The results obtained are conservative.

Predicting Oxygen Uptake of a Dredge Material Discharge

All data analyses were conducted on oxygen uptakes measured for a 1 hour period. The relationships derived from these analyses however, can be used to predict the oxygen status of dredge material discharge operations with dredge slurry pipe detention times less than one hour. Dredge slurries are a varying mixture of dredged sediment and dredging fluid, that is, dredge site water. In pipeline disposal operations, these slurries seldom have pipe detention times greater than 5 to 10 minutes. Knowing the oxygen concentration of the dredge site water and the 1 hour oxygen uptake of the dredged material, a dilution factor can be calculated to determine if adequate oxygen is available in the dredging fluid to satisfy the sediment demand. If the dilution factor is less than the site water to sediment ratio (v/v) in the dredge pipe, the discharge will be oxic. However, if the dilution factor is greater than the site water to sediment ratio, the oxygen uptake rate and the hydraulic detention time in the dredge pipe must be considered in order to determine the oxygen status of the discharge. From Table 26 it is decided whether the measured oxygen uptake is high, medium, or low rate. An appropriate k value is then selected and substituted into equation 3 to determine the ultimate oxygen uptake (TOD_u).

$$TOD_u = \frac{TOD_{60}}{(1-e-kt)}$$

Using the k value, TOD_u, and t (for the dredge pipe detention time) in the above equation, a new oxygen uptake value is obtained, TOD_t, for which a dilution factor must be calculated. If the volume of site water in the dredge pipe is not enough to satisfy this oxygen demand the discharge is anoxic. It is realized that hydraulic dredging operations have widely variable conditions for example hydraulic regime, detention time, sediment to water ratios, duration of discharge, etc. The above approach and methodology however may be used to determine the oxygen status existing at the discharge regardless of these operational differences. Such information is valuable to the evaluation of the environmental impact of dredge material discharge and can be gathered economically and without sophisticated equipment.

The following is an example of predicting the oxygen status of a dredge discharge.

Given: Temperature of site water = 25°C

D.O. of site water = 8.0 mg/l

Ratio of site water to dredge material = 5:1 (v/v)

Detention time of sediment in dredge pipe = 1 minute

Volatile solids of material to be dredge = 1.9%

Step 1: Determine 1 hour oxygen uptake based on sediment analysis

TOD25W = 19.48 + 143.73 (VSS)

TOD25W = 19.48 + 143.73 (1.9)

= 293 gO_2/m^3 dredge material for 1 hour

Step 2: Determine oxygen available in dredge slurry at 5 volumes of site water to 1 volume sediment

($5m^3$ site water) (8.0 mg/l) = 40 gO_2/m^3 of dredge material.

Since 293 >> 40 gO_2/m^3, the discharge will be anoxic if the dredge pipe detention time is 1 hour

Step 3: Determine oxygen uptake at the given dredge pipe detention time of 1 minute

a. From Table 26 select k value of 0.10/min at 25°C (293 ≅ medium rate)

b. Determine TOD_u, ultimate oxygen uptake

$$TOD_{60} = TOD_u(1-e^{-kt})$$

$$293 = TOD_u(1-e^{-0.10(60)})$$

$$TOD_u = 294\ gO_2/m^3 \text{ wet sed}$$

c. Determine TOD_5, oxygen uptake at 1 minute

$$TOD_5 = 294\ (1-e^{-0.10(1)})$$

$$= 28\ gO_2/m^3 \text{ wet sed}$$

The oxygen uptake of the sediment at 1 minute detention time, 28 g/m^3, is less than the oxygen available in the hydraulic dredging fluid (water), 40 g/m^3. The discharge therefore will be oxic, with a dissolved oxygen concentration of 2.4 mg/l.

CHAPTER VIII

RESULTS OF MATHEMATICAL MODELING AND KINETIC STUDIES

Steady State Model

The Langmuir adsorption isotherm holds that at equilibrium, the amount of pollutant adsorbed onto the solids r, is directly proportional to the dissolved pollutant concentration C, at low concentrations (Langmuir, 1918). However, as the pollutant concentration increases, one monolayer of pollutant is adsorbed onto the solids and a limiting solids capacity r_{max} is reached.

Langmuir adsorption kinetics may be expressed by the following equations for the dissolved and adsorbed pollutant concentrations. (See Figure 35).

$$\frac{dC}{dt} = -K_1 CM \left(r_{max} - r\right) + K_2 rM \qquad (4)$$

c = dissolved pollutant µg/l

r = adsorbed pollutant concentration, µg/kg, i.e., ratio of adsorbed pollutant to dry weight of solids

r_{max} = maximum adsorbed pollutant concentration, µg/kg

t = time, hours

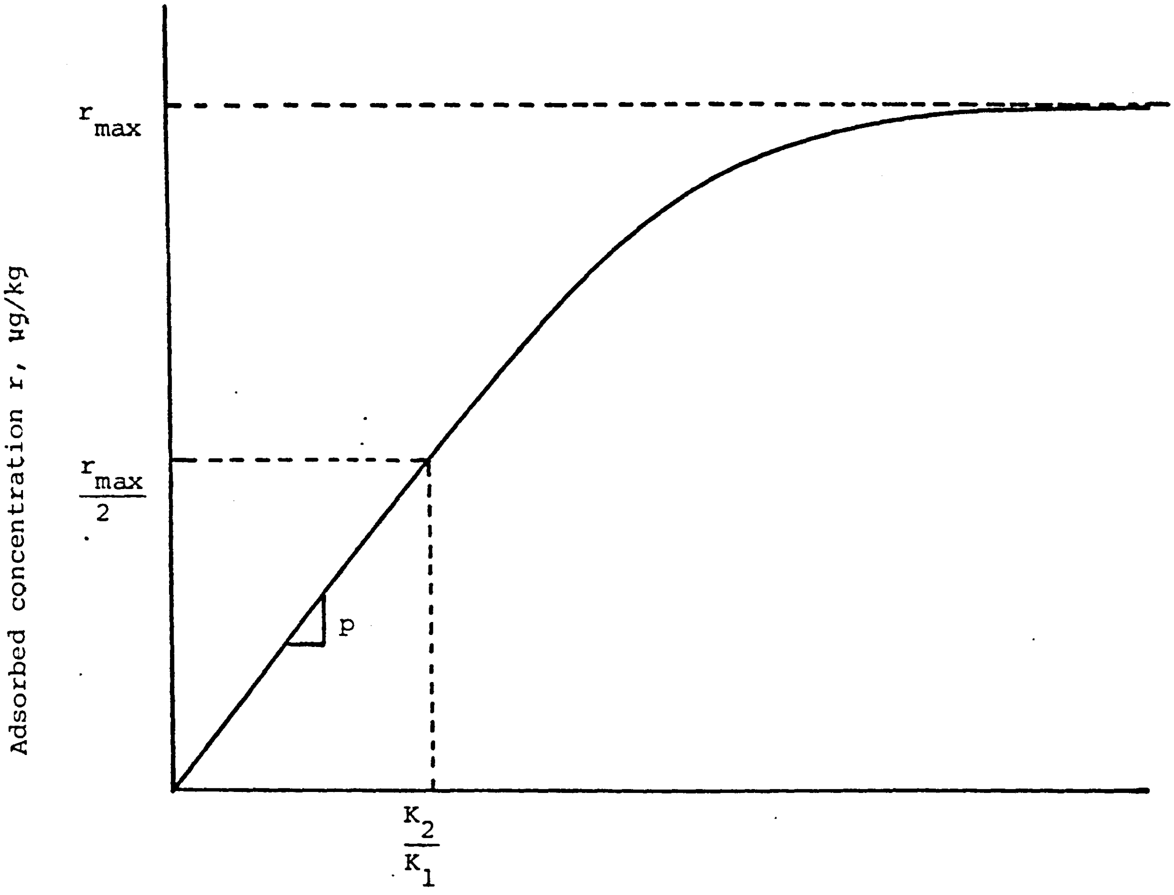
M = suspended solids concentration, kg/l

K_1 = adsorption rate constant, 1/µg hour

K_2 = desorption rate constant, 1/hour

$$\frac{dr}{dt} = K_1 C\left(r_{max} - r\right) - K_2 r \qquad (5)$$

$$\frac{dM}{dt} = 0 \qquad (6)$$



Dissolved Concentration C, μg/l

P = Partition coefficient, $\frac{\mu g/kg}{\mu g/l}$

Figure 35. Langmuir Adsorption Isotherm

At steady state, $\frac{dc}{dt} = 0$.

Solving equation (4),

$$r = \frac{r_{max}}{\frac{K_2}{K_1} + C} . C \tag{7}$$

At low concentrations, as is the normal case in the Mississippi River, $K_1C < K_2$.

$$r = \frac{K_1 r_{max}}{K_2 + K_1C} . C = \frac{K_1 r_{max} . C}{K_2} = P.C \tag{8}$$

P is the Partition Coefficient, expressed $\frac{\mu g/kg}{\mu g/l}$.

P is a measure of the ratio of adsorbed pollutant concentration to the dissolved pollutant concentration.

The total concentration of pollutant in a water sample is the sum of the dissolved and adsorbed (particulate) concentrations.

$$C_T = C + C_P = \frac{r}{P} + rM = r(M + \frac{1}{P}) \tag{9}$$

C_T = total pollutant concentration, μg/l

C = dissolved pollutant concentration, μg/l

C_P = adsorbed or particulate pollutant concentration, μg/l

r = adsorbed pollutant concentration, μg/kg

M = suspended solids concentration, kg/l

The Standard Elutriate Test consists of mixing site water and sediment in a 4:1 volumetric ratio. One may presume that in the raw water sample the aqueous phase is in sorptive equilibrium with its suspended solids (equation 10) and that in the sediment sample the solids are in sorptive equilibrium with the interstitial water (equation 11). (See Figure 36).

Initially, at time t = 0,

$$r_1 = PC_1 \tag{10}$$

$$r_2 = PC_2 \tag{11}$$

C_1 = dissolved pollutant concentration in raw water sample, μg/l

r_1 = adsorbed pollutant concentration in raw water sample, μg/kg

C_2 = dissolved pollutant concentration in the sediment, i.e., in the interstitial water, μg/l

r_2 = adsorbed pollutant concentration in the sediment, μg/kg

Total dissolved pollutant concentration in the Standard Elutriate Test,

$$\text{initially} = C_0 = \frac{4 \times C_1 + 1 \times C_2}{5} \tag{12}$$

Total adsorbed pollutant concentration in the Standard Elutriate Test,

$$\text{initially} = r_0 = \frac{4 \times r_1 \times M_1 + 1 \times r_2 \times M_2}{4 \times M_1 + M_2} \tag{13}$$

Total suspended solids concentration in the Standard Elutriate Test

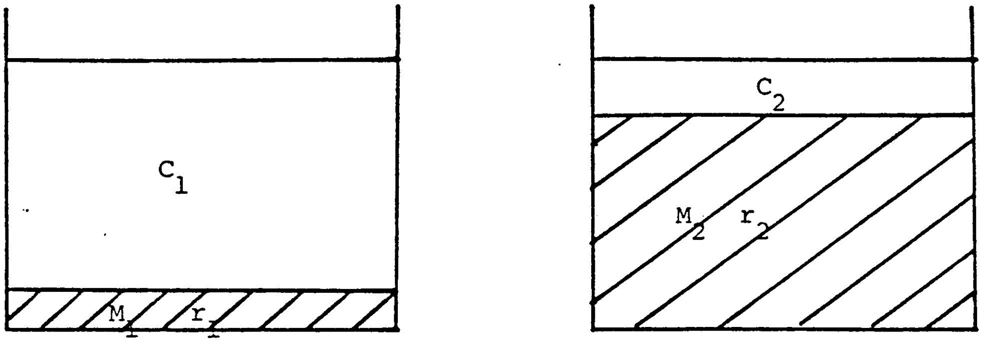
$$= M = \frac{4 \times M_1 + M_2}{5} \tag{14}$$

Before elutriation, after initial mixing, the total pollutant concentration $= C_t = C_0 + r_0M$ (15)

However, since there is no sorptive equilibrium initially, $r_0 \neq PC_0$

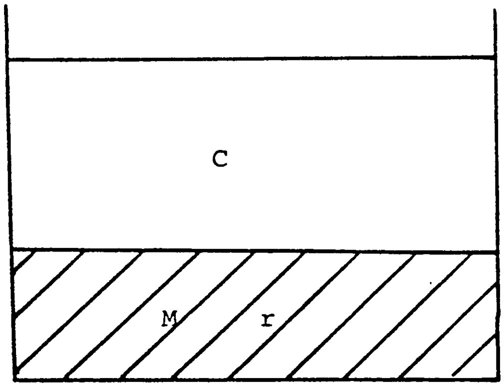
$$r_0 \neq PC_0 \tag{16}$$

After the elutriation and 60 minute settling, one may assume sorptive equilibrium to have been established.



Raw water sample
T = 0 minutes

Sediment sample
T = 0 minutes



Equilibrium
4:1 :: Water:Sediment
T = 90 minutes

Figure 36. The Standard Elutriate Test

Total pollutant concentration = $C_t = C + rM$ (17)

$$r = PC \qquad (18)$$

C = dissolved pollutant concentration or elutriate concentration, $\mu g/l$

r = final adsorbed pollutant concentration, $\mu g/kg$

M = dissolved solids concentration, kg/l

P = partition coefficient of the pollutant at that particular site, $\frac{\mu g/kg}{\mu g/l}$

Taking a mass balance on the pollutant,

$$C + rM = C_0 + r_0M \qquad (19)$$

$$C + PCM = C_0 + r_0M, \text{ using } (18)$$

$$C = \frac{C_0 + r_0M}{1 + PM} \qquad (20)$$

$$C = \frac{C_t}{1 + PM} \qquad (21)$$

The above equation is used to give an insight into the effects of the various parameters on the elutriate concentration, C.

While arriving at the Steady State models the following assumptions were made:

1. Purely physical phenomena - predominantly adsorption-desorption, perhaps some chemisorption and ion exchange.
2. Sorptive equilibrium is reached in the raw water before elutriation.
3. Sorptive equilibrium is reached in the sediment before elutriation.
4. Sorptive equilibrium is reached at the end of the elutriate test.

5. There is no biological or chemical activity.
6. Mixing is complete during elutriation.

As can be seen from equation (21), the value of the partition coefficient P, of the particular pollutant at the particular site is a very important factor in predicting the elutriate concentration, C. Values of partition coefficient P were calculated for various pollutants at the eight sites that were sampled on the Mississippi River. Tables 27 through 34 give the values of partition coefficients at the various sites. It was not possible to calculate partition coefficients when the concentration of the pollutant, either in the dissolved or particulate phase, was below the detectable limit.

Table 35, which summarizes the partition coefficients, clearly shows the variability of P, with both the site and the pollutant. The main reason for the variability is the nature of the sediment - particularly the size distribution and organic content (Karickhoff and Brown, 1978). It is possible that the ORP of the sediment would affect the ratio of adsorbed to dissolved concentration, especially with respect to Fe, Hg and Mn. It is also conceivable that the sampling techniques could have affected the concentration of the pollutant in the interstitial water. As the dredge which was used to sample the sediment is lifted through the water, there is always some mixing of the interstitial and silt water resulting in a concentration that is somewhere in between the two concentrations.

Figure 37 shows the variation in the ratio of dissolved pollutant concentration to the total pollutant concentration (C/C_t) versus the suspended solids concentration. The fraction in the dissolved phase

TABLE 27

Values of Partition Coefficients at Maquoketa

GREAT II Lab Simulation Study			May 29, 1979
Below Maquoketa River			M.P. 548
Pollutant	Interstitial µg/l	Sediment µg/kg	P µg/kg/µg/l
NH_3-N	-	13000	-
PO_4-P	30	9000	300
COD	46000	5×10^6	109
Mn	22.0	280	12.7
Ni	-	5500	-
Hg	0.53	440	830
Fe	475	8300000	17474

TABLE 28

Values of Partition Coefficients at Aspelmeier Ditch

GREAT II Lab Simulation Study May 29, 1979

Aspelmeier Ditch M.P. 545

Pollutant	Interstitial Water μg/l	Sediment μg/kg	Partition Coefficient $\frac{\mu g/kg}{\mu g/l}$
NH_3-N	-	9700	-
PO_4-P	30	11200	373
COD	46000	6.6×10^6	1435
Mn	22.0	170	7.7
Ni	-	20000	-
Hg	0.53	500	943
Fe	475	8.6×10^6	18105

TABLE 29

Values of Partition Coefficients at Montpelier

GREAT II Lab Simulation Study June 12, 1979

Montpelier M.P. 503-504

Pollutant	Interstitial Water μg/l	Sediment μg/kg	Partition Coefficient $\frac{\mu g/kg}{\mu g/l}$
NH_3-N	400	12000	30
PO_4-P	-	1500	-
COD	2700	475000	176
Mn	7.0	1260	180
Ni	2.0	159000	-
Hg	0.02	0.01	-
Fe	20	4.35×10^6	-

TABLE 30

Values of Partition Coefficients at Muscatine

GREAT II Lab Simulation Study June 12, 1979

Below Muscatine M.P. 448

Pollutant	Interstitial Water µg/l	Sediment µg/kg	Partition Coefficient $\frac{\mu g/kg}{\mu g/l}$
NH_3-N	300	11000	36.6
PO_4-P	-	0.1	-
COD	23000	205000	8.9
Mn	2.0	50	25
Ni	2.0	3400	-
Hg	0.2	0.1	-
Fe	20.0	2.908×10^3	-

TABLE 31

Values of Partition Coefficients at Keithsburg

GREAT II Lab Simulation Study — June 26, 1979

Keithsburg — M.P. 422

Pollutant	Interstitial Water µg/l	Sediment µg/kg	Partition Coefficient $\frac{\mu g/kg}{\mu g/l}$
NH_3-N	300	14000	47
PO_4-P	30	400	13
COD	34000	370000	10.9
Mn	1.9	1300	694
Ni	50	50.0	-
Hg	0.42	100	238
Fe	500	4.371×10^6	-

TABLE 32

Values of Partition Coefficients at Grey's Chute

GREAT II Lab Simulation Study			July 10, 1979
Grey Chute			M.P. 356
Pollutant	Interstitial Water µg/l	Sediment µg/kg	Partition Coefficient $\frac{\mu g/kg}{\mu g/l}$
NH_3-N	600	33000	55
PO_4-P	120	95000	792
COD	21000	1.8×10^6	85.7
Mn	9.5	70	7.4
Ni	2.5	10000	4000
Hg	0.2	120	-
Fe	20	3.83×10^6	-

TABLE 33

Values of Partition Coefficients at Keokuk

GREAT II Lab Simulation Study			July 10, 1979
Keokuk			M.P. 356
Pollutant	Interstitial Water $\mu g/l$	Sediment $\mu g/kg$	Partition Coefficient $\frac{\mu g/kg}{\mu g/l}$
NH_3-N	150	15000	100
PO_4-P	110	6000	54
COD	17000	360000	21
Mn	0.1	80	800
Ni	2.0	5800	-
Hg	-	0.1	-
Fe	20	2.45×10^6	-

TABLE 34

Values of Partition Coefficients at Quincy

GREAT II Lab Simulation Study June 25, 1979

Quincy M.P. 320

Pollutant	Interstitial Water µg/l	Sediment µg/kg	Partition Coefficient $\frac{\mu g/kg}{\mu g/l}$
NH_3-N	250	12000	48
PO_4-P	50	4000	80
COD	14000	290000	21
Mn	3.3	2100	636
Ni	2.0	1800	-
Hg	0.35	100	286
Fe	20	3.5×10^6	-

TABLE 35

Summary of Partition Coefficients

Great II Lab Simulation Study 1979

Partition Coefficients - in $\frac{\mu g/kg}{\mu g/l}$

Site	NH_3-N	PO_4-P	COD	Mn	Ni	Hg	Fe
Maquoketa	-	300	109	12.7	-	830	17474
Aspelmeier	-	373	1435	7.7	-	94.3	18105
Montpelier	30	-	176	180	-	-	-
Muscatine	36.6	-	8.9	25	-	-	-
Keithsburg	47	13	10.9	684	-	238	-
Grey Chute	55	792	85.7	7.4	4000	-	-
Keokuk	100	54	21	800	-	-	-
Quincy	48	80	21	-	636	286	-
Mean	53	269	233	245	2318	574	17789
Standard Deviation	23	269	162	321	1682	315	315
Coeff. of Variation	43.4%	100%	69.5%	131%	72.6%	54.9%	1.8%

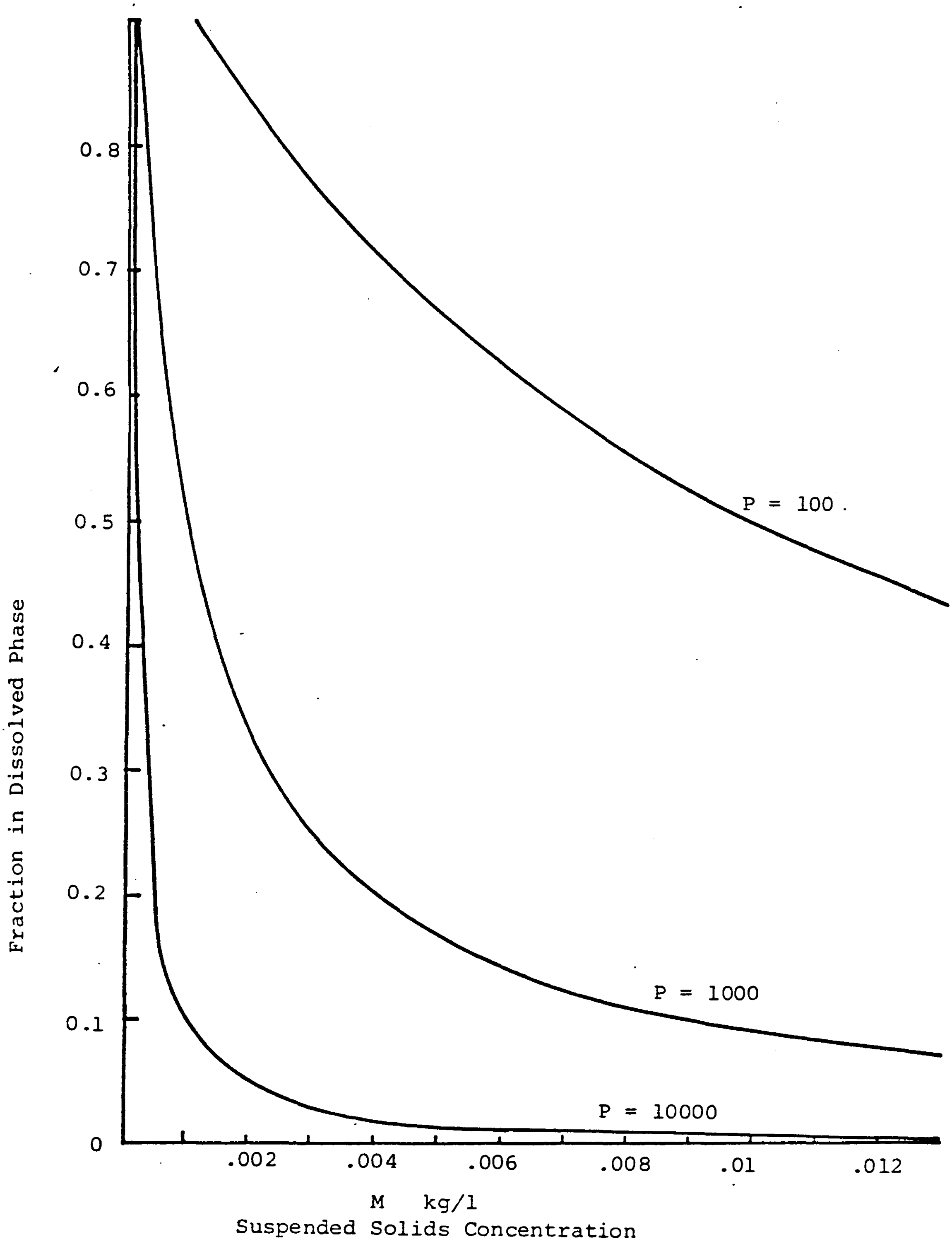


Figure 37. Fraction in Dissolved Phase Vs. Suspendend Solids Concentration

decreases with an increase in either suspended solids concentration M, or partition coefficient P. This is clearly indicated in Figure 37 for a few values of P at various values of M.

Figure 38 predicts the variation in the ratio of the dissolved to total pollutant concentration with a variation in the sediment suspended solids concentration. The data used was for average P values of NH_3-N, PO_4-P, and Ni equal to 53, 269, 2318 repectively. Iron, with a partition coefficient of almost 18,000, is greater than 99% in the adsorped-particulate phase.

Figure 39 indicates the variation in elutriate concentration C for a variation in total pollutant concentration, C_t. The figure shows the variation at particular values of PM - which is actually a measure of the ratio of the particulate to dissolved concentration of the pollutant.

The particulate concentration is proportional to the suspended solids concentration and the partition coefficient, $C_p = r \times M = PCM$. Therefore the ratio of the particulate concentration to the dissolved concentration is simply the suspended solids concentration times the partition coefficient:

$$\frac{C_P}{C} = \frac{PCM}{C} = PM$$

i.e., ratio of particulate to dissolved concentration is equal to PM.

Figure 40 shows the change in the elutriate concentration C for a change in (P + 1/M) when there is no initial dissolved concentration (i.e., $C_0 = 0$). It can be seen from Figure 40 that there is an exponential rise in the elutriate concentration with either an increase in the

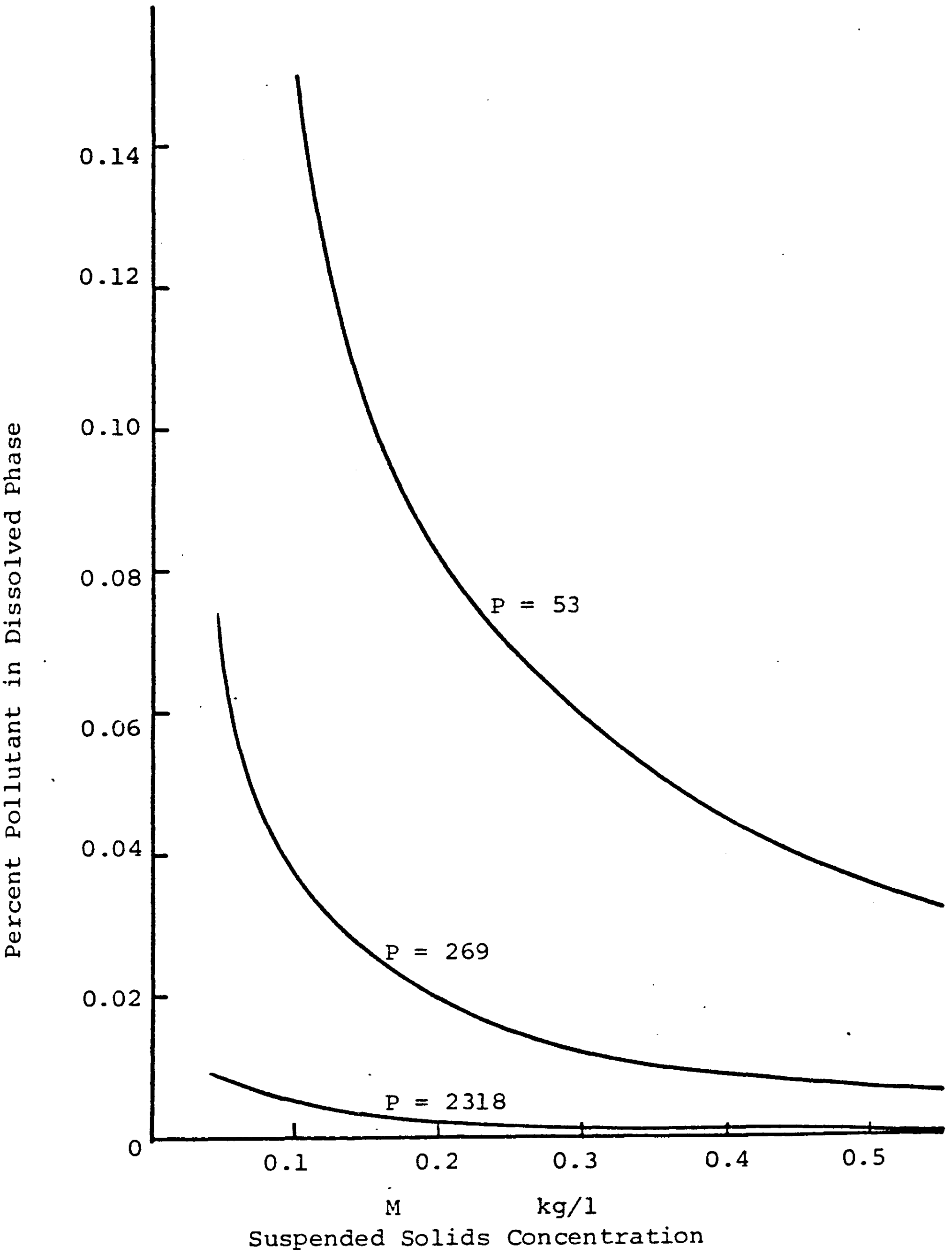


Figure 38. Percent Pollutant in Dissolved Phase Vs. Suspended Solids Concentration

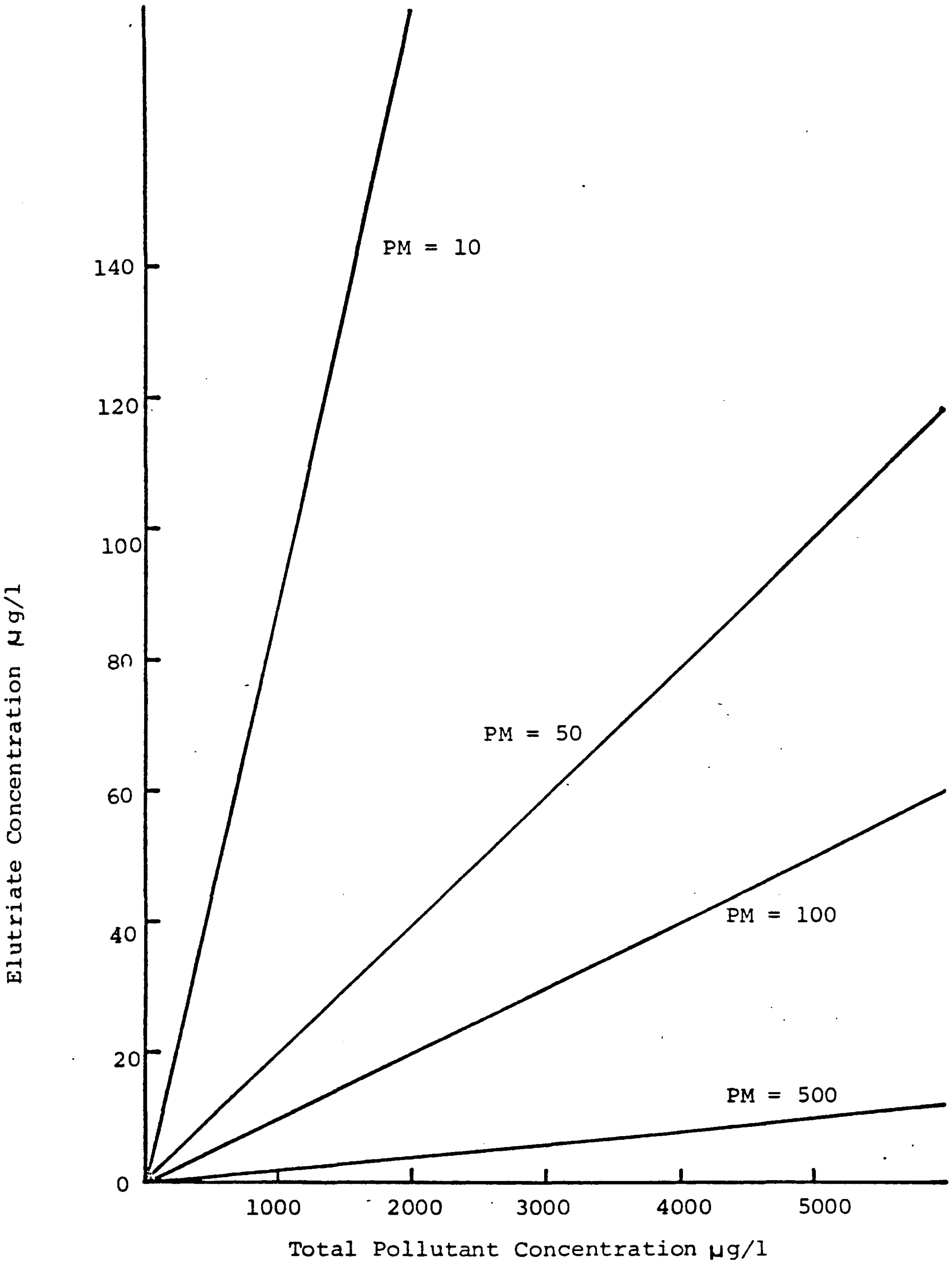


Figure 39. Elutriate Concentration Vs. Total Pollutant Concentration

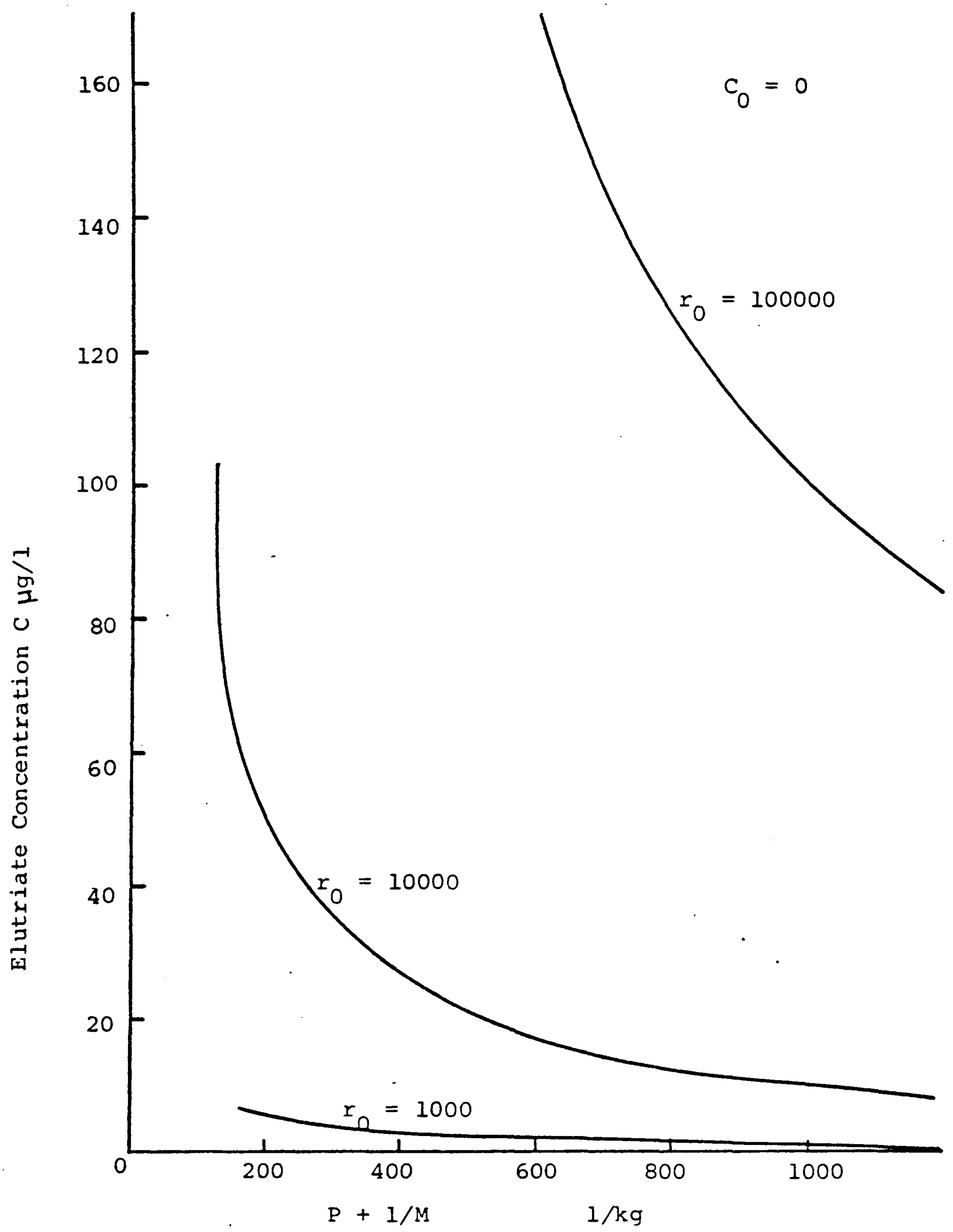


Figure 40. Elutriate Concentration Vs. P + 1/M

sediment suspended solids concentration, M or a decrease in the partition coefficient, P. The elutriate concentration is also directly proportional to the initial adsorbed pollutant concentration r_0.

Figure 41 predicts the elutriate concentration C, for changes in PM for particular values of initial dissolved pollutant concentration C_0, for a "clean" sediment, i.e., $r_0 = 0$. This could be used in the case of a pollutant spill in a river which has a "clean" sediment.

Use of Model to Predict Elutriate Concentration

The steady state model of the elutriate test could be used as a decision making tool to obviate the necessity of conducting expensive and time-consuming elutriate tests. Figure 42 gives the fraction in the dissolved phase at equilibrium conditions at various values of suspended solids M, for various values of partition coefficients P. This graph could be used to determine the elutriate concentration of a particular pollutant at a particular site if the sediment concentration, the site water concentration, and the suspended solids concentration are known.

Use of the Graph:

1. Determine the sediment concentration r_2 (μg/kg) at the site, the site water concentration C_1 (μg/l) and the suspended solids concentration of the sediment sample, M.
2. Calculate the total pollutant concentration, C_t.

$$C_t = C_0 + r_0 M$$

$$C_0 = \frac{4 \times C_1 + 1 \times C_2}{5}$$

C_1 = dissolved pollutant concentration in raw water sample, μg/l

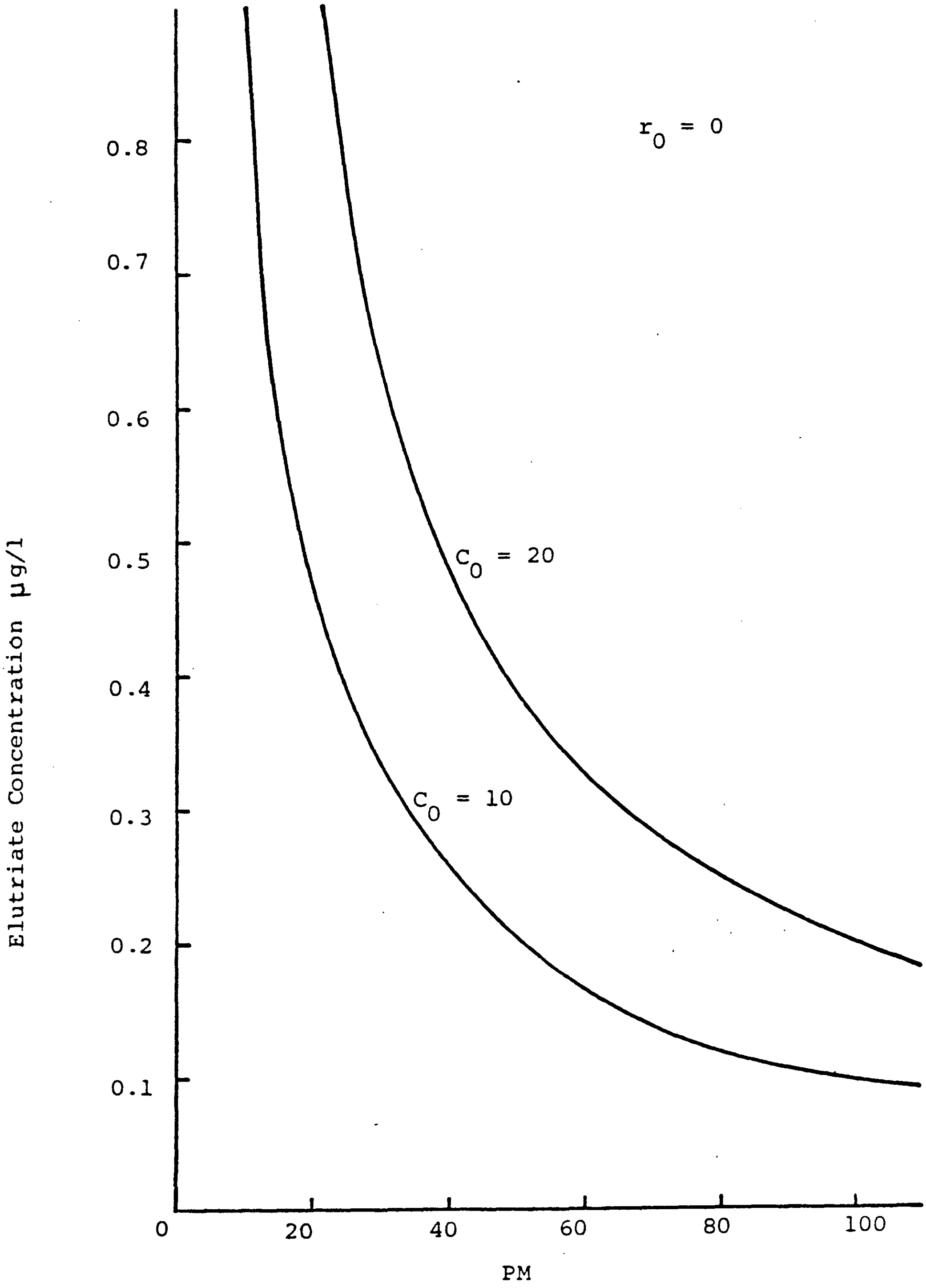


Figure 41. Elutriate Concentration Vs. PM

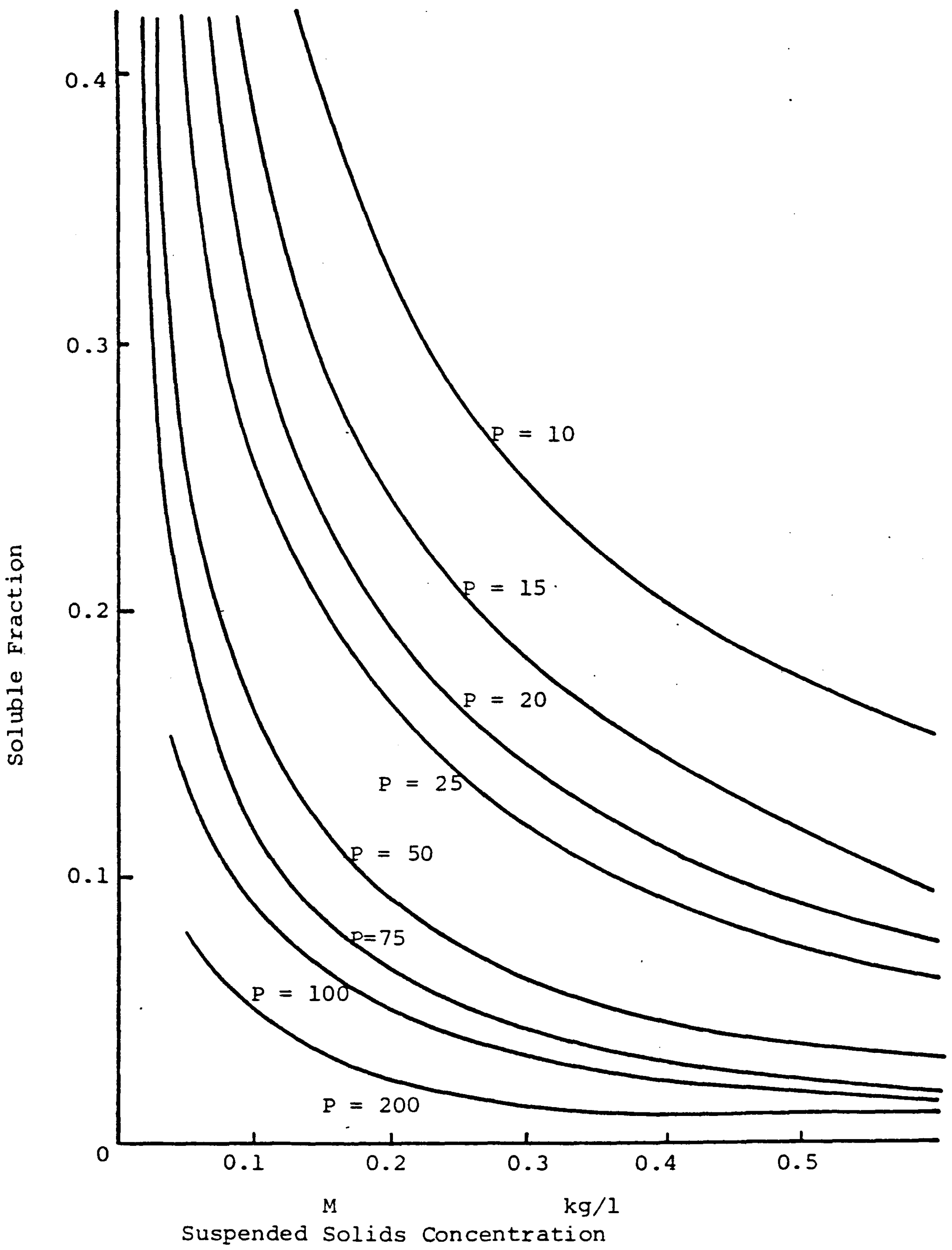


Figure 42. Soluble Fraction Vs. Suspended Solids Concentration

C_2 = dissolved pollutant concentration in the sediment, i.e., interstitial water, µg/l

However, since the volume of interstitial water remaining in the sediment is very small, it can be neglected, i.e., $C_2 = 0$.

$$C_0 = \frac{4C_1}{5} \tag{22}$$

$$r_0 = \frac{4 \times r_1 \times M_1 + r_2 \times M_2}{4M_1 + M_2}$$

r_1 = adsorbed pollutant concentration in raw water sample, µg/kg

r_2 = adsorbed pollutant concentration in sediment, µg/kg

M_1 = suspended solids concentration in raw water sample, kg/l

M_2 = suspended solids concentration in sediment, kg/l

Since the suspended solids concentration in the site water is very much less than the suspended solids concentration in the sediment, it can be neglected, i.e., $M_1 = 0$.

$$r_0 = r_2 \tag{23}$$

$$M = M_2/5 \tag{24}$$

The partition coefficient of the pollutant is initially determined and is used whenever the elutriate concentration is to be calculated. The same value of P can be used as long as the sediment characteristics - size distribution, organic content, etc., remain unchanged. The partition coefficient can be determined by finding out the sediment concentration, r_2 and the interstitial water concentration, C_2(µg/l).

Partition coefficient, $P\ (\frac{\mu g/kg}{\mu g/l}) = \frac{r_2}{C_2}$.

Knowing the sediment suspended solids concentration M and the partition coefficient P, the fraction in the soluble phase is determined, using the graph.

4. The fraction in the soluble phase multiplied by the total pollutant concentration C_t, gives the elutriate concentration C ($\mu g/l$).

Example:

COD at Keokuk.

Given $C_1 = 12000 \ g/l$, $C_2 = 17000 \ g/l$, $r_2 = 360000 \ \mu g/kg$

Suspended solids in sediment = 88.7%.

$$P = \frac{r_2}{C_2} = \frac{360000}{17000} = 21 \frac{\mu g/kg}{\mu g/l} .$$

$$C_0 = \frac{4 \times 12000}{5} = 9600 \ \mu g/l.$$

$$r_0 = 360000 \ \mu g/kg$$

$$M = 2.65 \ \frac{gm}{cm^3} \times \frac{0.887}{5} \times 1 \ \frac{kg/l}{gm/cm^3} = 0.47 \ kg/l.$$

$$C_t = C_0 + r_0 M = 9600 + 360000 \times 0.47 - 178800 \ \mu g/l.$$

From graph fraction in the soluble phase at M = 0.47 kg/l and

$$P = 21 \frac{\mu g/kg}{\mu g/l} , = .092.$$

Elutriate concentration C = 178800 x .092 = 16449 $\mu g/l$.

If the Standard Elutriate Test had been conducted using this sample, the equilibrium concentration would have been 16449 $\mu g/l$.

The actual elutriate concentration for the above example was 16000 $\mu g/l$.

Table (36) gives a list of predicted elutriate concentrations and the corresponding observed elutriate concentration. Figure (43) gives the observed elutriate concentrations versus predicted elutriate

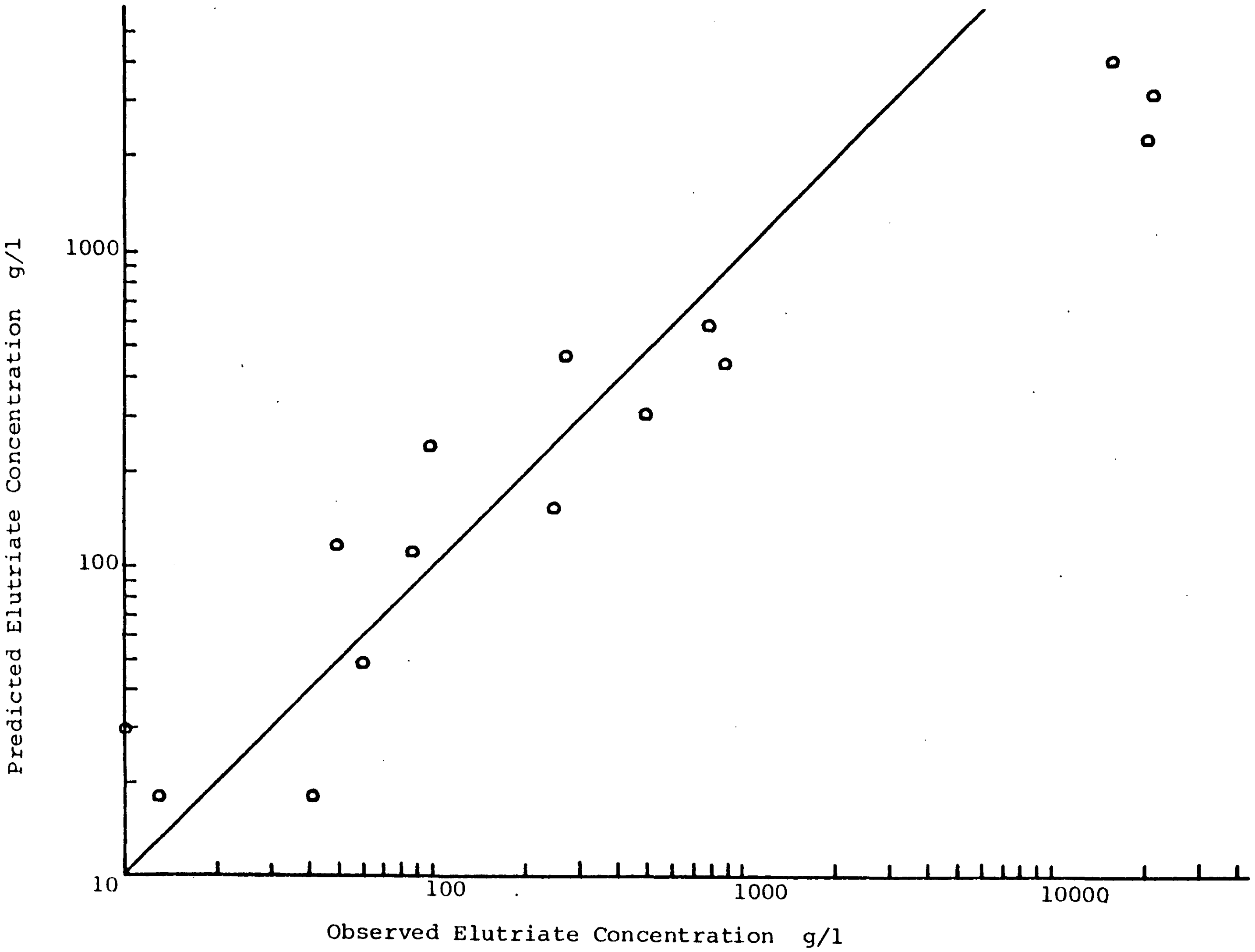


Figure 43. Predicted Elutriate Concentration Vs. Observed Elutriate Concentration.

TABLE 36

Observed and Predicted Elutriate Concentrations

GREAT II Lab Simulation Study 1979

Location	Pollutant	Predicted Concentration μg/l	Observed Concentration μg/l
Aspelmeier	PO_4-P	29.82	10
	COD	4626	16000
	Hg	0.537	1.2
Maquoketa	PO_4-P	29.75	10
	COD	44843	23000
	Mn	18.42	13.1
	Fe	472	274
Montpelier	NH_3-N	457	900
	COD	3209	22000
	Mn	8.0	18.6
Muscatine	NH_3-N	312	400
	COD	24781	12000
	Mn	6.91	4.3
Keithsburg	PO_4-P	260	10
	COD	31980	10000
	Mn	1.9	0.05
Grey Chute	NH_3-N	591	800
	PO_4-P	119	50
	COD	2293	21000
	Mn	7.09	0.59
	Ni	2.49	2.0
Keokuk	NH_3-N	153.6	250
	PO_4-P	110	90
	COD	16449	16000

TABLE 36 (continued)

Location	Pollutant	Predicted Concentration $\mu g/l$	Observed Concentration $\mu g/l$
Quincy	NH_3-N	242	100
	PO_4-P	49.2	60
	COD	13617	16000

concentrations for the GREAT II reach. The correlation coefficient between the two was found to be 0.55 which is significant at the 99% confidence level.

Reasons for Observed Elutriate Concentrations
Deviating from the Predicted Elutriate Concentrations:

1. The predicted concentration is the concentration that would have been achieved if the standard elutriate test were run for an infinitely long time. However, since mixing is for only 30 minutes, equilibrium is not achieved.
2. The partition coefficient is not the true partition coefficient. While removing the intersticial water from the sediment sample, it is often contaminated with site water leading to errors in the calculations of partition coefficient.
3. Mixing is not complete and hence all the sediment does not interact with the site water.

Dilution Factors on the Mississippi River

The Dilution Factor is the volume of disposal site water necessary to dilute a cubic meter of proposed dredge material discharge to acceptable levels using the results of the Elutriate Test and analysis of disposal site water in conjunction with appropriate water quality criteria. To calculate the dilution factor it is necessary to perform the Standard Elutriate Test to determine the concentration of pollutants of concern in the Standard Elutriate.

Taking a mass balance on the pollutant, since the mass of pollutant in one volume of Standard Elutriate is $1 \times C_e$, the mass of pollutant in

D volumes of disposal site water is D x C_a and the total volume is (D + 1).

$$1 \times C_e + D \times C_a = (D + 1) \times C_s \tag{25}$$

C_e = pollutant concentration in standard elutriate, μg/l

D = dilution factor required to dilute pollutant to a concentration equal to the numerical standard, vol/vol

C_a = pollutant concentration in disposal site water, μg/l

C_s = Numerical Standard of interest, μg/l, from U.S.E.P.A. Quality Criteria for Water, 1976.

Rearranging (25),

$$D = \frac{C_e - C_s}{C_s - C_a} \tag{26}$$

The total volume of water necessary to dilute a discharge of dredged material to acceptable levels is equal to the volume calculated in equation (26) multiplied by the total volume of dredged material.

$$M = D \times V_d \tag{27}$$

where

M = required volume of disposal site water, m^3

V_d = volume of dredged material discharge water, m^3

D is as defined above.

When using the above approach to calculate the dilution volume, the following facts are taken into account:

a. Acute toxicity criteria rather than chronic toxicity criteria are used to calculate the dilution factor.

b. Consideration is given to the basis of the criteria. The dilution volumes in this case are calculated on the basis of toxicity to fish, particularly those that were known to be found in the Mississippi River.

c. If the elutriate test concentration C is less than or equal to the standard concentration C_s, no calculation is necessary since no dilution is necessary.

d. If the elutriate test concentration C is greater than the standard concentration C_s, the required dilution volume is calculated using equation (26).

e. If the elutriate test concentration C is greater than the disposal site water concentration C_a, and the disposal site water concentration C_a is greater than or equal to the standard concentration C_s, then the standard cannot be achieved by dilution. Therefore, it is not possible to meet the standard (indicated by N.P. in the tables).

Tables (37) through (46) give the values of elutriate concentration C, site water concentration C_a and dilution factor D for the various sites.

The site water concentrations of unionized ammonia (as N) have been calculated at a mean pH of 7.6 and temperature of 20° C while for the elutriate concentration it has been calculated at a mean pH of 7.9 and temperature of 20° C (Birks, 1980). Figure 44 gives the relationship between pH and percent unionized ammonia (Quality Criteria for Water, U.S.E.P.A., July 1976, p. 11).

It is clear from Tables 37 through 44, that unionized ammonia, which is toxic to fish, is the most serious problem in the GREAT II

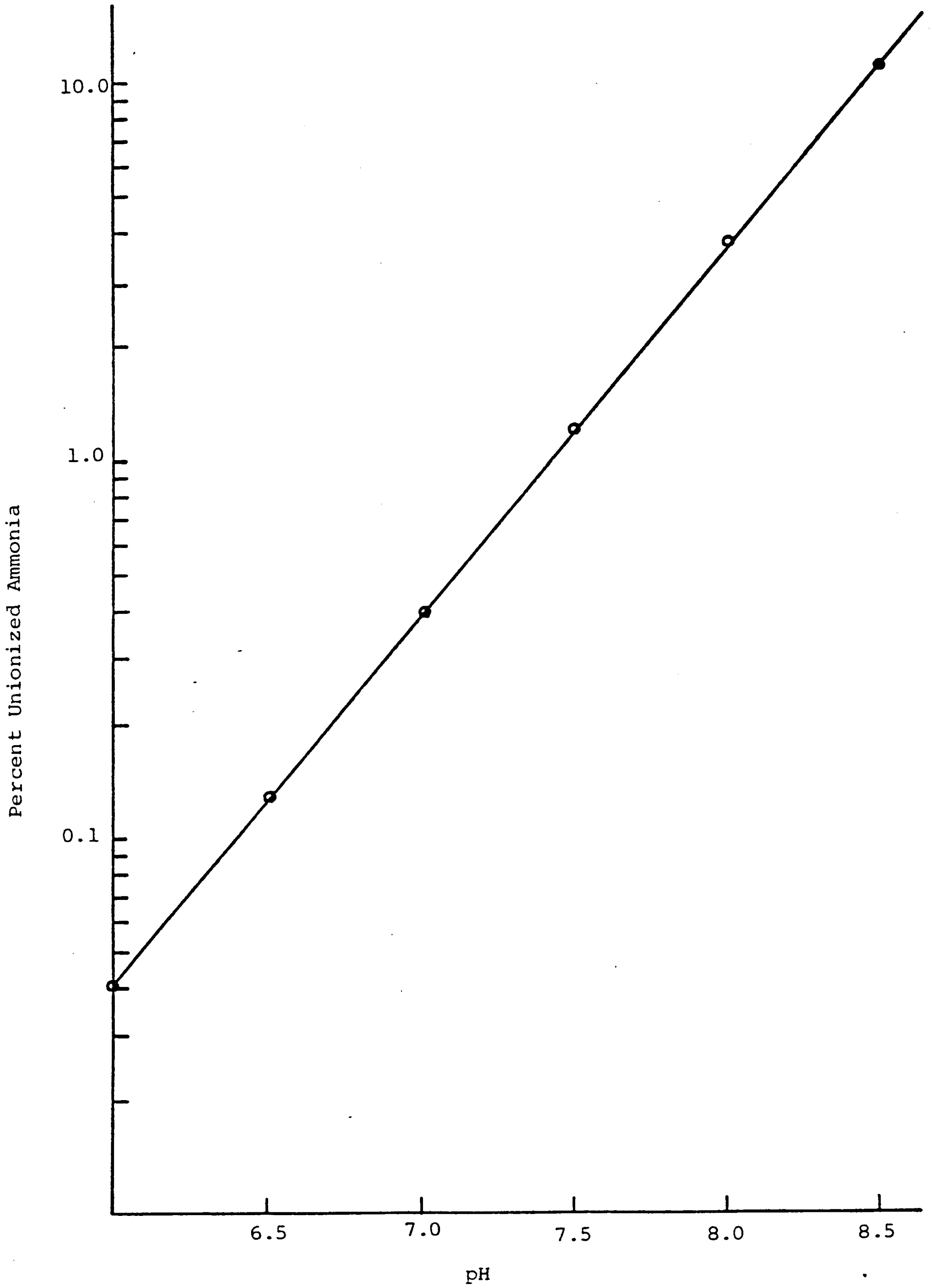


Figure 44. Percent Unionized Ammonia Vs. pH

TABLE 37

Dilution Factors for Maquoketa

GREAT II Lab Simulation Study	May 29, 1979
Below Maquoketa River	M.P. 548

Pollutant	Site Water Concentration C_a µg/l	Elutriate Concentration C µg/l	W Q Criteria C_s µg/l	Dilution Factor Vol/Vol
Unionized NH_3-N	2.25	23.78	16.5	0.51
Cadmium	0.06	0.3	1.2	0
Chromium	0.05	0.05	100	0
Copper	-	-	800	0
Iron	414	274	1000	0
Mercury	-	0.23	0.1	-
Manganese	0.21	13.1	100	0
Nickel	-	-	100	-
Lead	234	108	315	0
Zinc	-	-	136	-

TABLE 38

Dilution Factors for Aspelmeier Ditch

GREAT II Lab Simulation Study May 29, 1979

Aspelmeier Ditch M.P. 545.4

Pollutant	Site Water Concentration C_a $\mu g/l$	Elutriate Concentration C $\mu g/l$	W Q Criteria C_s $\mu g/l$	Dilution Factor Vol/Vol
Unionized NH_3-H	1.5	21.75	16.5	0.35
Cadmium	0.10	1.5	1.2	0.27
Chromium	0.06	0.34	100	0
Copper	-	-	800	-
Iron	10	703	1000	0
Mercury	-	1.2	0.1	-
Manganese	0.05	0.80	100	0
Nickel	-	-	100	-
Lead	0.05	184.67	315	0
Zinc	-	-	136	-

TABLE 39

Dilution Factors for Montpelier

GREAT II Lab Simulation Study June 12, 1979

Montpelier M.P. 469.5

Pollutant	Site Water Concentration C_a µg/l	Elutriate Concentration C µg/l	W Q Criteria C_s µg/l	Dilution Factor Vol/Vol
Unionized NH_3-N	90	26.1	16.5	1.28
Cadmium	0.91	3.42	1.2	7.6
Chromium	0.05	0.05	100	0
Copper	8.0	9.0	800	0
Iron	20	20	1000	0
Mercury	0.2	0.2	0.1	0
Manganese	4.76	18.6	100	0
Nickel	2.0	2.0	100	0
Lead	4.01	0.05	315	0
Zinc	1.76	9.5	136	0

TABLE 40

Dilution Factors for Muscatine

GREAT II Lab Simulation Study — June 12, 1979

Below Muscatine — M.P. 448

Pollutant	Site Water Concentration C_a µg/l	Elutriate Concentration C µg/l	W Q Criteria C_s µg/l	Dilution Factor Vol/Vol
Unionized NH_3-N	9.0	11.6	16.5	0
Cadmium	0.05	0.05	1.2	0
Chromium	0.05	0.05	100	0
Copper	5.3	1.1	800	0
Iron	20	20	1000	0
Mercury	0.2	0.2	0.1	0
Manganese	71	4.3	100	0
Nickel	2.0	2.0	100	0
Lead	0.05	0.05	315	0
Zinc	0.05	3.0	136	0

TABLE 41

Dilution Factors for Keithsburg

GREAT II Lab Simulation Study	June 26, 1979
Keithsburg	M.P. 422

Pollutant	Site Water Concentration C_a μg/l	Elutriate Concentration C μg/l	W Q Criteria C_s μg/l	Dilution Factor Vol/Vol
Unionized NH_3-N	0.75	6.38	16.5	0
Cadmium	15.0	2.2	1.2	N.P.*
Chromium	0.05	0.05	100	0
Copper	4.7	1.9	800	0
Iron	500	500	1000	0
Mercury	0.2	0.2	0.1	0
Manganese	0.76	0.05	100	0
Nickel	50	50	100	0
Lead	0.05	0.05	315	0
Zinc	50	1.9	136	0

*Not Possible to achieve water quality criteria by dilution.

TABLE 42

Dilution Factors for Keokuk

Great II Lab Simulation Study — July 10, 1979

Keokuk — M.P. 356

Pollutant	Site Water Concentration C_a µg/l	Elutriate Concentration C µg/l	W Q Criteria C_s µg/l	Dilution Factor Vol/Vol
Unionized NH_3-N	7.5	7.25	16.5	0
Cadmium	0.3	0.07	1.2	0
Chromium	0.05	0.05	100	0
Copper	3.3	1.2	800	0
Iron	177	20	1000	0
Mercury	0.2	0.2	0.1	0
Manganese	0.05	0.07	100	0
Nickel	2.1	7.0	100	0
Lead	5.5	0.75	315	0
Zinc	-	-	136	-

TABLE 43

Dilution Factors for Grey Chute

GREAT II Lab Simulation Study July 10, 1979

Grey Chute M.P. 356

Pollutant	Site Water Concentration C_a μg/l	Elutriate Concentration C μg/l	W Q Criteria C_s μg/l	Dilution Factor Vol/Vol
Unionized NH_3-N	7.5	23.2	16.5	0.74
Cadmium	0.11	1.3	1.2	0.1
Chromium	0.05	0.05	100	0
Copper	0.3	0.08	800	0
Iron	20	20	1000	0
Mercury	0.2	0.2	0.1	0
Manganese	0.1	0.59	100	0
Nickel	2.5	2.0	100	0
Lead	11.3	-	315	-
Zinc	-	-	136	-

TABLE 44

Dilution Factors for Quincy

GREAT II Lab Simulation Study June 26, 1979

Quincy M.P. 320

Pollutant	Site Water Concentration C_a µg/l	Elutriate Concentration C µg/l	W Q Criteria C_s µg/l	Dilution Factor Vol/Vol
Unionized NH_3-N	0.75	2.9	16.5	0
Cadmium	5.3	3.3	1.2	N.P.*
Chromium	0.05	0.05	100	0
Copper	7.8	4.6	800	0
Iron	20	20	1000	0
Mercury	0.2	0.2	0.1	0
Manganese	4.5	4.2	100	0
Nickel	2.6	2.0	100	0
Lead	0.05	0.05	315	0
Zinc	26	13.9	136	0

*Not Possible to achieve water quality criteria by dilution.

reach. Dilution factors ranging from 0.35 to 1.28 are required at 4 out of 8 sites to dilute the dredge effluent to safe levels. These dilution factors can be met easily since the minimum flow, at the highest mile point sampled is 16000 cfs, while the dredge flow rate is just 45 cfs. The problem due to ammonia, however, is largely due to dredging: it desorbs at all sites except Keokuk, where it adsorbs slightly. This means that the downstream ammonia concentration will be often higher than the upstream concentration during dredging and will return to the upstream concentration level when dilution is complete. Tables 45, 46 and 47 give dilution factors for the Mississippi River using data obtained from 16 sites on the GREAT II reach, sampled by the Corps of Engineers and analysed by the U.S.G.S. at various times of the year. From this data also it can be seen that in one case it is not possible to dilute unionized ammonia to acceptable levels through dilution and in one instance a dilution factor of 1.58 is required. It desorbs in all three instances.

Another pollutant of concern is cadmium, which desorbs at 4 out of 8 sites. A maximum dilution factor of 7.6 is required at Montpelier. The elutriate concentration exceeds water quality criteria at 5 sites. At one site, although there is adsorption, both the site water and elutriate concentration exceed the water quality criteria of 1.2 μg/l. However, it should be noted that due to very low concentrations of cadmium considered and the difficulty in measurement, the desorption phenomenon of cadmium is not statistically significant at the 90% confidence level in paired t-tests.

TABLE 45

Dilution Factors for Mississippi River-1

U.S.G.S. Analyses Mississippi River 14-18 August 1978

Pollutant	Site Water Concentration C_a µg/l	Elutriate Concentration C µg/l	W Q Criteria C_s µg/l	Dilution Factor Vol/Vol
COD	24440	70750	-	-
Unionized NH_3-N	13.5	14.72	16.5	0
PO_4-P	190	90	-	-
Arsenic	2.13	1.13	100	0
Beryllium	0.00	1.25	11	0
Cadmium	0.00	0.00	1.2	0
Chromium	1.88	1.25	100	0
Copper	4.63	3.44	800	0
Iron	22.50	57.50	1000	0
Lead	0.25	0.00	315	0
Manganese	2.5	99.38	100	0
Mercury	0.06	0.00	0.1	0
Nickel	0.75	4.00	100	0
Selenium	0.13	0.31	250	0
Zinc	3.75	10.00	136	0

TABLE 46

Dilution Factors for Mississippi River-2

Mississippi River Pre-Dredging Samples

August-November 1978 River Mile 323.5-489.4

Pollutant	Site Water Concentration C_a µg/l	Elutriate Concentration C µg/l	W Q Criteria C_s µg/l	Dilution Factor Vol/Vol
COD	18700	24100	-	-
Unionized NH_3-N	38.05	62.59	16.5	N.P.*
PO_4-P	50	110	-	-
Arsenic	-	-	100	-
Beryllium	-	-	11	-
Cadmium	2.27	1.39	1.2	-
Chromium	0.06	0.08	100	N.P.*
Copper	5.17	2.97	800	0
Iron	153.2	138.5	1000	0
Lead	3.44	1.24	315	0
Manganese	8.23	6.21	100	0
Mercury	0.55	0.27	0.1	N.P.*
Nickel	11.06	18.37	100	0
Selenium	-	-	250	-
Zinc	17.63	7.70	136	0

*Not Possible to achieve water quality criteria by dilution.

TABLE 47

Dilution Factors for Mississippi River-3

Mississippi River Pre-Dredging Samples

10-24 July 1979 River Miles323.5-489.4

Pollutant	Site Water Concentration C_a µg/l	Elutriate Concentration C µg/l	W Q Criteria D_s µgl/	Dilution Factor Vol/Vol
COD	27100	55900	-	-
Unionized Nh_3-N	1.35	40.45	16.5	1.58
PO_4-P	225	213	16.5	1.58
Arsenic	2.6	3.3	100	0
Beryllium	-	-	11	-
Cadmium	-	-	1.2	-
Chromium	-	-	100	-
Copper	1.6	2.2	800	0
Iron	10.7	154.7	1000	0
Lead	-	-	315	-
Manganese	0.61	402.9	100	
Mercury	-	-	0.1	-
Nickel	-	-	100	-
Selenium	-	-	250	-
Zinc	8900	19000	136	N.P.*

*Not Possible to achieve water quality criteria by dilution.

Manganese desorbs occasionally at the sites sampled by the GREAT II Simulation Study Group and in 2 out of 3 occasions in the U.S.G.S. samples. In fact, in one instance it requires a dilution factor of 3.04. Although most of the other pollutants analysed desorb at the two "dirty" sites - Aspelmeier Ditch and Grey's Chute, their concentrations hardly approach the Water Quality Criteria Concentrations.

Dilution Factor for Dissolved Oxygen

It has been shown that sediment dredged from a river bed, when mixed with site water, can exert an oxygen demand. In fact, the oxygen demand could even turn the dredge discharge anoxic, under severe conditions. The following calculations were made to determine whether the dredge discharge would have been anoxic at the eight sites sampled by the GREAT II Simulation Study Group and if so, the dilution volume required.

Taking the case of Keithsburg (Musgrove, 1980),

Total volume of water and sediment pumped

$$= 45 \text{ ft}^3/\text{sec} \times 3600 \text{ sec/hour} \times 18.5 \text{ hours} \times .02832 \text{ m}^3/\text{ft}^3$$

$$= 84875 \text{ m}^3.$$

Total sediment removed = 8885 m^3.

Ratio of water pumped to sediment removed

$$= \frac{84875 - 8885}{8885} = 8.55.$$

Taking a mass balance on the oxygen concentration,

$$1 \times (D.O.)_2 + D(D.O.)_1 = (1 + D) \times C_s \tag{28}$$

$(D.O.)_2$ = dissolved oxygen concentration at the exit of the discharge pipe, mg/l

$(D.O.)_1$ = dissolved oxygen concentration of the ambient site water, water, mg/l

C_s = Water Quality Standard, mg/l

D = dilution factor, vol/vol

Assuming $(D.O.)_1$ = 8 mg/l and C_s = 4 mg/l,

$$D = \frac{4 - (D.O.)_2}{8 - 4}$$

$$= \frac{4 - (D.O.)_2}{4} \qquad (29)$$

To calculate the D.O. concentration of the dredge discharge the oxygen demand of the discharge is determined.

Taking the data for Grey's Chute (Geadelmann, 1979),

$$\text{Oxygen uptake of sediment} = \frac{506 \text{ gm of } O_2}{m^3} \text{ in one hour.}$$

$$\text{Ultimate Total Oxygen Demand} = \frac{\text{(Total Oxygen Demand) 60 min.}}{(1 - e^{-Kt})}$$

K is the rate constant, K = 0.16/min., t = 60 min.

$$\text{Ultimate Total Oxygen Demand} = \frac{504}{1 - e^{-0.16 \times 60}} = 504 \text{ gm/m}^3.$$

Detention time in a pipe 1000 feet long and 20" in diameter with a discharge rate of 45 ft^3/second,

$$t = \frac{A \times 1}{Q} = \frac{\times (20/12)^2 \times 1000}{45 \times 60} = 0.808 \text{ min}$$

$$\text{Oxygen demand} = 504\ (1 - e^{-0.16 \times .808}) = 61 \text{ gm/m}^3.$$

$$\text{Available oxygen} = \frac{8.55 \text{ m}^3 \text{ of water}}{\text{m}^3 \text{ of sediment}} \times \frac{8 \text{ mg}}{1} \times \frac{1 \text{ g/m}^3}{\text{mg/l}} = \frac{68.4 \text{ gm of } O_2}{\text{m}^3 \text{ sediment}}$$

Since the available oxygen 68.4 gm/m^3 is greater than the oxygen uptake of the sediment 61 gm/m^3, the discharge is not anoxic.

$$\text{D.O. concentration of discharge} = \frac{68.4 - 61.0}{8.55} = 0.85 \text{ mg/l.}$$

Table 48 gives the oxygen demand at the other sites using appropriate K values as calcuated by Geadelmann (Geadelmann, 1979).

However, even if the discharge is deoxygenated, only if the discharge were submerged would reaeration be impossible, necessitating the calculation of dilution factor. Table 48 gives dilution factors if the dredge discharge is submerged.

$$D = \frac{4 - 0.85}{4} = 0.79 \text{ for above example.}$$

Kinetic Model of the Standard Elutriate Test

The objective of the kinetic model is to describe the dissolved concentration of the pollutant that has been adsorbed or desorbed from the sediment during the course of elutriation, according to the Standard Elutriate Test. Since the Standard Elutriate Test is a simulator of dredge disposal, the kinetic model would also simulate the effects of mixing bottom sediment and site water in the dredge line upto the point of discharge into the river during dredging.

Sorption is considered to be the physical phenomenon that predominates and the model takes into account only sorption kinetics. Complete mixing is assumed within the control volume - which is the volume of the beaker in which the elutriate test is conducted. The driving force in the kinetics is the difference between the equilibrium

TABLE 48

Dilution Factors for Dissolved Oxygen

Site	TOD_{60} $\frac{\text{g of } O_2}{m^3}$	TOD_U $\frac{\text{g of } O_2}{m^3}$	$TOD_{.808}$ $\frac{\text{g of } O_2}{m^3}$	Available O_2 $\frac{\text{g of } O_2}{m^3}$	Dil. Factor $\frac{\text{Vol}}{\text{Vol}}$	$(D.O.)_2$ $\frac{mg}{l}$
Maquoketa	272	273	21.2	68.4	0	5.5
Aspelmeier	392	392	47.5	68.4	0.39	2.44
Montpelier	96	97	7.5	68.4	0	7.12
Muscatine	62	63	4.9	68.4	0	7.43
Keithsburg	37	38	2.9	68.4	0	7.66
Grey Chute	504	504	61.1	68.4	0.79	0.85
Keokuk	149	149	11.6	68.4	0	6.60
Quincy	56	57	4.4	68.4	0	7.48

TOD_{60} = Total Oxygen Demand for 60 minutes.

TOD_U = Ultimate Total Oxygen Demand.

$TOD_{.808}$ = Total Oxygen Demand for 0.808 minutes.

$(D.O.)_2$ = Dissolved Oxygen Concentration of the discharge.

adsorbed concentration of the pollutant, r_{eq}, and the actual adsorbed concentration of the pollutant, r.

At equilibrium, the ratio of adsorbed pollutant concentration, r, to the dissolved pollutant concentration, C, is a constant - the partition coefficient, P.

i.e., $\frac{r}{C} = P$ at equilibrium

The equation governing the dissolved pollutant C, may be written as

$$\frac{dC}{dT} = KM\ (r - r_{eq}) \qquad (30)$$

At equilibrium, $r_{eq} = r = PC$, and therefore (30) may be written as

$$\frac{dC}{dT} = KM\ (r - PC) \qquad (31)$$

in which

C = dissolved pollutant concentration, µg/l

T = time, hours

K = sorption rate constant, 1/hour

M = suspended solids concentration, kg/l

r = adsorbed pollutant concentration, µg/kg

P = partition coefficient of the pollutant at that site, $\frac{\mu g/kg}{\mu g/l}$

<u>Solution</u>

The solution to equation (30) will give the dissolved pollution concentration at time, T.

$$\frac{dC}{dT} = KM\ (r - PC) \qquad (31)$$

If C_0 is the initial dissolved concentration of the pollutant in the control volume, and r_0 the initial adsorbed pollutant concentration in the control volume, then

$$C_0P \neq r_0.$$

However, mass must be conserved and the total pollutant concentration in the beaker must remain constant. The ratio of dissolved and adsorbed pollutant concentration will now be dynamic and change to approach an equilibrium state at which P = r/C.

Taking a mass balance, the total pollutant concentration,

$$C_T = C_0 + r_0M = C + rM \tag{32}$$

Rearranging equation (32),

$$r = \frac{C_0 + r_0M - C}{M} \tag{33}$$

Substituting for r in (31)

$$\frac{dC}{dT} = KM\ (\frac{C_0 + r_0M - C}{M} - PC)$$

$$\text{i.e.,}\quad \frac{dC}{dT} = CK\ (1 + PM) = K\ (C_0 + r_0M) \tag{34}$$

Comparing (34) to

$$\frac{dy}{dx} + P\ (x)\ y = Q\ (x)$$

the solution to which is

$$y.e^{\int P.dx} = \int Q.e^{\int P.dx} + C$$

Hence solution to (34) is

$$C.e^{\int K(1 + PM).dT} = \int K(C_0 + r_0M).e^{\int K(1 + PM).dT} + C \tag{35}$$

Using the boundary condition that, at T = 0, $C = C_0$ and simplifying,

$$C = C_0.e^{-K(1 + PM).T} + \frac{(C_0 + r_0M)}{(1 + PM)}\ (1 - e^{-K(1 + PM)T}) \tag{36}$$

where C_0 = dissolved concentration of pollutant at time T = 0, µg/l

K = sorption rate constant, 1/hour

P = partition coefficient of pollutant at the site, $\frac{\mu g/kg}{\mu g/l}$

M = suspended solids concentration, kg/l

T = time, hours

r_0 = adsorbed pollutant concentration at time t = 0, µg/kg

Experimental Methods and Results

Two sites near Keokuk (near M.P. 355) - one a main channel and one a slough (Grey Chute) were sampled in November, 1979. Both were proposed dredge sites. A Ponar Dredge Sampler was used to collect all the sediment samples. The Ponar Dredge Sampler is capable of sampling to a maximum depth of five inches and has a volume of nearly three liters. The site water was collected about a foot below the water level in 5 gallon Nalgene containers. The sediment container and the Nalgene container had been prewashed with acid and rinsed with deionized water.

The kinetic experiments were conducted within 2 days of sampling, in an open 5 gallon Nalgene container using the sediment and unfiltered dredge site water (see Figure 45). Three liters of sediment and 12 liters of site water were used for the test to give a sediment to water volumetric ratio of 1:4. A non-metallic propeller of diameter 20 cm with a stem of length 40 cm powered by a 1/80 HP, 5000 RPM motor, with a speed reducer capable of reducing the RPM to a fourth of the normal speed. Two large course bubble stone diffuser tubes were placed at the sides of the container, at the bottom, to aid in mixing and to

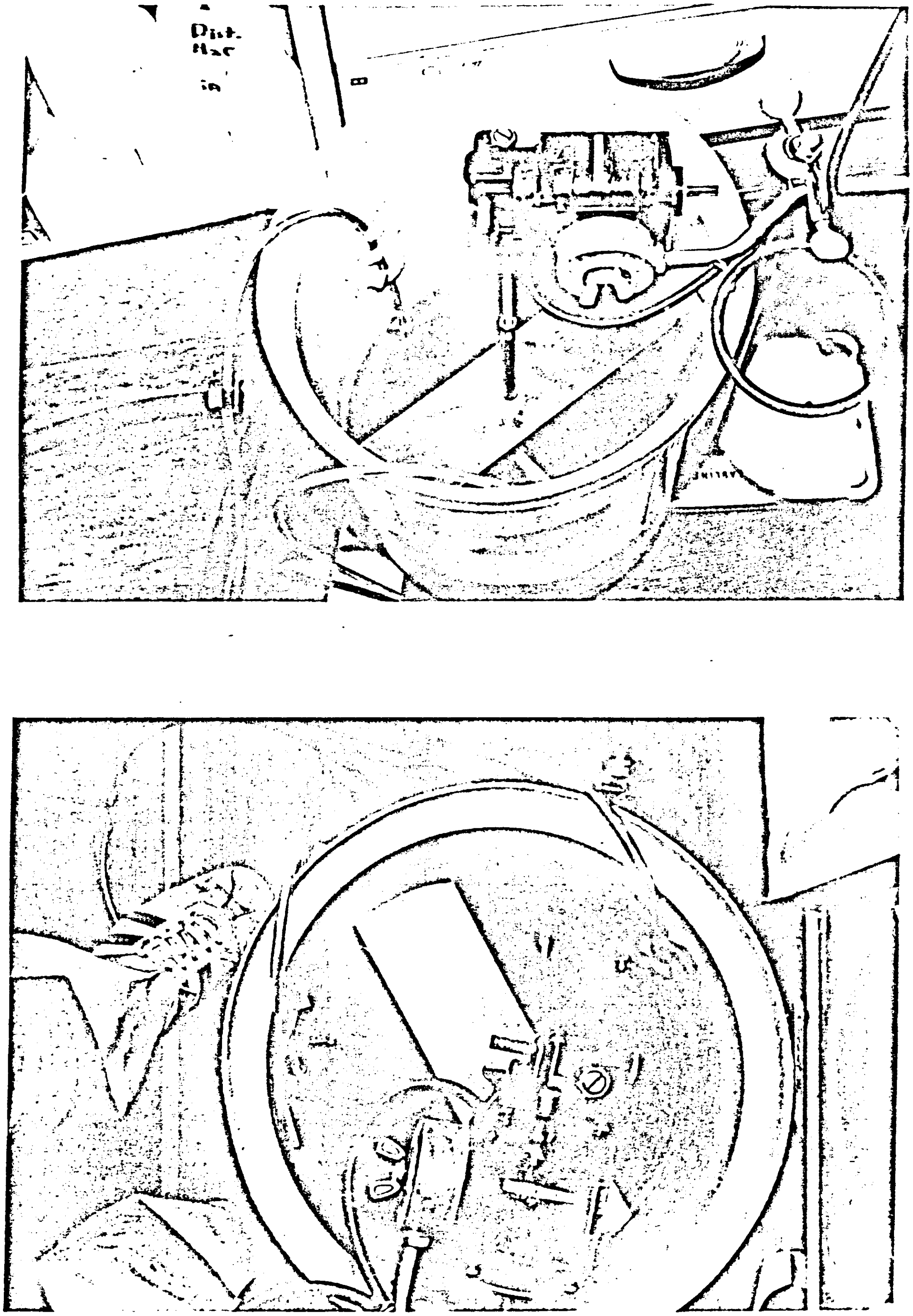


Figure 45. Apparatus for kinetic experiments.

avoid anoxic conditions. Compressed air was passed through a deionized water trap before entering the diffuser tubes and slurry.

Two tests were conducted at 7.5° C and two at room temperature. The motor was stopped during sampling. Samples were drawn off initially at 15 minute intervals and then at the second, fourth, fifth, sixth and twenty-fourth hours. The sampling does cause a reduction in volume of the overlying water since the samples taken do not contain much suspended solids. The final sediment to water ratio is approximately 3.7:1.

The samples were first centrifuged to reduce suspended solids and to expedite subsequent filtering. A 47 mm diameter, 5 micron filter was used initially followed by a 0.45 micron filter. The filtering apparatus was entirely made of glass (millipore) and a vacuum pump was used to facilitate filtering. The samples were then stored at 4° C until analysis for COD and NH_3 within a week.

Chemical Oxygen Demand was determined in accordance with Standard Methods (APHA, Standard Methods, 1975). Ammonia was determined according to procedures outlined in Standard Methods (APHA, Standard Methods, 1975).

The sorption rate constant for the four cases studied was calculated by trial and error. Constant values ranging from 0.01 to 1.0/hour were attempted until a rate constant of 0.1/hour was found to have a satisfactory fit to all the experimental values. This value of sorption rate constant was used to model the experimental data.

The kinetic model was solved using a FORTRAN computer program on the CDC CYBER 71. Assuming steady state to have been achieved after 24 hours, the total pollutant concentration was based on the 24 hour pollutant concentration. The mass of suspended solids in the control volume was found to be 0.43 kg/l in the case of Grey Chute. This value of $\underline{M}$ was used in all the cases. The values of partition coefficients were taken from data already available for the two sites (Table 35).

Figure 46 shows the model results and the experimental results of the kinetic experiment for COD at Grey Chute at 4.5° C. As can be seen, the model closely approximates the experimental values obtained, particularly until the second hour. It should be noted that, according to the model about 81% of the concentration change is complete within the first 30 minutes and that, from the experimental values, 95% of the concentration change is complete within the first 30 minutes.

Figure 47 gives the model result and the experimental values of the kinetic experiment for ammonia at Grey Chute at 7.5° C. Again, the model closely approximates the experimental values throughout the test period of 24 hours. Figure 48 shows the model results and experimental values for COD at Grey Chute at room temperature. After the 15th minute the highly variable experiments do not conform to the model predictions. Figure 49 gives the model results and experimental values for COD at Keokuk at room temperature. In this case the experimental values are quite close to the model predictions. In the 4 instances cited above the experimental values showed that, on an average, 72% of the concentration change is over within the first 30 minutes. According to the model, on an average, 68% of the concentration change is complete by 30 minutes.

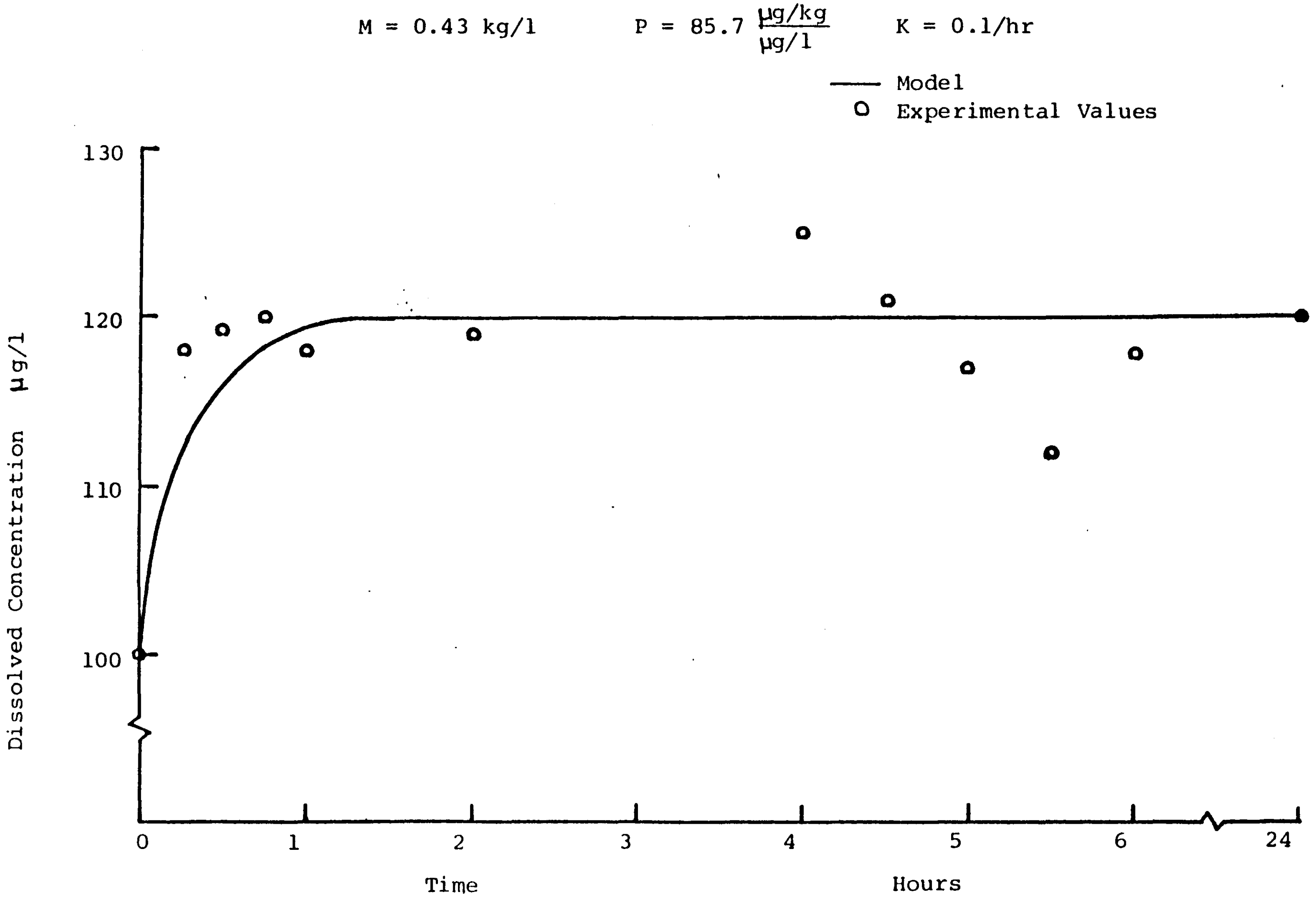


Figure 46. COD at Grey Chute -7.5° C. M.P. 356.

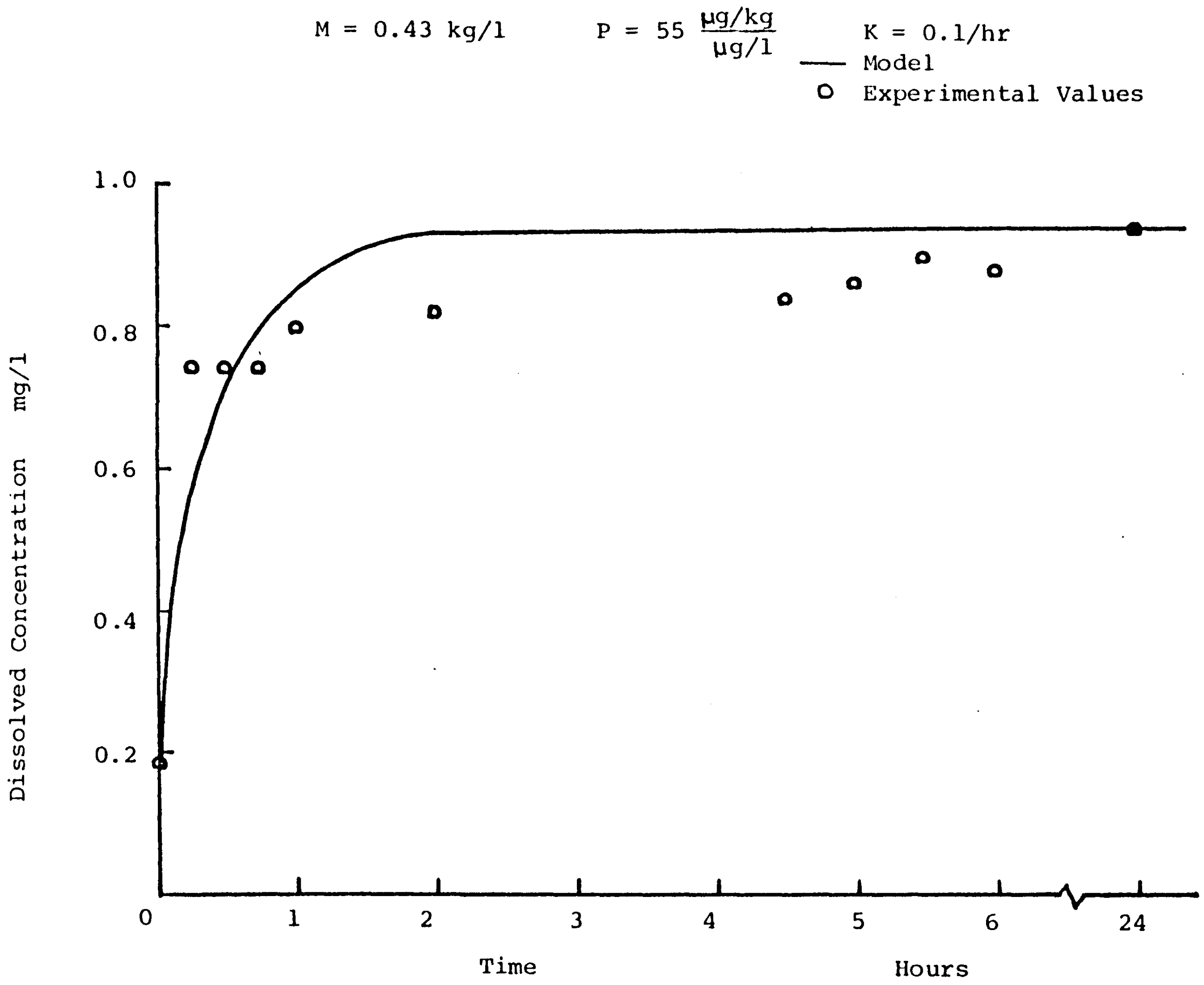
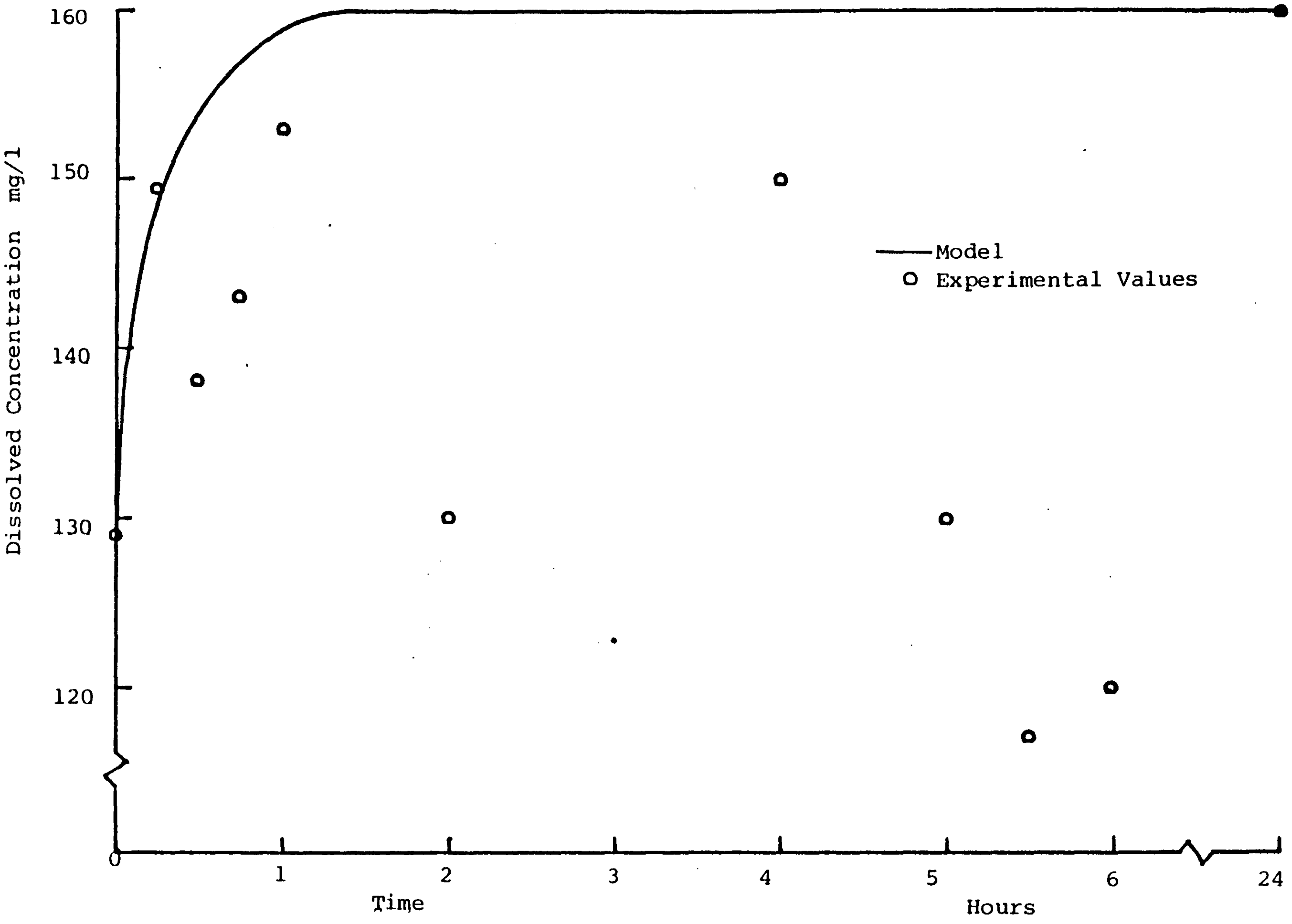


Figure 47. Ammonia at Grey Chute - 7.5° C M.P. 356.



M = 0.43 kg/l P = 85.7 $\frac{\mu g/kg}{\mu g/l}$ K = 0.1/hr

Figure 48. COD at Grey Chute - Room Temperature M.P. 356.

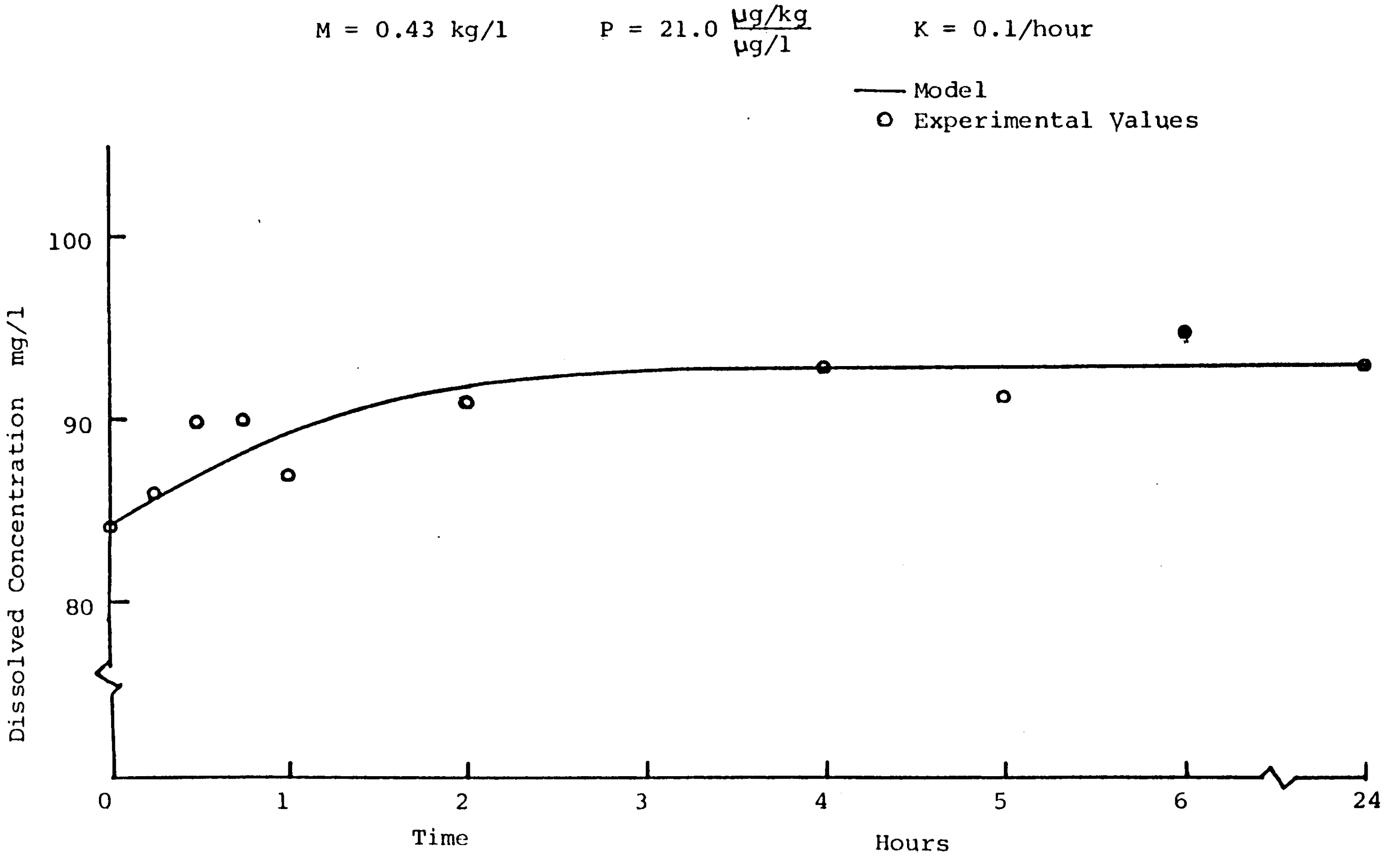


Figure 49. COD at Keokuk - Room Temperature M.P. 356.

In the case of COD at Keokuk, the ice bath malfunction led to a temperature rise from 8° to 18°. A scrutiny of the experimental results suggested either volatilization of biological degradation of the COD. Assuming an additional first order reaction, a degradation or volatilization term was added to the original equation (equation 31). The equation governing the kinetics are now as follows:

$$\frac{dC}{dT} = KM\ (r - PC) - K_a C \qquad (37)$$

$$\frac{dr}{dT} = -K\ (r - PC) \qquad (38)$$

Since there is no conservation of mass, due to either volatilization or biological degradation of COD, the assumption of a constant total pollutant concentration cannot be made. Also, it is not possible to calculate the total pollutant concentration from the 24 hour pollutant concentration as steady state is not achieved. The adsorbed pollutant concentration used was achieved by trial and error. The degradation rate constant used was calculated through a sensitivity analysis. The simultaneous equations (equations 37 and 38) were solved using GASP IV, which is a Combined Continuous/Discrete FORTRAN based Simulation Language. The model results and experimental values are given in Figure 50.

The Kinetic Model attempts to explain the mechanics of sorption during the process of elutriation. The experimental results showed that the elutriate test with 30 minutes of agitation is a fair approximation (72%) of equilibrium. The Kinetic Model shows that besides the sorption constant there are two more factors - the partition coefficient, P, and the suspended solids concentration, M, that affect the dynamics of

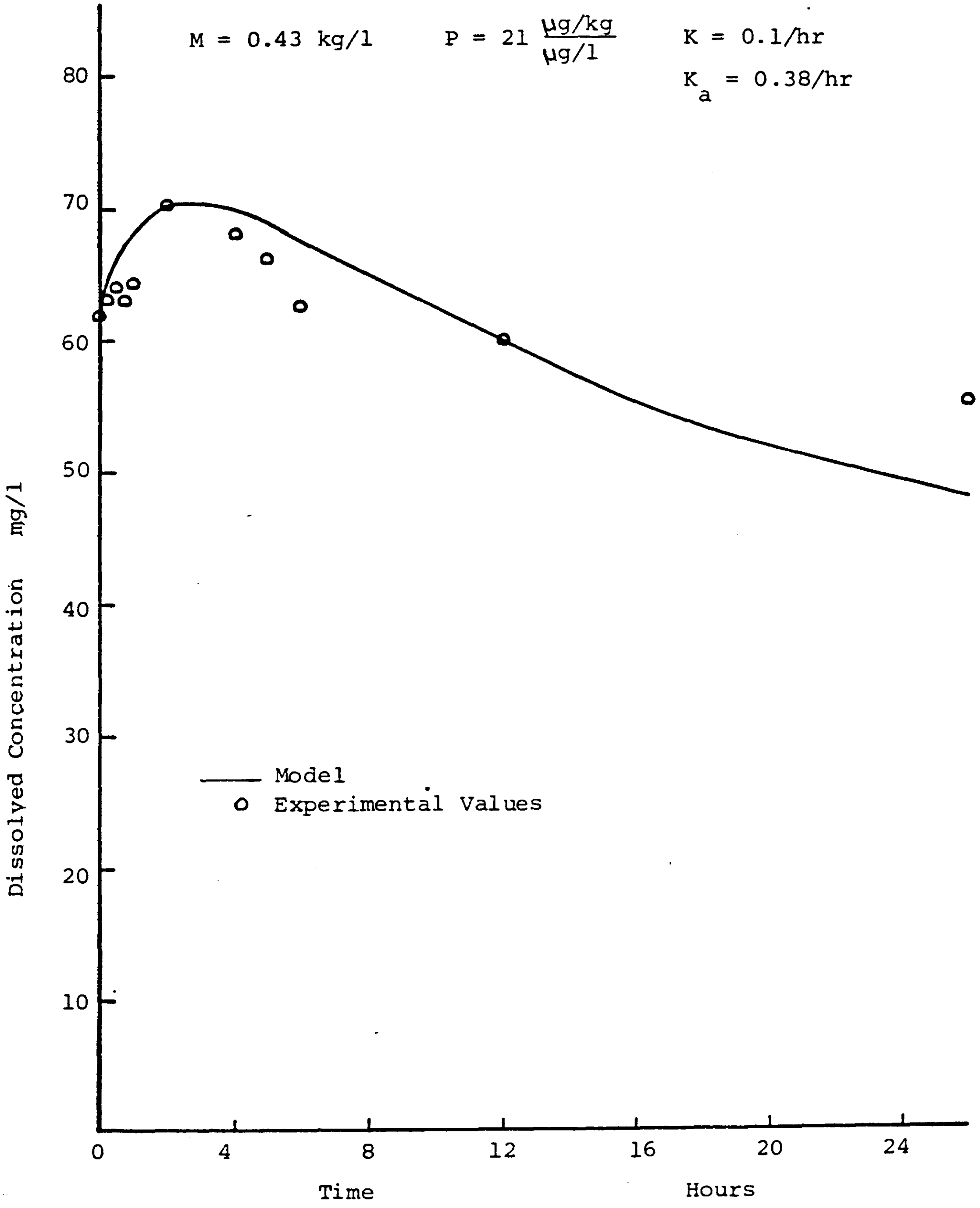


Figure 50. COD at Keokuk - 8°-18° C M.P. 356.

elutriation. The Kinetic Model could be used to model the concentration plume of a pollutant during disposal, as is shown subsequently.

Proposal of Plume Model

The model characterizes the pollutant plume for open water dredge disposal from the pipe line of a hydraulic dredge. The pollutant is thoroughly mixed in the pipe line before disposal. On disposal, the assumption made is that there is no dispersion so that the plume concentration represents the worst case. The model is one dimensional along the center line of the plume. The kinetics of sorption and sedimentation are assumed to predominate to the exclusion of all others.

Formulation

The driving force in the sorption kinetics is assumed to be the difference between the actual adsorbed concentration, r, and the equilibrium adsorbed concentration, r_{eq}. At equilibrium,

$$r_{eq} = PC \tag{38}$$

The model itself is divided into two stages. The first stage of model describes the pollutant concentration within the pump and pipe, which is similar to the kinetic model. The second stage describes the pollutant concentration and suspended solids concentration of the plume on discharge from the pipe. The second stage has a term to take into account the settling of the suspended solids.

Stage I:

$$\frac{dC}{dT} = K\,M\,(r - PC) \tag{39}$$

$$\frac{dr}{dT} = -\,K\,(r - PC) \tag{40}$$

$$\frac{dM}{dT} = 0 \tag{41}$$

$T = 0$ to T_1

$$T_1 = \frac{A \times l}{Q} \tag{42}$$

C = dissolved pollutant concentration $\mu g/l$

r = adsorbed pollutant concentration, $\mu g/kg$

K = sorption rate constant, 1/hour

M = suspended solids concentration, kg/l

P = partition coefficient, $\frac{\mu g/kg}{\mu g/l}$

T_1 = detention time in pipe - hours

A = area of pipe - m^2

l = length of pipe - m

Q = flow rate of dredged material, m^3/hour

Stage II:

$$U.\frac{dC}{dx} = K\ M\ (r - PC) \tag{43}$$

$$U.\frac{dr}{dx} = -\ K\ (r - PC) - K_s r \tag{44}$$

$$U.\frac{dM}{dx} = -\ K_s M \tag{45}$$

$$x = T_1/U \text{ to } 500 \text{ m} \tag{46}$$

U = velocity of river downstream, m/hour

K_s = sedimentation constant, 1/hour

x = distance downstream, m

The above equations were incorporated in a GASP IV computer program and solved. GASP IV is a Combined Continuous/Discrete FORTRAN based Simulation Language (Pritsker, 1974). Three of the examples of the

Kinetic Model were used to model the plume. Since no in-situ dredging data was available it was not possible to either calibrate or verify the model.

Figure 51 shows the predicted COD plume of open water dredge disposal, had there been dredging at Grey Chute at the given conditions, assuming no dispersion. Since the sediment is highly polluted there would be considerable desorption both in the pipe and while flowing downstream in the river. At a distance of 500 meters downstream of the dredge location the dissolved COD concentration would have reached 0.95 mg/l from a low 0.1 mg/l upstream of the dredge location. There is a reduction in the adsorbed solids concentration due to the settling of the suspended solids. There is no significant change either within the discharge pipe. A flow velocity of 1.0 m/sec was encountered during sampling on the Mississippi River. This figure was used for all the simulations. The sorption rate constant of 0.038/hour was taken from the kinetic experiments. The value of K_s = 14.4/hour is for a sand particle with a settling velocity of about 0.025 ft/sec and a river depth of 6 feet. The partition coefficient for COD was taken from Table 35. The adsorbed pollutant concentration of COD was taken from Table 32.

Figure 52 predicts the ammonia plume at Grey Chute. Ammonium ions are active in ion exchange with clay minerals. Since the sediment ammonia concentration is relatively low, ammonium ions being active in ion exchange with clay minerals, the dissolved ammonia concentration would reach a maximum of 189 μg/l and then start decreasing due to the sorbed concentration decreasing. The sorbed concentration would

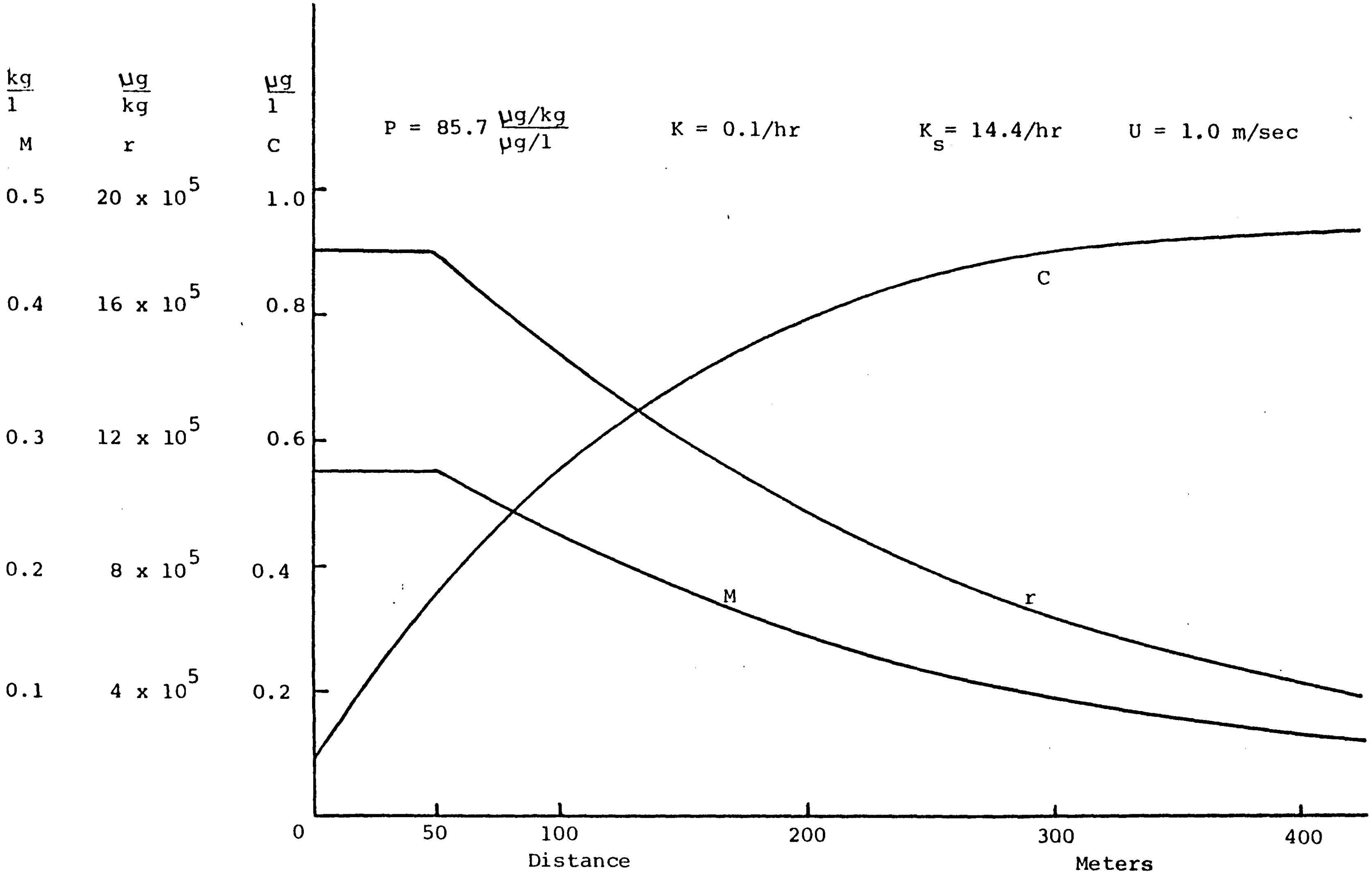


Figure 51. Plume Model of COD at Grey Chute.

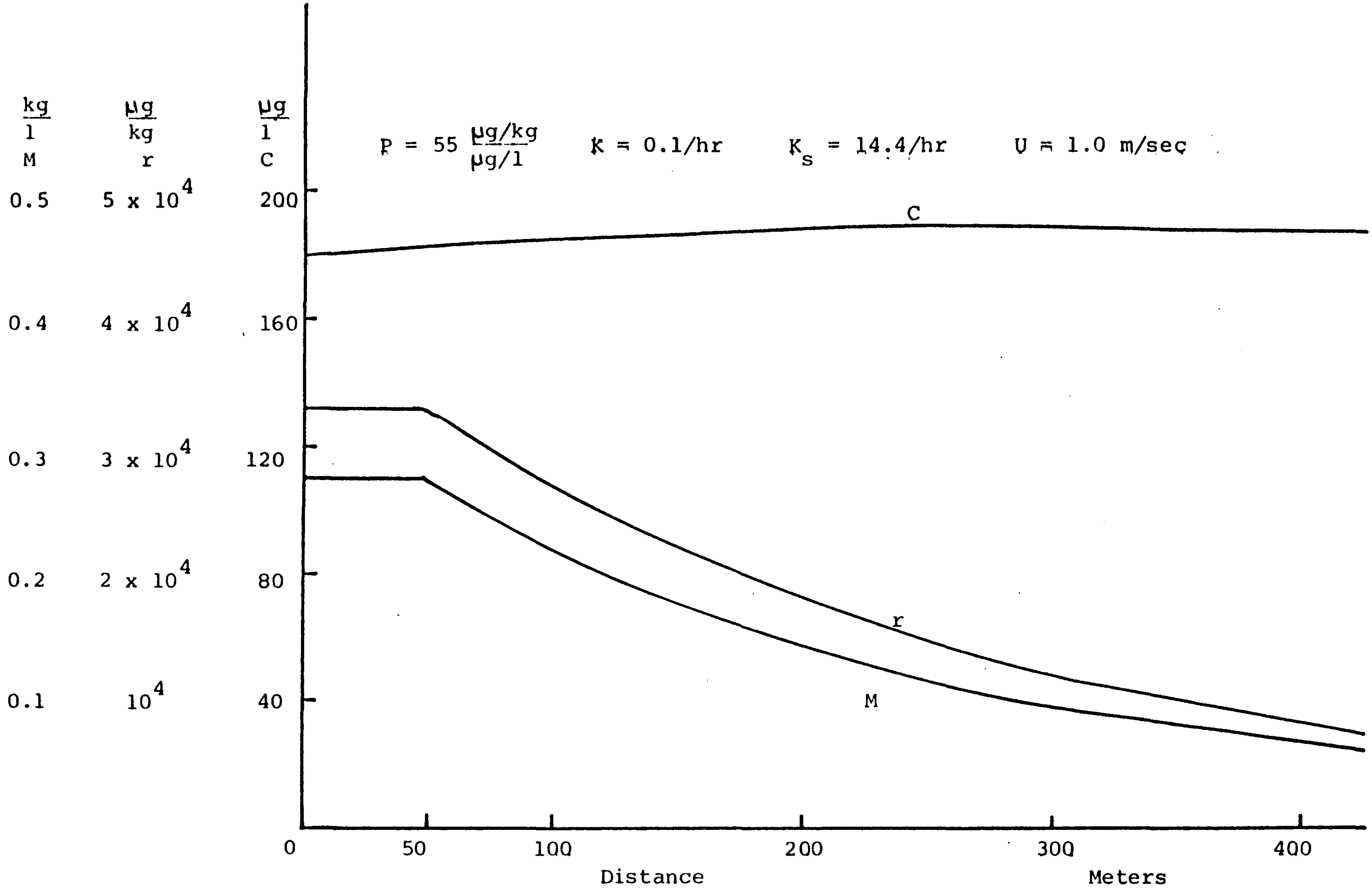


Figure 52. Plume Model of Ammonia at Grey Chute

decrease due to sedimentation. There would be no decrease for the first 50 meters which corresponds to travel within the pipe.

Figure 53 gives the plume model for COD at Keokuk. Due to a very high COD concentration in the sediment there will be rapid desorption leading to an increase in the dissolved COD concentration.

The plume model serves to give an idea about the magnitude of the maximum dissolved pollutant concentration and the approximate distance downstream that this maximum would occur. The model gives us an idea about the distance downstream that the effects of dredging are observed.

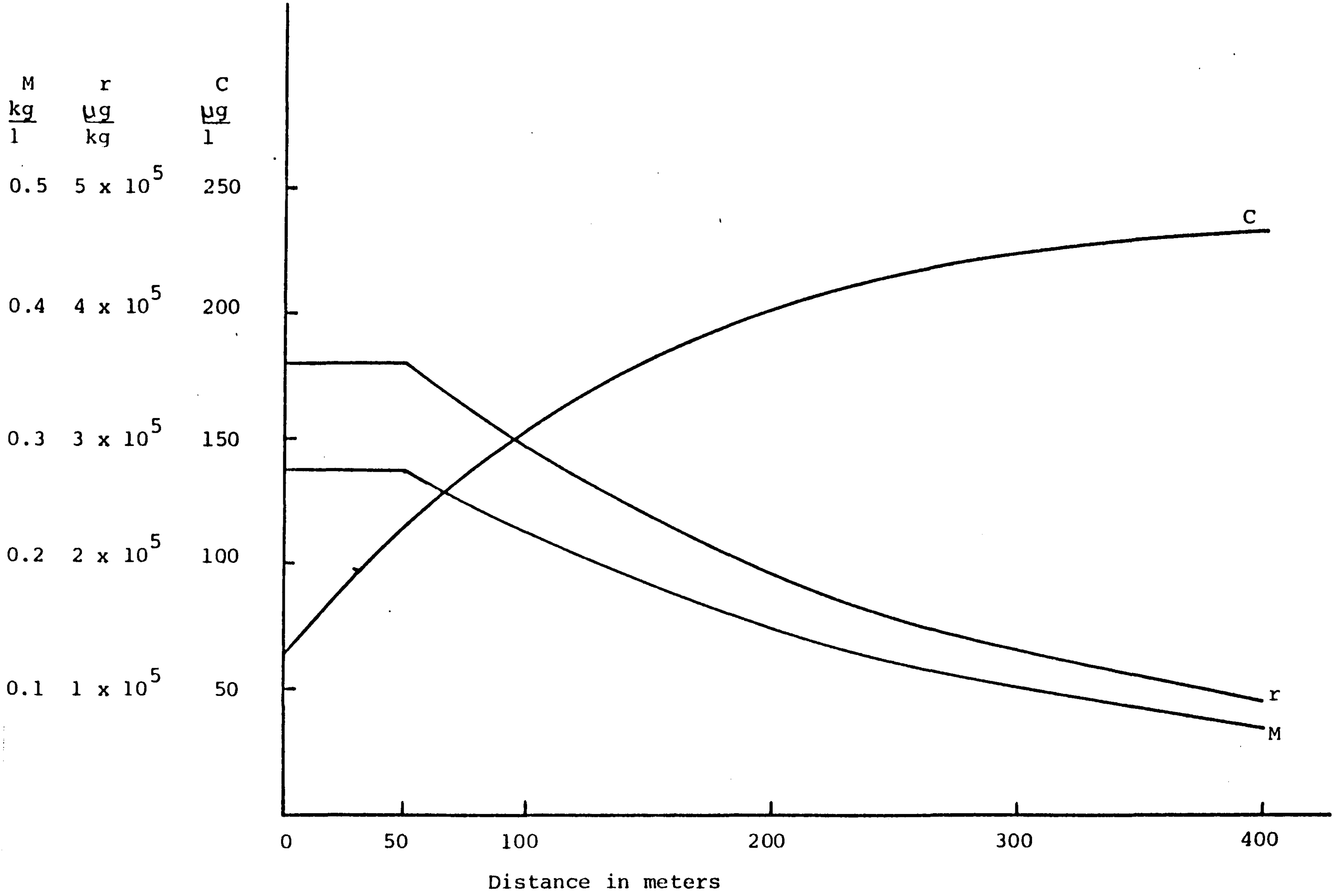


Figure 51. Plume Model of COD at Keokuk

CHAPTER IX

CONCLUSIONS AND RECOMMENDATIONS

The conclusions of this study were six:

1) Water quality criteria (USEPA, 1976) were seldom exceeded in standard elutriate tests. Presuming that the elutriate test simulates conditions at the point of discharge, dilution factors are not needed to meet water quality criteria.

2) Manganese, ammonia, COD, and oil and grease were the most frequently desorbed pollutants in the standard elutriate tests. Samples which displayed the largest desorption characteristics were generally "dirty" sediments (usually slough sediments) with finer grain size (more silt and clay), darker color, lower total solids content, and higher percent volatile solids.

3) Total iron and ortho-phosphate were the most frequently "adsorbed" (the effect would include precipitation phenomena) in the standard elutriate test. Trace metals, such as copper and zinc, were sometimes adsorbed.

4) The pesticides DDT, DDE, dieldrin, and PCB's were generally less than detectable in sediment and site water samples. Herbicides Lasso (alachlor) and Aatrex (atrazine) were detected in site water at approximately 1 ppb but were neither significantly adsorbed nor desorbed during elutriation.

5) Oxygen uptake of the sediment samples correlated quite well with the percent volatile solids content of the sediment ($r = 0.96$). A respirometer apparatus was developed to assess the oxygen demand of discharged dredge material. Oxygen uptake increased with the depth of material in sediment cores and with temperature. Oxygen demand was primarily due to chemical rather than biochemical reactions. Estimates showed that depletion of oxygen in the water column should not be serious with most sediment in the GREAT II reach.

6) Particle size distribution analyses indicated that most heavy metals were in the particulate state, especially as coatings on sand particles (greater than 62 microns) and in the clay fraction (0.45-2.0 microns nominal diameter).

7) Mathematical models were developed to describe the elutriate test, its kinetics, as well as the discharge of dredge material into navigable waters. The important model parameters include the sorbed pollutant concentration of the dredged sediment, the equilibrium partition coefficient of the pollutant on sediment, the suspended solids concentration of the discharge, and the dissolved pollutant concentration of the site water. The kinetic model for COD and NH_3 indicated that 70% of the change in concentration due to elutriation is complete within 30 minutes.

Recommendations include:

1) Sufficient elutriate tests have been performed to show that maintenance dredging of main channel sediments does not exceed water quality criteria. Attention should now be focused on water quality effects of opening sloughs and harbor dredging.

2) Sampling of the sediment intersticial water should be accomplished

with corers to be more representative of the actual intersticial water. There must be no mixing with the overlying site water during sampling.

3) The partition coefficient gives an indication of the pollution potential of a particular pollutant. A range of partition coefficients for each pollutant of concern should be established for the different kinds of sediments found in the Mississippi River.

4) Further study of the kinetic model using other pollutants is required if the kinetics of the discharge plume are to be modeled.

5) In situ-sampling, during dredging, would facilitate calibration of the plume model. The model could then be verified under various conditions - highly polluted sediment and clean water, clean sediment and polluted water, polluted sediment and water.

6) Sediment samples cannot be preserved for oxygen uptake measurements for more than 1-2 days.

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APPENDIX A

SITE MAPS

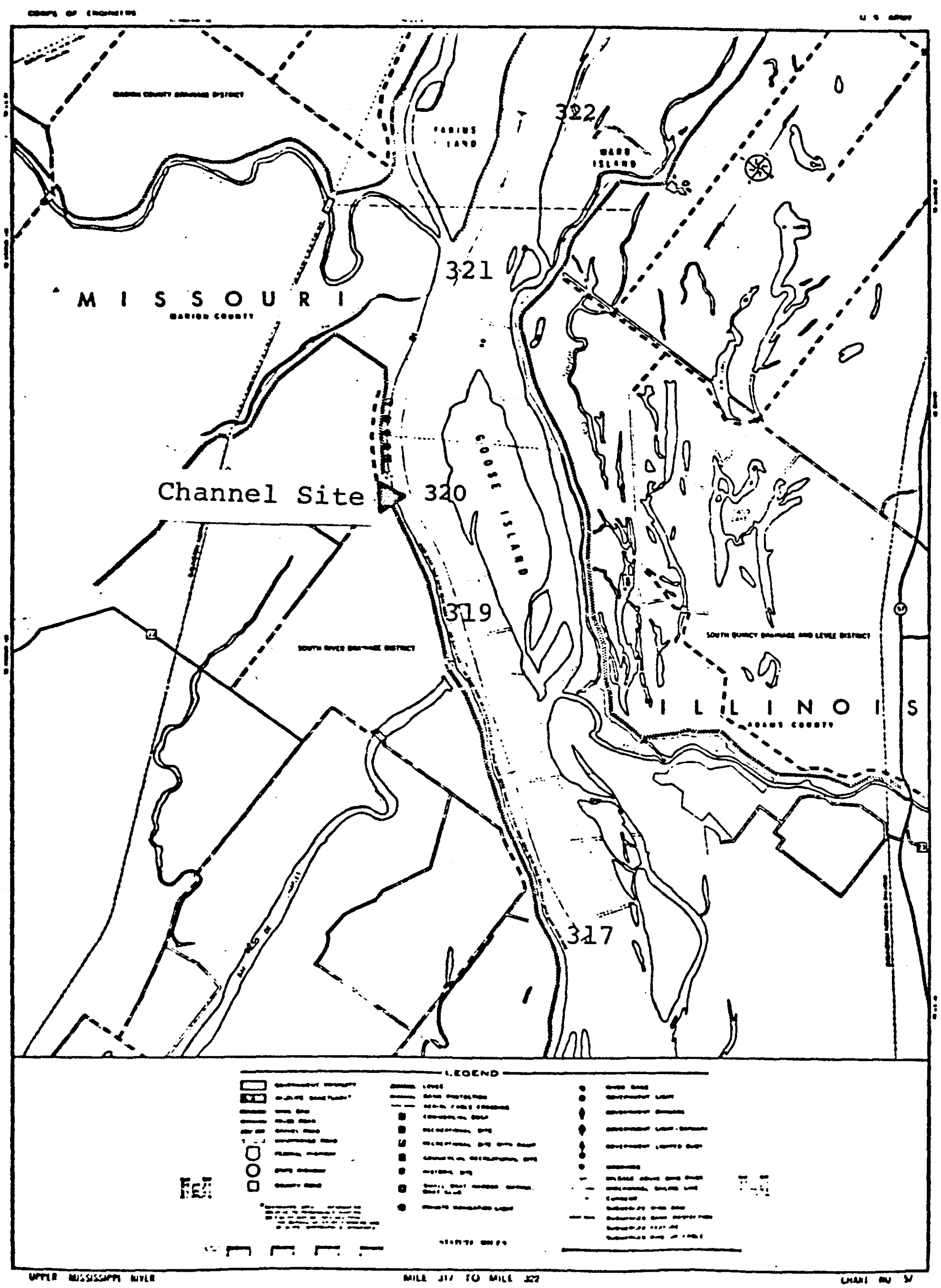


Figure A-I. Sample site at M.P. 320.0 below Quincy, IL at North East Power Company.

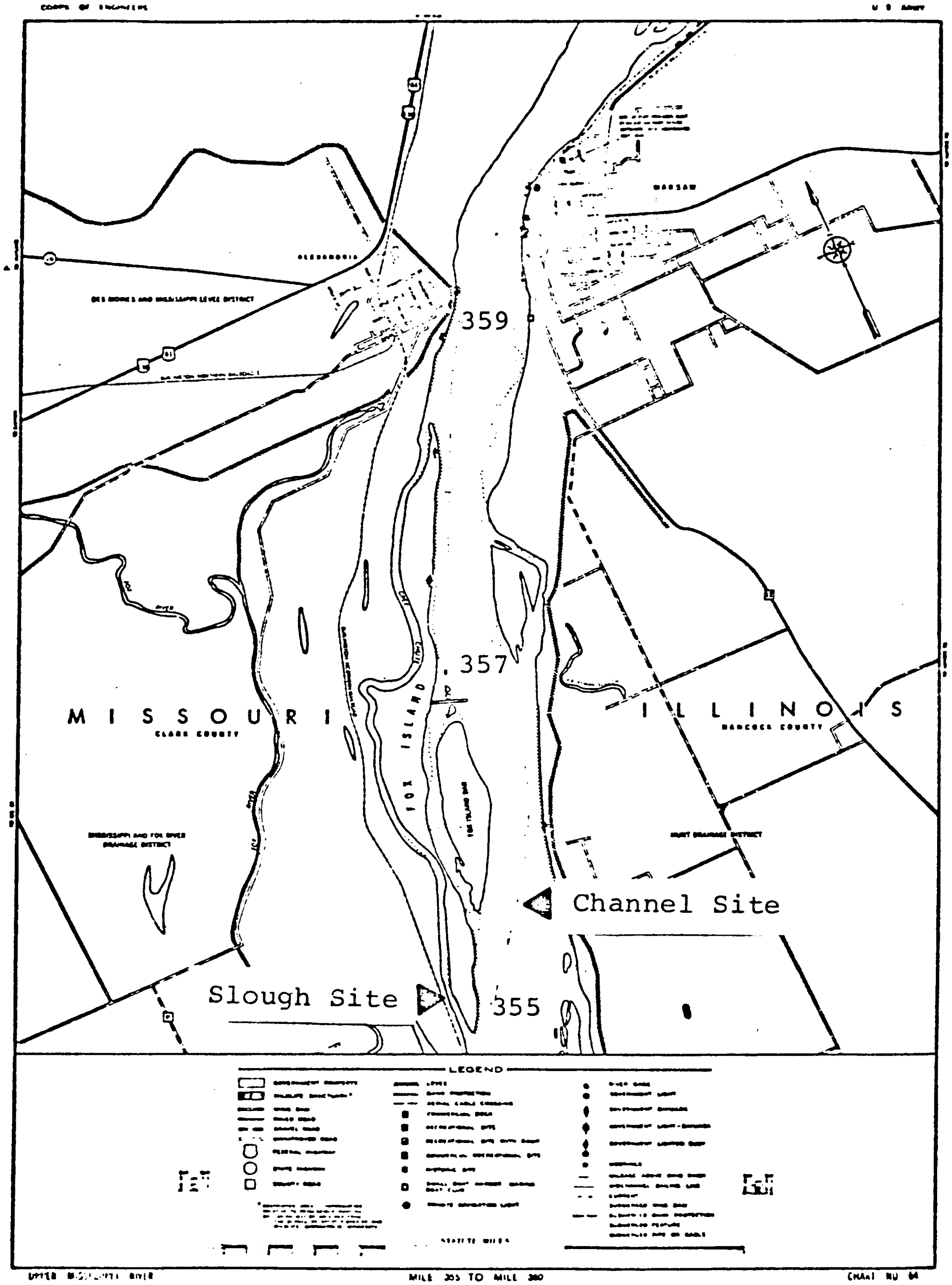


Figure A-II. Sample Sites at M.P. 355.5 below Keokuk, IA at Fox Island and in Grey's Chute.

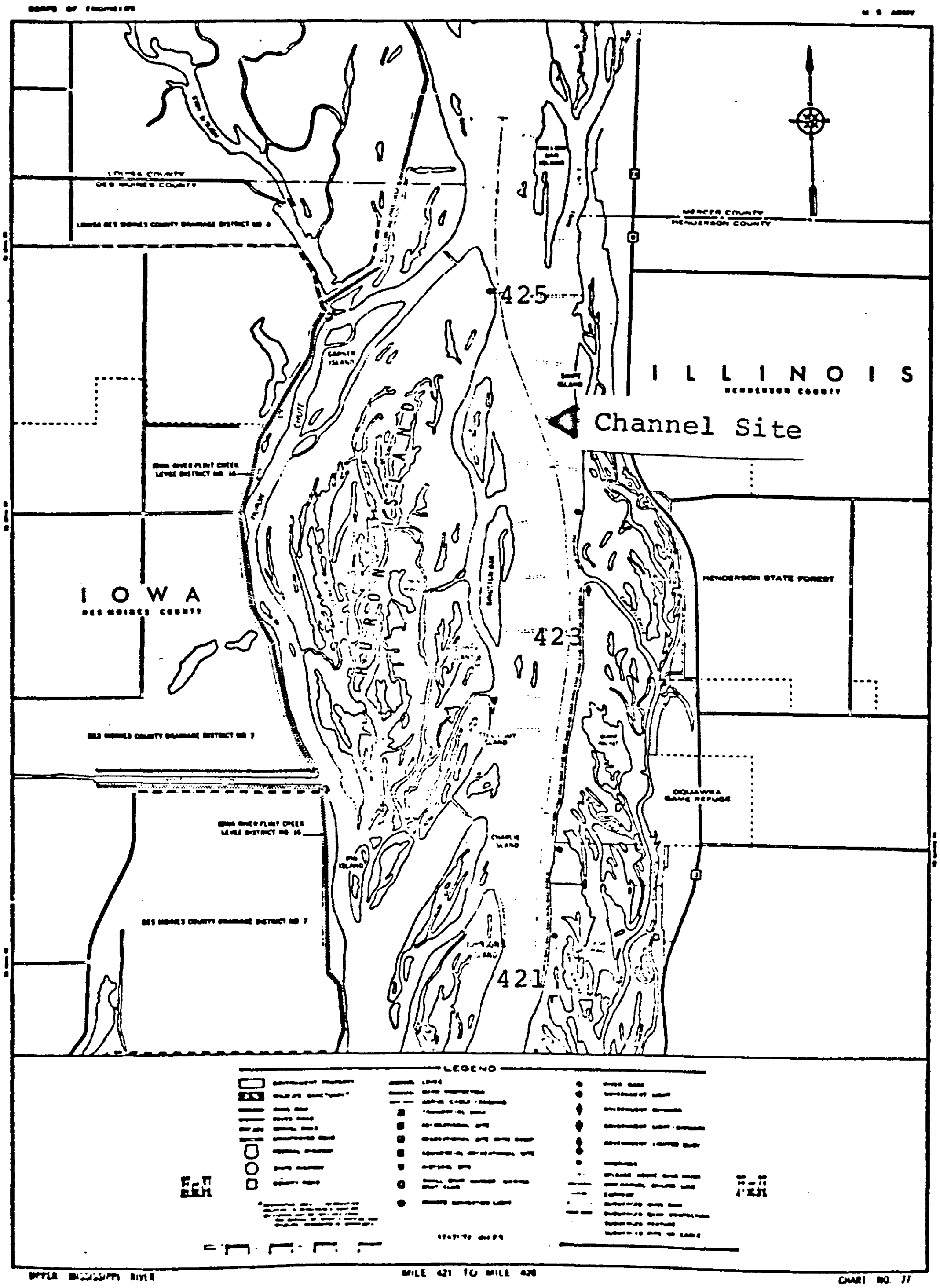


Figure A-III. Sample Site at M.P. 424.0 below Keithsburg, IL.

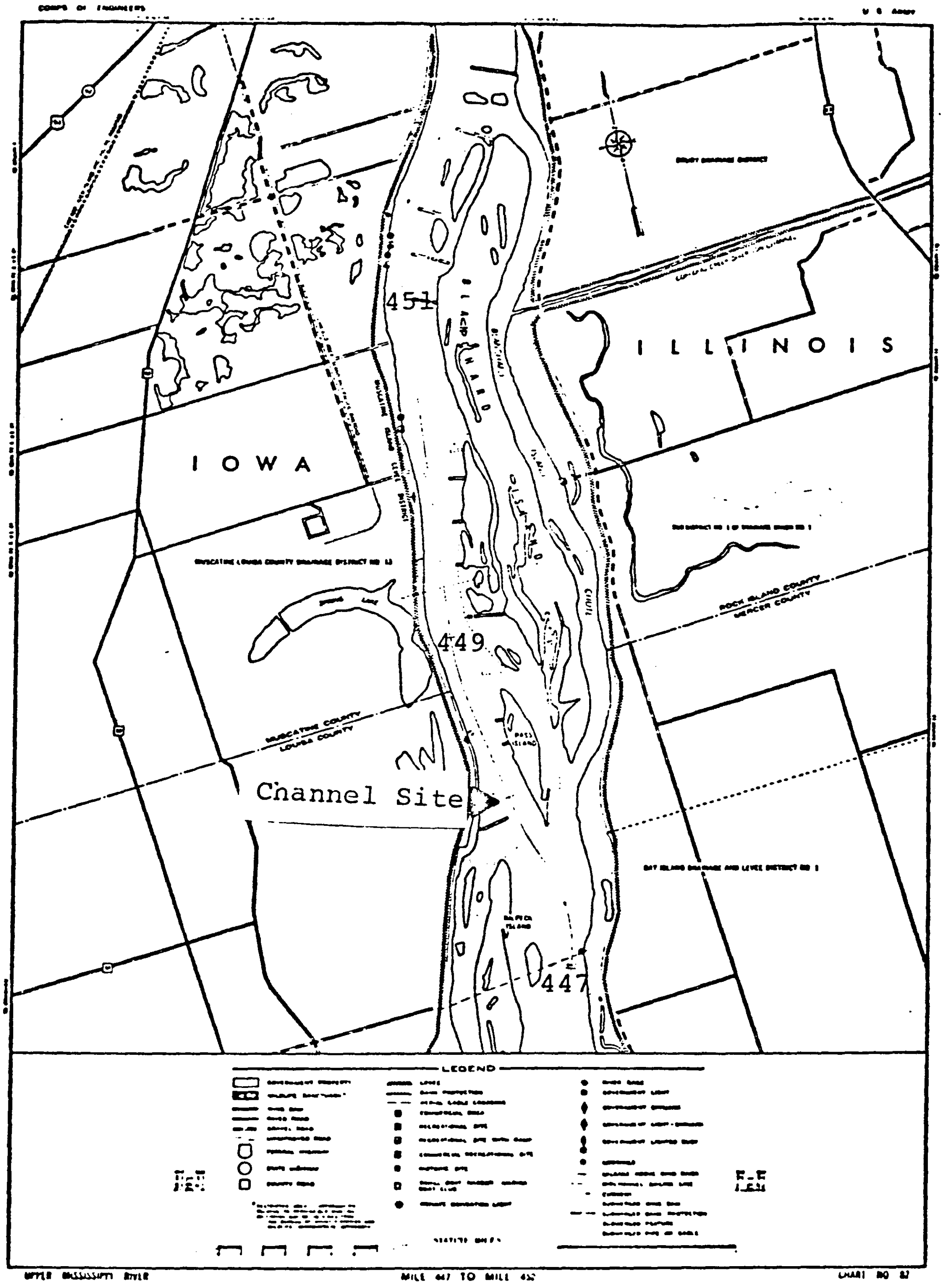


Figure A-IV. Sample Site at M.P. 448.0 below Muscatine, IA at Bass Island.

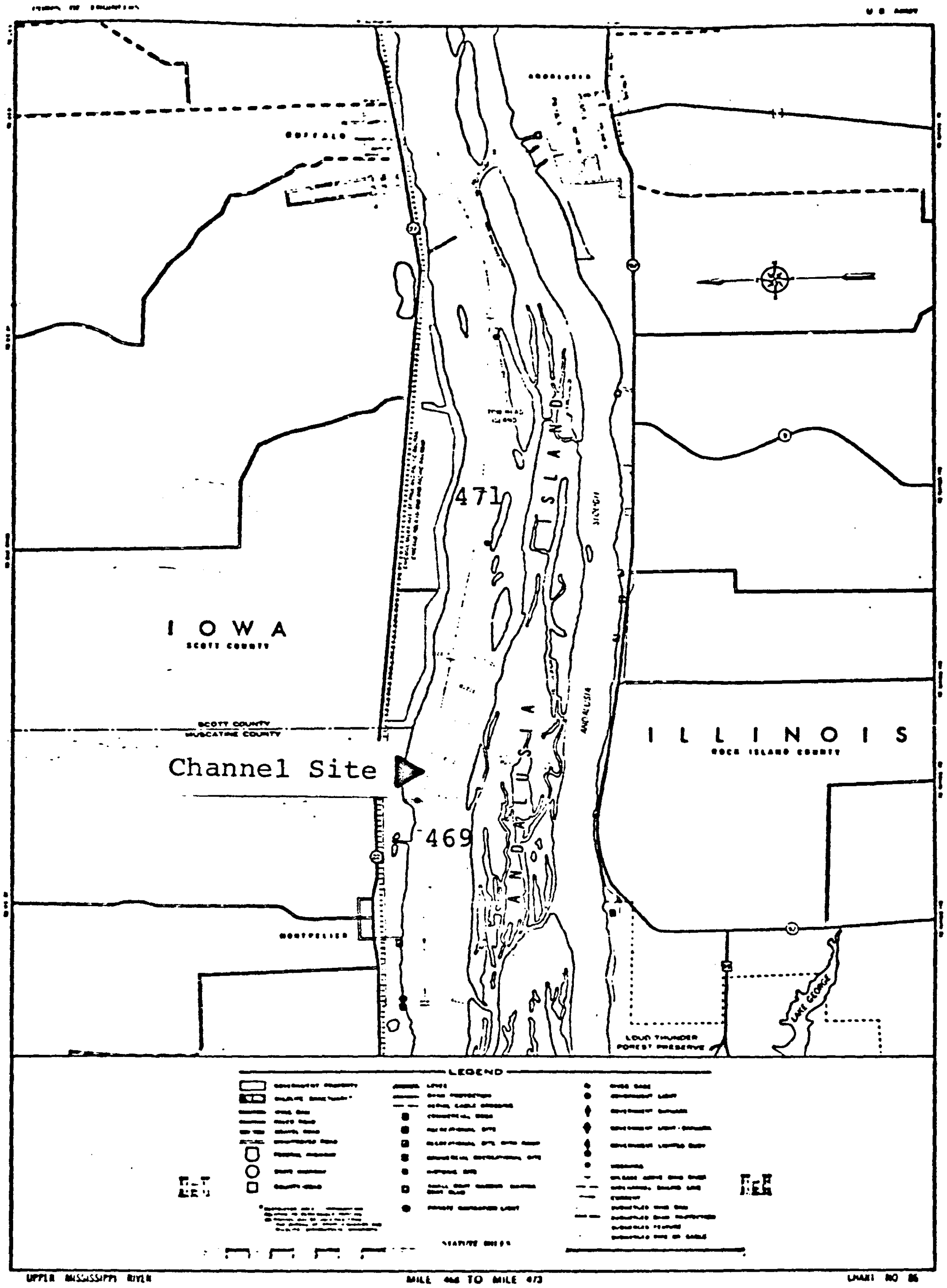


Figure A-V. Sample Site at M.P. 469.5 below Davenport, IA at Montpelier, IA.

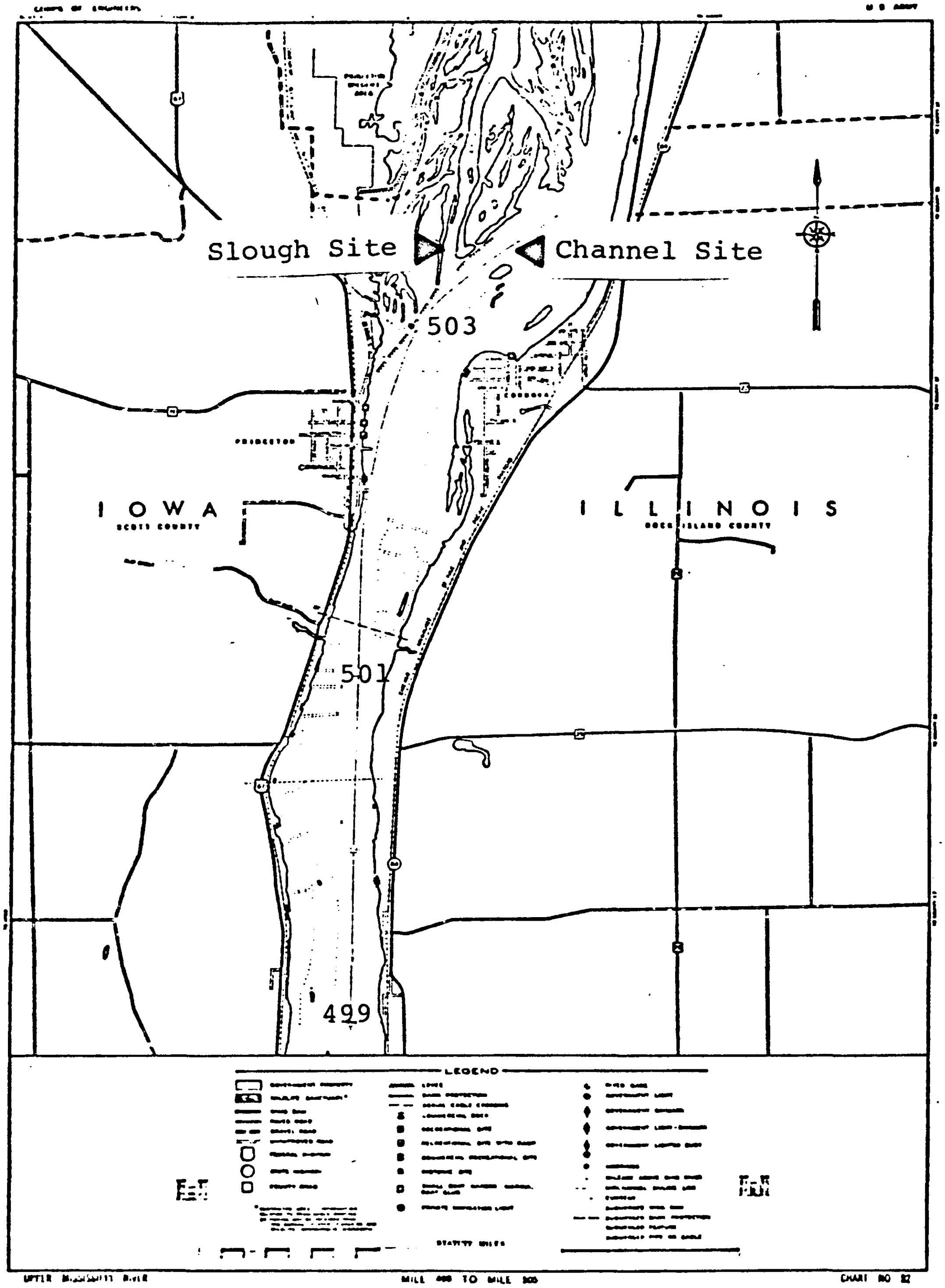


Figure A-VI. Sample Sites at M.P. 503.5 above Princeton, IA and in Steamboat Slough.

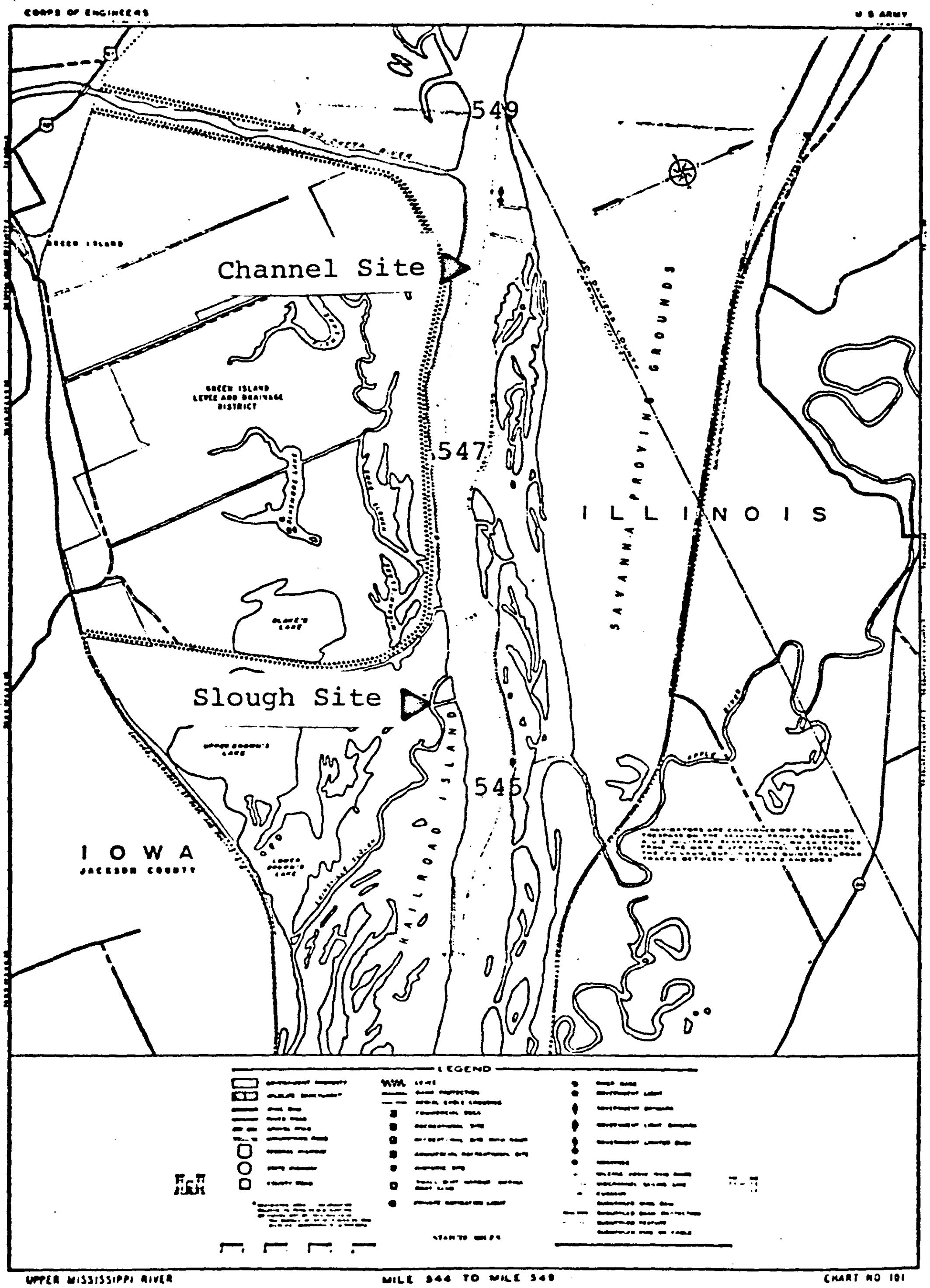


Figure A-VII. Sample Sites at M.P. 548.0 below mouth of Maquoketa River and at M.P. 545.8 in Apple-Meier Ditch.

APPENDIX B

PHYSICAL PARAMETER AND ELUTRIATE TEST DATA

Table B-I. Physical Parameters M.P. 320 (Channel)

Temperature 24°C

Depth 16.3 ft, 15.6 ft, 18.1 ft

Dissolved Oxygen 6.5 mg/l

	Raw	Interstitial	Elutriate I	Sediment I	Elutriate II	Sediment II	Elutriate III	Sediment III
ORP (mV)	411	-	361	361	371	361	371	361
pH	7.6	-	8.0	6.5	8.0	6.4	8.1	6.7
TSS (mg/l)	1.7	7	64	-	40	-	52	-
TVS (mg/l)	-	-	-	-	-	-	-	-

Table B-II. Physical Parameters M.P. 356 (Slough)

Temperature 24°C

Depth 10.2 ft, 12.2 ft, 8.6 ft

Dissolved Oxygen 6.5 mg/l

	Raw	Interstitial	Elutriate I	Sediment I	Elutriate II	Sediment II	Elutriate III	Sediment III
ORP (mV)	356	-	336	281	351	301	261	81
pH	7.9	-	8.1	7.4	8.1	7.4	7.4	7.1
TSS (mg/l)	56	60	154	-	314	-	1130	-
TVS (mg/l)	24	26	36	-	57	-	155	-

Table B-III. Physical Parameters M.P. 356 (Channel)

Temperature 24°C

Depth 14.0 ft, 18.4 ft, 14.6 ft

Dissolved Oxygen 6.2 mg/l

	Raw	Interstitial	Elutriate I	Sediment I	Elutriate II	Sediment II	Elutriate III	Sediment III
ORP (mV)	346	-	366	321	376	361	376	331
pH	7.8	-	8.0	7.8	8.0	7.6	8.2	6.8
TSS (mg/l)	88	27	78	-	118	-	56	-
TVS (mg/l)	32	17	30	-	34	-	28	-

Table B-IV. Physical Parameters M.P. 424 (Channel)

Temperature 24°C

Depth 14.0 ft, 16.4 ft, 14.2 ft

Dissolved Oxygen 7.2 mg/l

	Raw	Interstitial	Elutriate I	Sediment I	Elutriate II	Sediment II	Elutriate III	Sediment III
ORP (mV)	391	-	391	366	386	381	386	351
pH	8.1	-	8.1	6.4	8.0	5.8	8.1	5.6
TSS (mg/l)	157	43	63	-	93	-	93	-
TVS (mg/l)	-	-	-	-	-	-	-	-

Table B-V. Physical Parameters M.P. 447 (Channel)

Temperature 21°C

Depth 13 ft

Dissolved Oxygen 6.0 mg/l

	Raw	Interstitial	Elutriate I	Sediment I	Elutriate II	Sediment II	Elutriate III	Sediment III
ORP (mV)	394	-	394	344	394	344	394	344
pH	6.9	-	7.4	-	7.3	-	7.4	-
TSS (mg/l)	282	272	108	-	72	-	232	-
TVS (mg/l)	-	-	-	-	-	-	-	-

Table B-VI. Physical Parameters M.P. 469.5 (Channel)

Temperature 21°C

Depth 13 ft

Dissolved Oxygen 6.0 mg/l

	Raw	Interstitial	Elutriate I	Sediment I	Elutriate II	Sediment II	Elutriate III	Sediment III
ORP (mV)	394	-	334	344	334	394	334	344
pH	7.2	-	7.6	-	7.7	-	7.7	-
TSS (mg/l)	94	324	176	-	132	-	64	-
TVS (mg/l)	-	-	-	-	-	-	-	-

Table B-VII. Physical Parameters M.P. 545.5 (Slough)

Temperature 17°C

Depth 12-13 ft

Dissolved Oxygen 9.7 mg/l

	Raw	Interstitial	Elutriate I	Sediment I	Elutriate II	Sediment II	Elutriate III	Sediment III
ORP (mVO	644	-	344	344	334	44	274	44
pH	-	-	-	-	-	-	-	-
TSS (mg/l)	44	51380	960	-	980	-	6380	-
TVS (mg/l)	-	-	-	-	-	-	-	-

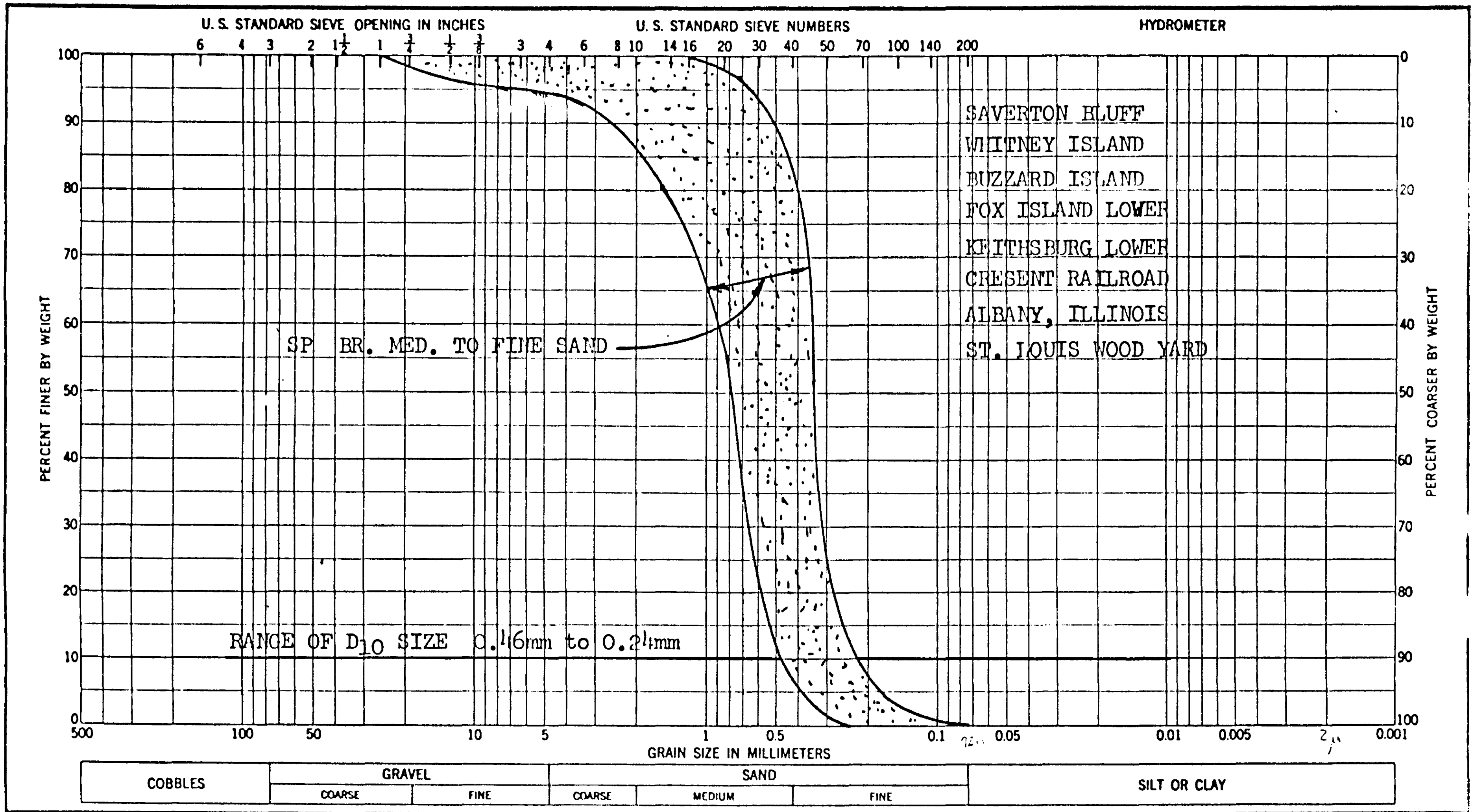
Table B-VIII. Physical Parameters M.P. 548 (Channel)

Temperature 18°C

Depth 10 -20 ft

Dissolved Oxygen 9.6 mg/l

	Raw	Interstitial	Elutriate I	Sediment I	Elutriate II	Sediment II	Elutriate III	Sediment III
ORP (mV)	544	-	444	144	444	44	444	44
pH	-	-	-	-	-	-	-	-
TSS (mg/l)	43	73400	1750	-	2260	-	1400	-
TVS (mg/l)	-	-	-	-	-	-	-	-



SAVERTON BLUFF
WHITNEY ISLAND
BUZZARD ISLAND
FOX ISLAND LOWER
KEITHSBURG LOWER
CRESENT RAILROAD
ALBANY, ILLINOIS
ST. LOUIS WOOD YARD

SP BR. MED. TO FINE SAND

RANGE OF D_{10} SIZE 0.16mm to 0.24mm

Sample No.	Elev or Depth	Classification	Nat w %	LL	PL	PI

Project MISSISSIPPI RIVER DREDGE

Area

Boring No. RANGE OF GRADATION CURVES

Date 1 September 1978

GRADATION CURVES

ENG FORM 1 MAY 63 2087