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INFLUENCE OF THE SEDIMENT/WATER INTERFACE ON THE AQUATIC CHEMISTRY OF HEAVY METALS

ENVIRONMENTAL CHEMISTRY RESEARCH DIVISION
ENVIRONICS DIRECTORATE
TYNDALL AIR FORCE BASE, FLORIDA 32403

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The mechanisms controlling the transport of three heavy metals: cadmium, chromium, and silver, in natural water systems are evaluated following a review of the scientific literature and laboratory studies of adsorption/desorption behavior and the interaction of these metals with phytoplankton. In fresh water, chromium as chromate is not appreciably taken up by model inorganic or organic particulates, but after (continued)

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reduction to Cr(III) is rapidly and irreversibly taken up by clay particles, hydrous iron oxide and phytoplankton. Cadmium and silver are more reversibly adsorbed by clay particles, are strongly adsorbed by hydrous manganese oxide, and are concentrated by phytoplankton. Once a part of reducing bottom sediments, the availability of all three metals to the aqueous phase is further reduced so that they are not released by short term resuspension. With prolonged resuspension of anoxic sediments some cadmium may redissolve, but chromium and silver will remain in the solid phase.

PREFACE

This report documents work performed during the period February 1975 through September 1976 by the New England Aquarium under contract F29601-75-C-0062 with the Air Force Civil Engineering Center, Air Force Systems Command, Tyndall Air Force Base, Florida 32401. Major Michael G. MacNaughton, EVC, managed the program for the Center.

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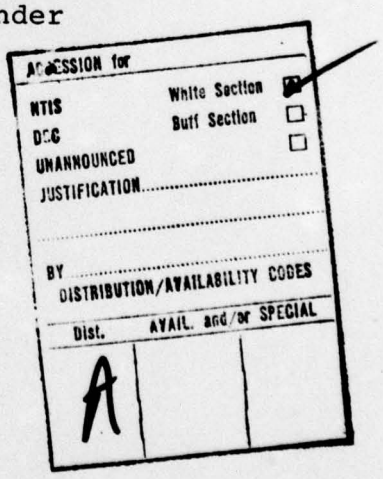
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SECTION I

INTRODUCTION

Heavy metal chemistry in natural waters is characterized by several phase changes. Metals may be present in the aqueous phase through the dissolution of minerals during natural erosion processes or the discharge of mining and industrial wastes. The metal ions are then adsorbed on, coprecipitated with, or occluded within various organic and inorganic matrices. As this suspended solid matter settles out of the water column, the metals are stripped from the aqueous phase into the sediments. Further chemical alteration occurs largely as the result of the change from an oxygenated to an anaerobic environment.

A study of the sediment/water interface behavior of cadmium, chromium and silver must first include a study of the dominant mechanisms which control the uptake of the dissolved metals by suspended particulate matter. This process will depend on such water quality parameters as pH, salinity, oxidation potential, temperature, and, in particular, the concentrations of naturally occurring ligands which may form stable ion pairs or complexes with the metals under study. Included in this group would be such inorganic ligands as carbonate, hydroxide, and chloride, and organic chelating agents such as EDTA and NTA, amino acids, and the array of compounds known collectively as humic substances. The degree to which such metal-ligand association occurs may be determined two ways: through models based on thermodynamic equilibria, or by empirical observation. Mathematical models provide a useful base of information on which to design analytical testing, but, as will be shown, are in themselves inadequate in describing the chemistry of most natural waters.

In the work described here, information from a literature survey was combined with the results of laboratory simulation experiments to form a theoretical model describing the transport of the three metals in natural waters. Then a detailed examination was made of the distribution of these metals in a polluted river/estuary system, the lower Charles River near Boston, Massachusetts. The results of metal analyses of the aqueous and sediment phases were then compared with the behavior predicted by the model.

SECTION II

LITERATURE REVIEW

2.1 Introduction

While adsorption and possibly coprecipitation processes have been implicated as the principal means by which trace metal concentrations are regulated in the water column, detailed analyses of the critical scavenging mechanisms are generally lacking for most metals. As Sayre, et al. (1963) pointed out, a comprehensive model of transport mechanisms must address the questions:

1. What are the chemical forms involved?
2. What factors control the extent of adsorption (organic ligand complexation, ionic strength, etc.)?
3. To what extent does adsorption occur?

Our attempt to answer these questions as they apply to three trace elements - chromium, cadmium, and silver - has entailed an extensive review of the existing literature. The information obtained in this review and its application to the present study are discussed in the following paragraphs.

2.2 Inorganic Species Distribution

The most straightforward aspect of a transport model would appear to be that which predicts the distribution of each element among soluble inorganic complexes, including uncharged ion pairs, and such sparingly soluble metal salts as the hydroxides and sulfides and the silver halides. For many such complexes, the formation constants and solubility data are fairly accurately known. A compilation of those constants pertinent to the present study is presented in Tables 33-35. To use these data in transport models requires that such water quality parameters as pH, oxidation potential, ionic strength and the concentrations of complexing anions be known, at least approximately. In marine systems, and especially in open ocean waters, these parameters are reasonably constant and well characterized. Fresh water systems are another matter, however, since pH, dissolved oxygen levels, and the concentrations of the major ionic species can vary significantly with time as well as location.

Moreover, in formulating model systems, two assumptions are made, neither of which may be valid. Since these are equilibrium constants, they necessarily apply only to systems

or regions within systems which have reached thermodynamic equilibrium. However, the literature contains numerous examples of reactions implicated in trace metal transport which are not at equilibrium in natural water systems. According to Morgan (1967), the surfaces of aluminosilicates may be near equilibrium in sea water but are far removed in fresh water. The kinetics of many redox processes are quite slow, so that, for instance, in the diagenesis of organic-rich sediments the oxygen used in early degradation comes from sulfate and not from hydrous ferric oxide as would be predicted from reaction thermodynamics (Bostrom, 1967). Similarly, from thermodynamic considerations the oxidation state of manganese in aerated seawater should be Mn(IV). However, the very slow kinetics of Mn(II) oxidation, possibly catalyzed on mineral surfaces or by microbial action, accounts for the presence of Mn(II) in seawater.

A second assumption made in equilibrium modeling is that the formation constant values in the literature are accurate. Actually there can be wide variations in these values, even when corrected for ionic strength effects. The significant impact such variability can have on modeling results was illustrated recently by Morgan and Vuceta (1976). The selection of the most accurate or most applicable data values is not always straightforward. For example, Murray, et al. (1968), list ZPC values, the pH at which the solid surface charge from all functional groups is zero, for manganese dioxide from 1.5 to 7.3 depending on crystal structure. By electing to use a value >7, Parks (1967) concluded that cationic adsorption in fresh water on manganese oxides would be minimal, while in sea water, colloidal MnO_2 may control trace metal levels. However, in their study of trace metal adsorption on hydrous ferric oxide (HFO) and hydrous manganic oxide (HMO), Gadde and Laitinen (1974) interpreted their results in terms of the ZPC for HMO of 2.8 given by Morgan and Stumm (1964).

Given the above uncertainties, one may conclude that the predictions from an equilibrium model are far from definitive. However, they can provide a useful starting point in formulating a more empirical evaluation. Also the results of most metal speciation models found in the technical literature seem to agree with one another. Thus, the principal dissolved cadmium species in sea water was computed to be $CdCl_2$ and $CdCl^+$ (Krauskopf, 1956), with much smaller proportions of $CdCl_3^-$ and Cd^{+2} (Zirino and Yamato, 1972). Similarly, Morel and Morgan (1972) predicted that cadmium would exist in a model sea water-like medium exclusively as chloro complexes. They also calculated the principal Cr(III) complexes to be hydroxides, presumably $Cr(OH)_2^+$, and the likely form of silver to be AgI. The latter result does not coincide with the common assumption

that silver exists in sea water in chloro complexes, probably $AgCl_2^-$ and $AgCl_3^=$ (Krauskopf, 1956; Horn, 1969; Gilbert, 1971).

The chemistry of chromium presents an additional complication to a modeling scheme in that it may be present in natural waters in two oxidation states. Not only are the kinetics of the $Cr(VI)+3e^- \rightarrow Cr(III)$ couple not documented for natural waters, but the thermodynamically favored oxidation state is somewhat in doubt. Thus, Elderfield (1970), Fukai and Huynh-Ngoc (1968), Goldschmidt (1954), and Krauskopf (1955) theorized the Cr(VI) was the stable form in open ocean water at pH 8, while Sillen (1961) and Chuecas and Riley (1966) concluded that Cr(III) should be the favored state.

Published experimental data on the subject do little to resolve the question. In their study of the distribution of ^{51}Cr in the Columbia River and Oregon coastal water, Curl, et al. (1965) noted that the metal was in the hexavalent state when introduced to the river, but that a portion was reduced to the trivalent state in flowing to the sea. Once in the Pacific Ocean, no further reduction appeared to take place (Cutshall, et al., 1966). Fukai (1966), who theorized that chromium should be present in sea water in the hexavalent state, found both forms in coastal water samples. However, Chuecas and Riley (1966) reported that 99% of the chromium in samples from the Irish Sea was trivalent, the form the authors considered to be thermodynamically stable. Finally, Elderfield (1970), using the analytical method of Fukai and Vas (1967), found that in 8 of 10 samples of coastal sea water over 90% of the chromium was in the trivalent state, while in one of the remaining two, 88% was hexavalent.

This variability in both theoretical and observed distributions between oxidation states arises from at least two sources. The stability of trivalent chromium may be enhanced by the presence of naturally occurring organic chelators, as yet not characterized. Also the kinetics of chromium redox processes in natural waters are not accurately known. Cr(VI) can oxidize organic matter in natural waters (Elderfield, 1970). Presumably in slightly acidic fresh water, production of Cr(III) in this manner would be greater than in sea water, given the strong pH dependence of the $Cr(VI)+3e^- \rightarrow Cr(III)$ half reaction. On the other hand, oxidation of Cr(III) may be a very slow process, even in pH 8 sea water, given the high overpotential of most redox reactions involving molecular oxygen. The net effect of these processes appears to agree with the partial reduction of Cr(VI) observed in the Columbia River and with the apparent stabilization of Cr(VI) in oceanic waters.

2.3 Dissolved Organic Species

An important factor in metal transport may be the association between the metal and dissolved organic chelating agents. Florence and Batley (1976) calculated that 99% of the Cr(III) in sea water made 2 x 10^{-8}M in EDTA would be present as the EDTA complex. In their model seawater systems, Morgan and coworkers have included among the ligands a number of amino acids and aminocarboxylate chelating agents. Their computations indicate that none of the three metals were present principally in an organic complex. The Cr(III)-EDTA complex was proportionately the most abundant, making up 0.3% of the total chromium concentration. However, no formation constant values were available for many of the organic-Cr(III) complexes. This lack of thermodynamic data may contribute greatly to the inability of such models to predict metal complex distributions, and, in the case of chromium, to indicate the favored oxidation state.

While the formation of dissolved organic complexes of cadmium and chromium has been considered in several theoretical treatments, there has been little experimental verification of their presence in natural waters. In their electrochemical studies of metal chelates in Great Lake water, Matson and coworkers (Matson, et al., 1969; Allen, et al., 1970) did not characterize cadmium complexation. Using similar techniques, Chau and Lum-Shue-Chan (1974) analyzed a number of lake samples for four metals including cadmium, but found no detectable cadmium levels (0.4 ppb) in most of them. In a study of the ability of Chelex-100 resin to adsorb trace metals from sea water, Florence and Batley (1975) concluded that cadmium and several other metals are likely adsorbed on or occluded within colloidal organic and inorganic particulates rather than present as soluble organic chelating agents. Further investigation (Florence and Batley, 1976) showed that ultraviolet irradiation of sea water samples generated more freely soluble cadmium. Whether this release of "bound" metal was due to the destruction of organic colloids or organic complexing agents was not discussed by the authors.

2.4 Adsorption on Particulates

2.4.1 Theoretical Models

Adsorption processes on metal oxide surfaces have been extensively studied. As Morgan and Vuceta (1976) pointed out, there are essentially two different theoretical models used to describe adsorption processes, the "adsorption-hydrolysis, ion-solvent interaction" (AHIS) model of James and Healy (1972b),

and the "surface complex formation" (SCF) model of Stumm and associates. The AHIS model considers the free energy of adsorption as the sum of coulombic, solvation and chemical components:

$$\Delta G_{ADS} = \Delta G_{COUL} + \Delta G_{SOLV} + \Delta G_{CHEM}$$

Values for the first two components can be calculated a priori knowing the hydrated radius of the adsorbed ion, the charge on the ion and on the surface, and the dielectric constants of the bulk solution and of the interfacial region. The ΔG_{CHEM} term is then usually employed to fit the total free energy equation to the observed adsorption behavior. In the AHIS model the adsorption of an uncharged complex, or of any species on a surface at ZPC, must be due solely to this chemical interaction. Thus, Gadde and Laitinen (1974) observed appreciable adsorption of cadmium in the region of the ZPC for HMO which they attributed to the chemical or "specific" adsorption of the metal ion. Morgan and Vuceta (1976) reported that adsorption on clay particles involves little chemical interaction. Similarly an extrapolation of the adsorption isotherm for Cr(III) on silica observed by James and Healy (1972a) indicates little adsorption in the pH region of the ZPC. Fukai and Vas (1967) reported the quantitative adsorption of Cr(III) from pH 8 sea water using a suspension of HFO. Since the ZPC for amorphous hydrous ferric oxide has been reported to be 8.5 (Parks, 1965), the adsorption process presumably entails significant chemical interaction.

The SCF model considers adsorption on a hydrous oxide as an exchange reaction with a surface proton of the -MOH moiety. Thus, the model considers only the freely dissolved metal as the adsorbed species and the formation of hydroxide or other complexes as side reactions which compete with surface complexation. The implications of this model appear to contradict the conclusion of James and Healy (1972a) that there exists at least a qualitative positive relationship between metal hydroxylation and adsorption on a variety of surfaces.

It should be pointed out that both models, despite their different approaches, can be fitted to experimental data. In the AHIS model, as noted above, the ΔG_{CHEM} term is essentially a fitting parameter, i.e., a chemical correction to the electrostatic model. The SCF model employs "apparent constants" for the acid dissociation equilibria of -MOH groups and for the formation of metal complexes. These modified constants contain electrostatic terms to account for the interaction between metal ions and the charged surface layers. In other words, the model has an electrostatic correction for its chemical approach. The use of these correction factors to fit experimental data gives no clue as to the theoretical accuracy of either of the two

models, or to their applicability to complex environmental systems. In the work reported here, physical adsorption was evaluated simply in terms of the Freundlich isotherm:

$$\frac{X}{M} = kc^n$$

where X = wt of material adsorbed
M = grams of adsorbent
c = concentration of adsorbate in solution at equilibrium
k = empirical constant
n = empirical constant (≤ 1)

A measure of adsorption specificity (chemical interaction) was determined through the extrapolation of adsorption isotherms through the region of ZPC, and by measuring adsorption and desorption in the presence of much higher levels of alkaline earth cations.

2.4.2 Adsorption on Natural Suspended Solids

A number of studies have examined the adsorption of trace metals on such naturally occurring particulates as the clay minerals, viable and detrital organic matter, and the hydrous oxides of iron and manganese. Krauskopf (1956) examined the adsorption of chromium(VI), silver and a number of other metals from seawater onto a variety of model particulates. He found that silver was not adsorbed by HFO, HMO, apatite (calcium phosphate fluoride) and clay, but that it was adsorbed by plankton and peat moss. Cr(VI) was only slightly affected by HFO, apatite, clay and the organic particulates, but was strongly adsorbed by HMO. Curl, et al. (1965) reported the rapid uptake of Cr(III) by 10 species of marine phytoplankton. They found no significant differences in adsorptive behavior between species or between viable and dead cells. Johnson, et al. (1967) observed that the chromium adsorbed on suspended particulates in the Columbia River was not desorbed by the major cations of sea water or by copper sulfate. Knauer and Martin (1973) reported that the cadmium concentrations in onshore marine phytoplankton were almost an order of magnitude higher than in offshore samples, a trend which reflected the higher dissolved cadmium levels onshore. Cadmium was extensively adsorbed on HMO between pH 5 and 8 in distilled water-based media; it was adsorbed on HFO to a lesser degree at pH 8 and only slightly at pH 5 (Gadde and Laitinen, 1974).

In their study of the stream supply of 8 trace elements in 12 of the world's rivers, Kharkar, et al. (1968) investigated the adsorptive properties of three clay minerals, ferric oxide, manganese dioxide, and freshly precipitated ferric hydroxide. Hexavalent chromium was not extensively adsorbed by any of the

particulates. About 20-30% of 1 µg/l Ag in distilled water was adsorbed by 1000 ppm suspensions of illite and montmorillonite; 13% was adsorbed by 1000 ppm kaolinite; 60% by 1000 ppm HFO, and 80-85% by 1000 ppm MnO_2. Between 25% and 30% of the adsorbed silver was released from the first two clay particles on mixing with sea water, while almost all of the silver adsorbed by MnO_2 was released. After analyzing the particulate and dissolved levels of trace elements from numerous samples, the authors concluded that the dissolved concentration is independent of the concentration on particulate matter and that there is no correspondence between suspended load and dissolved trace element concentration. This inert quality of trace elements associated with suspended particulates was developed further in a related paper by Turekian and Scott (1967), who found that the concentrations of chromium, silver, and four other metals were generally higher on suspended particulates in eastern U.S. streams than on those in the Mississippi and western streams, despite the fact that the cation exchange capacity of the suspended load is similar in eastern streams. The authors concluded that simple cation exchange is not the principal mechanism in the association of these metals with suspended particulates.

The phase distribution of cadmium in fresh water systems has been characterized in two papers. Gardiner (1974) measured the ability of silica, kaolin, humic acids and several river muds to adsorb cadmium from a hard, untreated ground water medium. Of the model materials only humic acid approximated the adsorptive ability of the river muds. Both adsorption and desorption on humic acid appeared to be rapid processes, approaching equilibrium within a few minutes. These results led the author to conclude that humic substances in river sediments would act as an effective buffer maintaining a constant dissolved cadmium level. In a study of nine trace metals in the waters and sediments of several eastern Tennessee streams, Perhac (1974) found that most of the cadmium in the water column was consistently in the dissolved phase or associated with colloidal material of less than 0.01 µm. Understandably, the highest proportion of waterborne cadmium present in the particulate phase was found in the sample containing the highest suspended load. Whether these solids significantly decreased the dissolved concentration of cadmium is not clear given the uncertainty of the data. However, for several other metals, the independence of dissolved levels from suspended solid loading observed by Kharkar, et al. (1967) appeared to be followed.

2.4.3 Sediment Chemistry

Once a part of the sediment phase, the particulate trace metals will likely undergo further phase transformation. Of particular interest are the mechanisms which may release adsorbed metals and allow their migration through the sediment

interstitial water. One cause of metal mobilization in reducing sediments is the reduction of such efficient metal scavengers as hydrous ferric and manganese oxides to their soluble divalent ions, accompanied by the release of associated trace metals into solution (Duchart, et al., 1973).

In a study of the interstitial waters of sediments from off the coast of southern California (Brooks, et al., 1968), dissolved cadmium levels were found to be enriched near the top of each core sample, but were depleted with depth. The source of surface enrichment appeared to be settling organic matter. During the diagenesis of this material in the near-surface layers, its trace metal load would be released into the sediment pore waters. The decrease with depth coincided with the decrease in oxidation potential and increase in sulfide levels. However, the observed cadmium concentrations were 10^{11} greater than predicted from the solubility product of CdS. This behavior may be accounted for by complexation reactions, or, more likely, by the solubility of metal-polysulfide species.

An examination of fresh water and coastal sediments of the Big Cypress region in southern Florida showed that only about 4% of the total cadmium concentration was exchangeable, i.e., leached with 1 M ammonium acetate (Mattraw, 1973). Perhac (1974) found no detectable levels of chromium or cadmium in the exchangeable fraction of the bottom sediments of Joe Mill Creek, Tennessee. Regrettably, no detection limit values were given. The results of density gradient centrifugation of these sediment samples showed that most of the cadmium, and several other metals, was associated with carbonate minerals such as dolomite and calcite. The author observed that because of its mineral association, cadmium would have little biological availability. This inert character was supported by the fact that while dissolved levels of cadmium were comparable to those found in other streams in the region, the sediment concentrations of Joe Mill Creek were by far the highest encountered.

Finally, Chen, et al. (1976) have recently reported an extensive examination of the mineral association and mobility of a number of chemical constituents, including the three metals of interest, in marine and fresh water sediments. They found that under a variety of experimental conditions there was no significant short-term release of silver or cadmium upon the suspension of marine sediments in sea water media; chromium was released from 3 to 10 times over background levels. Sequential extraction of the sediment samples gave these results: cadmium was mostly associated with reducible phases, i.e., iron and manganese hydrous oxides. The next largest proportion of the metal was associated with organics and sulfides, and an average of only 8% of the Cd of marine sediments was of lithogenous origin. The chromium content of the various types of sediments was between 60 and 74% lithogenous. Of the remainder, 75-88% was associated with iron and manganese oxides either as

discrete micronodules or as coatings on clay particles. About 8% was associated with organics and sulfides. Of the total concentration in the sediments, which varied between 67 and 178 ppm, between 4 and 11 ppb was water soluble and from 2 to 16 ppb was in an iron exchangeable form.

The most significant result of the study may have been the results of long-term (120 days) desorption experiments. While there was no measurable release of Cd from sediments in a slightly oxidizing or reducing environment, there was a 15-fold increase in Cd levels in oxygen saturated interfacial water after 4-5 months contact, with most of this release occurring within 15 days. There was no such long-term release for either chromium or silver. The authors attempted a mechanistic interpretation of these results to account for trace metal transport across the sediment water interface. Their explanation of the observed release of cadmium consisted of an accounting of the inorganic complexes formed in sea water. However, stabilization of the dissolved metal in this manner would have argued against its incorporation in coastal sediments in the first place. The inert character of sedimentary silver in these experiments was explained by invoking the theoretical solubility of AgCl in sea water. In this argument, side reaction coefficients accounting for the formation of $AgCl_2^-$ and $AgCl_3^=$, the theoretically stable ionic forms in seawater, were not considered.

2.5 Summary

The scientific literature contains a number of theoretical models describing the dissolved species of cadmium, chromium and silver likely to be found in natural waters. There are two significant deficiencies limiting the utility of these models: (1) There is insufficient analytical and thermodynamic data to calculate the abundance of metal complexes with all significant naturally occurring ligands; (2) the assumption that the natural water system being characterized is at thermodynamic equilibrium is probably incorrect, especially with respect to redox processes.

Analogous models predicting adsorption/desorption processes have also been developed. These models are generally based on short-term laboratory simulations with model particulate phases. The results of such experiments reveal these processes to be quite rapid. However, analyses of environmental suspended solids and sediments indicate that most of the naturally occurring heavy metal content is not readily exchanged with dissolved ionic species. There is apparently much more metal occlusion and incorporation within the lattice structures of, for example, expanded layer clays like montmorillonite, rather than simple surface adsorption. An indication of the reverse of this geochemical morphisism can be seen in the 120-day studies of Chen, et al. (1976). Thus, the effective buffering ability of suspended and interfacial

sediments on dissolved metal levels may have been exaggerated by previous investigators. The slow rates of the associated geochemical transformations would account for the apparent inert character of the solid phase in flowing fresh water systems cited in the discussion above.

SECTION III

PROCEDURES

3.1 Test Materials for Laboratory Simulation

3.1.1 Aqueous Media

Three different aqueous media were employed. Adsorption studies on model inorganic particulates were carried out in distilled water. The only addition of ionic species other than the metal standard took place during pH adjustment with either 1 N hydrochloric acid, prepared from the "Ultrex" (J. T. Baker Chemical) grade reagent, or 1 N sodium hydroxide (Fisher Certified Solution).

A synthetic fresh water medium (SFW) was used for culturing the test algae prior to their use in metal uptake studies. The ingredients of the media are listed in Table 1, and resemble a number of similar mixtures developed for the culturing of fresh water algae. The test media used in metal uptake experiments was SFW': SFW without the trace metal and vitamin mixtures. SFW' was also used in adsorption and desorption studies with natural sediments and in one desorption scan with model inorganic particulates. Desorption was also measured in a sea water medium, filtered Boston Harbor water: salinity = 32 $^{o}/oo$, pH = 7.8.

Standard solutions of silver and cadmium were prepared from 1000 ppm commercial atomic absorption standards. A 1000 ppm Cr(VI) stock was prepared from K_2CrO_4 reagent; a 1000 ppm Cr(III) solution was made by dissolving up the free metal in hydrochloric acid and diluting to volume with water. In adsorption studies on inorganic particulates, the most commonly used test concentrations were 5-10 ppb Cd, 20 ppb Cr, and 10 ppb Ag. These values were selected in an attempt to approach environmentally observed levels while providing a sufficient FAA signal so that substantial decreases in dissolved metal concentration could be precisely followed.

3.1.2 Model Inorganic Particulates

Three clay minerals were used: kaolin - acid washed American standard (Fisher Scientific Co.); fuller's earth (Matheson, Coleman & Bell Manufacturing Chemists); and API standard montmorillonite No. 31-Arizona (Ward's Natural Scientific Establishment). After grinding in a mortar, 20-30 grams of each clay was suspended in about 900 ml of 1 N HNO_3, stirred for about 24 hours, then centrifuged, and the supernatant discarded. This process was repeated until the acid leachate showed insignificant levels of chromium, cadmium and silver. Both fuller's earth and montmorillonite required 4-5 washes before the leachate chromium concentration was less than 5 ppb.

Each clay sample was then washed three times with distilled water in a similar manner and placed in a settling cone. After the appropriate time, that fraction of the final suspension (pH >3.5) with a particle size of less than 10 μm was siphoned off and its suspended load determined by gravimetric analysis of a 25 ml subsample.

Suspensions of hydrous ferric and manganese oxides were prepared using the procedure of Gadde and Laitinen (1974). Analysis of HMO and HFO in the suspensions involved centrifugation of 10 ml subsamples for 30 minutes at 15,000 RPM, dissolution of the pellet in 6 N hydrochloric acid, and analysis of the HCl solution for Mn or Fe by either atomic absorption or plasma emission spectrometry. Final suspension concentrations were calculated on both a molar and a weight basis for the presumed species: $MnO_{1.95}$ and FeOOH.

3.1.3 Phytoplankton Species

To evaluate whether morphological differences would affect the ability of fresh water algae to take up the metals of interest, three phytoplankton of varied size and shape were selected for study. They were the morular green Chlorella vulgaris, the chaining blue-green Anabaena constricta, and the diatom Melosira varians. All stock cultures were obtained from the Carolina Biological Supply Co. and maintained under sterile conditions on a 14 hour light/10 hour dark cycle at 19° C.

3.2 Procedures for Laboratory Simulation

3.2.1 Adsorption on Inorganic Particulates

Each test metal was run in duplicate and usually with two controls consisting of trace metal solution with no added particulates. Equal volumes of suspension and of metal ion solution were prepared in Teflon beakers such that the concentration of each component was twice the desired experimental level. The two portions were mixed together and then redivided into two approximately equal volumes. The contents of each container were agitated by means of a Teflon coated stirring bar driven by a water-powered stirring motor. All tests were run in constant temperature environments, either a water bath for tests at slightly below room temperature to 30° C or a refrigerator held at 4° C. In adsorption rate experiments, each test solution was subsampled periodically over four hours and again after 24. Each subsample was centrifuged and the supernatant analyzed for dissolved metal content by flameless atomic absorption (FAA). In other tests where only equilibrium data were sought, samples were analyzed before mixing and only once thereafter, usually four hours after mixing.

Centrifugation, rather than filtration, was the method chosen for phase separation since it was our intent to measure adsorption on settleable solids that could prove effective in removing metals from the water column. In early experiments

samples were centrifuged for 2 minutes at 1500 RPM, which would remove clay particles greater than 1 μm. Longer, higher speed centrifugation was found not to significantly change test results for most particulates. However, the apparent adsorption on HFO and montmorillonite suspensions was significantly greater when phase separation was carried out at 16,500 RPM for 15 minutes, which would remove the particles with the density of clay 0.05 μm in diameter.

Adsorption/desorption behavior was determined for the three metals on three of the model particulates: kaolin, montmorillonite and HMO. Because of anticipated analytical difficulties in metal analyses in sea water, higher metal concentrations were used: 50 ppb Cd, 50 ppb Ag, and 100 ppb Cr. The clay suspensions were each 1000 ppm; the HMO concentration was 10^{-4} M. After two hours mixing, 40 ml aliquots were centrifuged, and the particulate pellets resuspended in either SFW or in sea water. After 16 hours the suspensions were again centrifuged and the dissolved metal concentrations determined. To account for adsorption/desorption processes occuring on the walls of the polypropylene centrifuge tubes as well as background metal levels, duplicate blanks with no particulates added were carried through the experiment. SFW' samples were analyzed directly by FAA. A 5 ml subsample of each sea water supernatant was oxidized with $KMnO_4$ at 50° C for 30 minutes and allowed to cool. Then 0.2 ml of 5% ammonium pyrrolidine-carbodithioate and 5 ml of 2-pentanone were added, the mixture was vigorously shaken for 1 minute, and the phases were allowed to separate. Through this procedure, Cr(III) is first oxidized to Cr(VI) and then complexed and extracted, with Ag(I) and Cd (II), into the organic phase. Metal concentrations in the 2-pentanone layer were determined by FAA.

3.2.2 Uptake by Phytoplankton

Initial phytoplankton adsorption and metal toxicity studies were carried out in Pyrex flasks. Toxicity scans for each metal were carried out using 12 algal cultures; each initially contained 2×10^4 cells/ml. Two of these served as controls; to the others were added various concentrations of each of the four metal species: Ag, Cd, Cr(III) and Cr(IV). Each culture was maintained at 19° C on a 14 hour light/10 hour dark cycle, and subsampled periodically over about 30 days. In addition, samples of media were spiked with metal but not with algae and maintained under the same conditions as the test cultures. These samples were subsampled periodically over a 10-day period and the dissolved metal concentrations determined. As a result of metal losses apparently due to adsorption on the Pyrex containers, subsequent uptake scans were carried out in Teflon beakers.

At the start of each uptake experiment, equal volumes of trace metal solution and of phytoplankton culture were prepared in the beakers such that the concentration of each component

was twice the desired level. The two portions were blended and then redivided into approximately equal volumes. Subsamples from each portion were taken periodically, centrifuged, and the supernatant analyzed for dissolved metal content by flameless atomic absorption.

In the first test series, Chlorella cultures with initial densities of 0, 10^3, 10^4 and 10^5 cells/ml were treated with cadmium, silver, and trivalent chromium. Significant uptake of cadmium was observed only in the highest density cultures; any uptake of silver and chromium, however, was completely masked by the decrease in concentration of control samples with no phytoplankton added.

To isolate phytoplankton uptake from losses apparently due to adsorption on container walls, high density cultures of the three species were treated with each of the metals of interest, and subsamples were taken several times within two hours of mixing. After 72 hours each culture was autoclaved and then suspended an additional three days before a final set of samples was taken.

3.3 Analysis of Environmental Samples

3.3.1 Sampling

Water and sediment samples were taken from the lower Charles River, a body of water which receives partially treated waste water from several heavily industrialized cities and towns, and also untreated wastes from numerous combined sewer outfalls. Three station locations, shown in Figure 1, were chosen after a preliminary survey of river sediments showed that they consisted of unconsolidated anoxic ooze in the lower basin, but mostly of sand with some silt near the Newton Yacht Club (Station 3). Single sediment grab samples were taken at each location, placed in polyethylene bags, and stored frozen. Subsampling was routinely accomplished by chipping off a portion of the frozen mass with hammer and chisel.

Water samples were collected on ten occasions between October 1975 and June 1976. Samples were taken with a 3-liter Teflon sample bottle which had an exterior structure of brass and external stainless steel closing springs. All metallic parts were coated with either Teflon or epoxy resin. Samples were poured into polypropylene bottles which had been soaked in 3 M HCl, distilled water rinsed, and then rinsed with river water from near the collection site. Large volume (48 liter) surface water samples were collected with an 18-liter plastic bucket and poured into a 48-liter polyethylene carboy cleaned in the manner described above. All samples were returned to the laboratory and either frozen or processed the same day.

3.3.2 Separation of Suspended Solids

Initially the separation of suspended matter was done by vacuum filtration. Because of high particulate levels:

10.9 ± 1.2 mg/l. for the ten samples taken on the first cruise, most filter membranes became clogged with a passage of less than one liter of sample. Therefore, a combination of preliminary centrifugation followed by pressurized filtration (40 psi) of the supernatant was employed for processing up to 4 liters of sample through a single 47-mm filter membrane.

The selection of the filter membrane to be used was made following the evaluation of four materials: 0.45 µm cellulose acetate (Millipore), 1 µm glass fiber ("Metrigard Superfine" - Gelman), 1 µm nylon (Millipore), and 0.5 µm Teflon/polypropylene ("Fluoropore" - Millipore). Standard volumes of SFW' were passed through each to measure leachable metal content. Then SFW' spiked with 10 ppb Cd(II), Ag(I), Cr(III), or Cr(VI) was passed through each to measure any adsorption on the filter material. The results of the first set of experiments indicated that none of the filters leached significant levels of the three metals. Both nylon and glass fiber filters showed significant adsorptivity for silver. As a result of these tests, and because it is a widely used filter material, 0.45 µm Millipore cellulose acetate membranes were selected.

In an effort to separate substantially larger quantities of suspended solids for the sequential extraction procedure described below, a third phase separation technique was employed. A flow-through centrifugation system was constructed, similar to that employed by Perhac (1974), using a high speed refrigerated centrifuge (Sorvall Model RC2-B) with 400-ml stainless steel continuous flow attachment (Model KSB-4). All metal surfaces in contact with the samples were coated with Teflon. Connections from the reservoir to the centrifuge and to the collection bottle were made of cleaned silicone tubing. The siphon system from the reservoir was constructed so that the carboy served as a mariotte bottle and was adjusted to provide a constant flow rate of 100 ml/min. With centrifugation at 16,500 RPM (32,800 x gravity), clay particles greater than 0.12 µm in diameter were removed.

3.3.3 Analysis of Suspended Solids

The suspended solids recovered from the filtration procedures were used only to calculate total suspended solid levels. Each sample from the large volume centrifugation was combined into a single mass from the 8 flow-through tubes, freeze dried, and sequentially extracted as follows:

1. Suspended for 1 hour in 1 M NH_2OH in 25% HOAc
2. Centrifuged and washed twice in distilled water
3. Freeze dried
4. Soxhlet extracted with chloroform (40 cycles)
5. Oven dried at 80° C
6. Digested in aqua regia
7. Digested in 30% hydrogen peroxide

This essentially four-stage extraction scheme was devised to determine that portion of each of the three metals associated with non-silicate ferromanganese minerals and carbonates (step 1, see Holmes, et al., 1974), that portion occluded within relatively non-polar organic compounds (step 4), and that which is located within silicate layers, in hydrophylic organic matrices, or present as a sulfide (steps 6, 7). The initial sample weight (usually 0.5 to 0.6 g) and the weight transferred for and remaining after each extraction step was measured to 0.1 mg. The hydroxylamine hydrochloride/acetic acid extract was also analyzed for manganese and iron.

3.3.4 Analysis of the Aqueous Phase

A number of water quality parameters were measured which were believed to influence the distribution of Cd, Cr, and Ag among the likely dissolved species and which could have also effected association with solid phases. Temperature, dissolved oxygen (Winkler titration), pH, and salinity/conductivity were measured shortly after collection. Further characterization in the laboratory included the determination of total halides by potentiometric titration with a silver selective ion electrode, alkalinity by standard acid titration, calcium and magnesium concentration by plasma emission spectrometry (PES), and metal complexation capacity. The last parameter was determined using two techniques: The first made use of differential pulse polarography to measure that proportion of a cadmium addition which was present in solution as the freely dissolved metal or as an electrochemically active complex. Test samples included centrifuged river water before and after irradiation with ultraviolet light and before and after concentration in a rotary vacuum evaporator. The complexation capacity of these samples for copper was also determined using a ligand competition procedure developed recently in this laboratory (Stolzberg and Rosin, 1976). The technique entails the addition of 10 $\mu\underline{M}$ copper to a 10 ml sample followed by its elution through a 2 cm x 6 mm diameter column of Chelex-100 resin (100-200 mesh, sodium form). The first 3-4 ml of sample through the column were discarded; the remainder was collected for copper analysis. The presence of copper in the eluant would be due to the metal forming strong or nonlabile complexes or its association with colloidal particles that are excluded from the resin interstices.

To determine the nature of the dissolved metal species on a more empirical basis, a number of extraction procedures were used. In the first series of samples taken, 100 ml aliquots of each surface and bottom water filtrate were successively extracted with 10 ml $CHCl_3$ at natural pH, with 10 ml $CHCl_3$ following acidification to pH 2.5, and with a mixture of 10 ml $CHCl_3$ and 1 ml of 5% ammonium 1-pyrrolidine carbodithioate (APCD) at pH 2.5. Internal standards were run through all three steps using 0.25, 0.50, and 0.75 ppb spikes of Cd, Cr(VI) and Ag. The intent of this sequential extraction

procedure was to differentiate between metals complexed with or sequestered within organic matter and the freely dissolved or reversibly complexed concentration that would be complexed with APCD and extracted with $CHCl_3$.

Since both the concentration and the composition of the ligands were unknown, internal standards were run for each metal, and the size of the additions was kept low to reduce the probability of saturating all available ligand sites. However, no detectable metal concentrations were found in either of the first two chloroform extracts, and the efficiency of the APCD/$CHCl_3$ extraction was less than 30% for all three metals.

In an effort to improve extraction efficiency, samples from the second cruise were extracted in a similar manner, but using 1-methyl-2-pentanone (MIBK) as the organic solvent. The APCD/MIBK extraction system has been successfully used in the analysis of chromium (Gilbert and Clay, 1973a) and other metals (Stolzberg, 1975) in brackish and sea water samples. However, MIBK alone did not extract detectable levels of any of the trace metals, and only silver was efficiently and reproducibly extracted from the river water samples with APCD added. The method which has given the most consistent dissolved metal analysis result has been direct injection of the water sample into a pyrolytic graphite furnace followed by flameless atomic absorption. Using a prototype atomizer system with temperature feedback control and either a hydrogen or deuterium lamp for the correction of background absorption, the detection limits for the three metals in 10 µl samples were: Cd = 0.05 ppb; Cr = 0.4 ppb; and Ag = 0.05 ppb. All metal concentrations were determined by the method of standard additions.

3.3.5 Sediment Analysis

Sediment subsamples were partially thawed, and the outer layer, including ice granules, was removed with a Teflon spatula. The remainder was placed in a Teflon beaker and thawed in a glove box under a nitrogen atmosphere. Six 50 g portions of the blended material were transferred to polypropylene centrifuge tubes; the tubes were capped and the samples centrifuged for 10 minutes at 10,000 RPM to separate solids 0.1 µm in size and larger from the interstitial water. The supernatant from three of the six tubes was immediately analyzed for free sulfide using a silver sulfide selective ion electrode. In this technique the sample was made basic with an anti-oxidant buffer, and after the electrode potential had stabilized with respect to a double junction reference electrode, the free sulfide concentration was determined by the method of standard subtraction using a 1000 ppm Cd stock solution. The complete sulfide analysis was carried out in a nitrogen atmosphere to minimize losses due to air oxidation. The supernatant from one of the remaining tubes was analyzed for pH and salinity/conductivity. Samples from the other two were decanted into recappable polyethylene tubes, acidified with "Ultrex" nitric acid and analyzed for the three metals by FAA. The moist

sediment samples obtained following decantation of the interstitial water were sequentially extracted in the following manner: Ten gram portions from three of the centrifuge tubes were transferred to Pyrex beakers, 50 ml of 1 M NH_2OH. HCl in 25% HOAc was added to each, and the mixture was warmed to near boiling for 2 hours. After cooling, the samples were centrifuged; the supernatant was poured into a Pyrex crystallization dish, and the sediment pellet was resuspended and re-extracted. The supernatant was taken to near dryness and the residue digested with 3 ml of hot nitric acid for approximately 15 minutes, or until a clear solution was obtained. The digested extract was then taken to volume and the concentrations of the three metals determined by plasma emission spectrometry. Results of these analyses indicated that four extractions were necessary to remove all available chromium from these samples.

The extracted sediment was washed with distilled water, freeze dried, and 3.0 grams were transferred to a cellulose extraction thimble and soxhlet extracted with chloroform. After the solvent in contact with the thimble was no longer colored, the extraction was continued an additional 20-25 cycles. At that time, the chloroform extract was transferred to a round-bottom flask, dried, and the residue digested in nitric and sulfuric acid at reflux temperature.

The contents of the extraction thimble were air dried and a 2.0 gram sample transferred to a round-bottom flask and digested in 20 ml of aqua regia at reflux temperature for 1 hour. The remaining suspension was then filtered and the digestate taken to volume. The sequential extraction procedure is summarized in Table 2.

The procedure reported by Peech (1945) was used to measure the cation exchange capacity and the exchangeable concentrations of calcium, magnesium, cadmium, chromium and silver. Twenty-five grams of freeze dried sample were leached for approximately 15 minutes with 1 M ammonium acetate. After a wash with 150 ml of 95% ethanol, the sample was leached with 10% NaCl in 0.005 N HCl. The concentration of ammonia in the sodium chloride leachate was determined by a selective ion electrode technique (Gilbert and Clay, 1973b). The ammonium acetate leachate was analyzed for the five metals by PES.

To simulate the release of metals during sediment resuspension under, for example, high flow conditions, 0.50 g of freeze dried sample was suspended in 500 ml of SFW' in a Teflon beaker. Subsamples were taken 4 hours and 24 hours after mixing. Then the suspension was acidified to pH 4.0 with "Ultrex" hydrochloric acid and additional subsamples taken at 4 and 24 hours. Sample pH was then lowered to 2.5, and a third set of samples were taken after 4 and 24 hours and 7 days.

3.3.6 Adsorption on Natural Sediment Samples

The residual metal binding capacity of the resuspended silt and clay fractions of the river sediments was determined.

SECTION IV

RESULTS AND DISCUSSION

4.1 Metal Interaction with Phytoplankton

4.1.1 Toxicity

The results of toxicity studies indicated that up to 100 ppb Cd or 250 ppb Cr(III) or Cr(VI) did not significantly decrease the growth rate of Chlorella (see Tables 3-5). Silver, however, appeared to inhibit cell growth at a concentration of 25 ppb and in cultures with 50, 100, and 200 ppb added, no growth occurred (Table 6, Figure 2). Microscopic examination of the cultures indicated that few organisms were viable after several days of exposure to the higher doses of silver.

The greater toxicity of silver for phytoplankton may be explained by its strong affinity for the sulfhydryl groups that are present on the cell membranes of these organisms. Strongly bound to these groups, silver may disrupt the usual transport processes across the cell membrane. A toxicity mechanism of this sort has been implicated in the notable toxicity of Cu(II) and Hg(II) to phytoplankton (see, for example, Rice, et al., 1973); these two metals closely resemble silver in the insolubility of their sulfides and in their affinity for sulfhydryl groups. Moreover, the activity of silver ions may not be reduced to the same extent as that of Cd, Cr(III), Cu(II), or Hg(II) by complexation with extracellular chelator compounds. Watts and Harvey (1963) have argued that production of these in batch culture phytoplankton studies limit the reliability of these techniques in modeling naturally occurring interactions with trace metals. Recent studies in this laboratory tend to support this conclusion. Therefore, the toxicity results reported here should not be extrapolated to natural water systems. The extent to which the presence of extracellular chelators may have affected metal uptake studies is discussed below.

4.1.2 Adsorption on Container Walls

A second factor contributing to the uncertainty of metal uptake experiments is the adsorption of metal ions on container walls. The results of the first adsorption test, run in acid-leached Pyrex flasks, indicated losses due to the apparent adsorption of Cr(III) and Ag on the culture vessels (see Table 7). Similar adsorption of silver from sea water stored in borosilicate containers was reported by Robertson (1968). The remaining uptake scans were run in Teflon beakers. The only results discussed below from the first test are for Cr(VI) uptake by Chlorella, since adsorption of this metal species on Pyrex was not observed.

In tests similar to those conducted with the clays, freeze dried samples from the three stations were suspended in SFW'; the coarse material was allowed to settle out, and the fraction made up of particles less than 10 μm in diameter was collected. Test suspensions were prepared so that, when mixed with metal solution, the particulate loading was 1000 ppm. A 2 hour preliminary test series was carried out in 50 ml polypropylene tubes to determine whether significant adsorption of Ag, Cd, or Cr(III) would occur. Since that was found to be the case, an additional series of large volume tests were run. In each test six one-liter 1000 ppm suspensions of sediment from station 2 were spiked with three concentrations of one of the metals. Two other solutions, containing the metal species but no suspended solids, served as controls.

4.1.3 Metal Uptake

Uptake of the four metal species was evaluated as a function of phytoplankton species, cell density, culture viability, and the time of contact. The adsorption of Cd, Cr(III) and Ag on duplicate cultures of 0, 10^3, 10^4, and 10^5 cells/ml Chlorella is described by the data in Tables 8 to 10. Significant adsorption of cadmium occurred only in the samples with an initial cell density of 10^5/ml. Dissolved silver levels were significantly lower in samples containing between 4×10^4 and 2×10^5 cells/ml. For both metals cell destruction had little effect on adsorption. While some losses in the cadmium and silver concentrations of the controls were observed, adsorption of Cr(III) on the Teflon culturing apparatus was considerable. Any Cr(III) uptake by Chlorella was completely masked by the decrease in the metal concentration of the control samples: from 10 to 2.6 ppb after 72 hours.

To better separate phytoplankton uptake from wall adsorption, high density cultures of Chlorella and Anabaena were spiked with 2 ppb of Cd and Ag and 10 ppb Cr(III), and subsampled three times within an hour of mixing, and again after 24 hours. The results (Tables 11 to 13) indicated that cadmium adsorption proceeded relatively rapidly, approaching equilibrium within one hour of mixing. No loss of cadmium due to wall adsorption was observed over 24 hours. The uptake of chromium (III) was also rapid, with the maximum loss observed 5 minutes after mixing. Thereafter any decrease in dissolved metal concentration in the phytoplankton cultures was matched or exceeded by losses in the controls. After 24 hours, the controls contained less chromium in solution than any of the test cultures. This behavior may have been due to the excretion of chelator substances which could complex with and essentially stabilize Cr(III) in solution. A similar decrease in the adsorptive properties of copper after complexation with citrate was reported by Morgan and Vuceta (1976). The uptake of silver followed the same pattern as chromium; maximum adsorption occurred within 5 minutes, and any longer-term losses in the test cultures were offset by greater losses in the control samples.

The data in Tables 14 to 17 offer a comparison of the adsorptive properties of the three phytoplankton species toward all four metal species. These results indicated that at a given cell density, cadmium was more strongly taken up by Melosira than by Chlorella, and hardly at all by Anabaena. Chromium(III) and silver followed the same trend except that significant uptake of both by Anabaena was also observed. None of the three species exhibited a strong affinity for Cr(VI).

Since the size and shape of the test phytoplankton varied considerably between species, the metal uptake data have been summarized in terms of concentration factors, i.e., the ratio of the concentration of the metal in the phytoplankton over the concentration in solution at equilibrium. With each concentration expressed on a weight basis, the concentration factor

is essentially the Freundlich isotherm constant, "k", for the case where the dissolved metal concentration is small and the adsorbed metal occupies a negligible fraction of the total number of adsorptive sites. Under these conditions the second constant "n" of the Freundlich equation approaches unity and the ratio of the adsorbed metal concentration to the dissolved concentration at equilibrium is a constant. Table 18 lists these concentration factors for the three algal species and four metal species. Of the three species, Melosira, a diatom, took up more of all four metal species. Since it is of approximately the same size and shape as the individual cells of Anabaena, the higher adsorption capacity of the diatom is probably due to its textured, siliceous test which would likely possess more ion exchange sites than the polysaccharide sheath of the blue-green.

The data in Table 18 show that Anabaena would take up four times more silver and six times more trivalent chromium than a Chlorella culture of equal mass. These ratios are not surprising since the individual cells of Chlorella appeared several times larger and their dry weight was five times greater than those of Anabaena. This pattern agrees with the conclusion of Harvey and Patrick (1967) that variations in the ability of algae to accumulate trace metals arise from differences in cell morphology, particularly surface area to volume ratios, rather than systematic relations between the algae. Riley and Roth (1971) similarly observed no correlation between trace element distribution and phytoplankton taxonomy.

4.2 Adsorption on Inorganic Particulates

4.2.1 Kinetic Studies

Adsorption on inorganic particulates was found to be a rapid process. In those tests where the loss of dissolved metal approached 100%, equilibrium was almost completely reached before the first subsample could be taken and centrifuged, that is, within 3 minutes of mixing (see, for example, Figure 3). Several adsorption rate experiments were run over 24 hours to examine longer-term adsorption processes. None of the results show the slower uptake which Gardiner (1974) reported for cadmium interactions with environmental particulates and which he concluded involved chemisorption or reaction at sterically hindered sites.

4.2.2 Temperature Dependence

Previous studies have shown that adsorption processes on metal oxides and clay surfaces may have significant heats of reaction. Endothermic adsorption was reported for Co(II) on montmorillonite between 25° and 55° C (Hodgson, 1960), and for Co(II) on MnO_2, Al_2O_3, and Fe_3O_4 between 30° and 100° C (Tewari, et al., 1972). Chester (1965) found that the adsorption of Zn(II) was exothermic. Dyck (1968) saw no temperature effect

for the adsorption of Ag(I) on ferric oxide between 25° and 50° C.

In the study reported here, cadmium adsorption of fuller's earth and on kaolin at pH 6 was studied at 12°, 20° and 30° C. Chromium adsorption on kaolin at pH 6 was run at 6°, 16°, 20° and 30° C. The results showed no significant differences in the adsorption of cadmium on either particulate material. There appeared to be a slight increase in chromium adsorption on kaolin with increasing temperature; however, the differences were so small as to be statistically insignificant over the temperature range studied.

4.2.3 pH Dependence

Variation in pH had a pronounced effect on metal adsorption for all the particulate material studied. Such behavior has been observed by many others and is believed to be a function of two principal factors: (1) the net surface charge on the particulate phase changes from (+) to (-) as solution pH is increased through the point of zero charge (ZPC); and (2) the hydrolysis of metal ions increases with increased pH. The more hydrolyzed a metal ion is, the less its hydration sphere must be restructured in the adsorption process. In terms of the AHIS model, a more hydrolyzed species is adsorbed with a less positive ΔG_{SOLV} term in the free energy of adsorption expression. While there is no universal function, or set of functions, that accurately predicts the relationship between adsorption and hydrolysis, there is a well-documented qualitative dependence of adsorption on metal hydrolysis (James and Healy, 1972a).

The pH dependence of adsorption isotherms for cadmium, silver and trivalent chromium on each of the inorganic solids is presented in Figures 4 to 7. Hexavalent chromium was not significantly adsorbed by any of these particulates.

Adsorption isotherms for all three metals on kaolin (Figure 4) show that abrupt increases in adsorption occur within the same pH range for all three metals. Metal hydrolysis appears to play a negligible role in this case; rather adsorption seems to depend principally on the surface charge of the particulate phase. Parks (1967) calculated ZPC values for hydrous and anhydrous kaolinite of 5.5 and 4.8, values which bracket the region of maximum adsorption change for the three metals. That substantial chromium adsorption occurs at pH values below ZPC indicates that in addition to simple ion exchange, this metal may be "specifically" adsorbed; that is, chemically bonded to the surface.

Adsorption on montmorillonite exhibited an unusual pH dependence. Trivalent chromium was extensively adsorbed over the pH range of 3-7. Adsorption through the region of ZPC, calculated by Parks (1967) to be 4.2 for hydrous montmorillonite, indicated significant chemisorption. As with kaolin, however, the free energy of the chemical interaction cannot be accurately calculated by extrapolation of the isotherms to zero

adsorption as described by Murray, et al. (1968). Silver was not significantly adsorbed at pH 3, but about 40% was taken up at pH 5 and 7. However, the maximum adsorption occurred near the ZPC at pH 4. Cadmium behavior complemented that of silver with no adsorption at the ZPC but substantial dissolved metal losses at pH 3 and even more adsorption at pH 5 and 7. Excluding the data from near the ZPC, the pH dependence of cadmium and silver adsorption follows the usual trend. The reasons for the discontinuous behavior at pH 4 is not obvious to the authors.

HMO proved to be an effective adsorber of both Ag and Cd, but had little effect on Cr(III) (Figure 6). As with kaolin, the increase in adsorption with increasing pH is not predicted by the bulk solution hydrolysis constants for either silver or cadmium given by Ringbom (1963) and Sillen and Martell (1964). Extrapolation of the data through ZPC indicates that there is little chemical interaction in the adsorptive reactions of any of the metals. These results vary from those of Gadde and Laitinen (1974), who concluded that cadmium adsorption on HMO contained a significant chemical contribution. Their similar conclusion regarding adsorption processes on hydrous ferric oxide was supported by the extensive adsorption of Cr(III) from pH 3 to 7. Since the ZPC of HFO is reported to be 8.5, the adsorption of cationic species from acidic media would have to be due to a chemical reaction on the particulate surface with a large, negative free energy. On the adsorption isotherm for Cr(III) on HFO, zero adsorption is approached near the inflection point, or -4.0 pH units from the ZPC. The corresponding specific adsorption potential is:

$$\frac{RT}{F} \ln 10^{-4} = -236 \text{ mV or } -5.6 \text{ kcal/mole}$$

The results of adsorption from distilled water at pH 6-7 for all model inorganic particulates and metal species are summarized in Table 19. They show that the metals tended to be adsorbed on clay particles in the order Cr(III) > Cd > Ag > Cr(VI). On hydrous manganese oxide the Cd and Ag were much more strongly adsorbed that Cr(III), while on HFO this order was reversed: Cr(III) > Cd > Ag. Hexavalent chromium was not significantly taken up by any of the particulate phases.

4.2.4 Influence of Complexing Anions

Cadmium is present in plating baths and, presumably, in the effluent from metal finishing plants as a cyanide complex. To examine the differences in adsorptive properties between the free and complexed metal, adsorption of cadmium on kaolin, montmorillonite and HMO in the presence of cyanide was also measured. The results of these tests are listed in Table 20 with the results of comparable tests run in distilled water.

The slight differences observed in the adsorptive properties of the metal after complexation do not coincide with the behavior of mercuric ion in the presence of chloride reported by MacNaughton and James (1974), who found that the chloro complexes competed with adsorption on silica. The reason for the variable influence of complexation is not clear since the cadmium-cyanide complexes, like those of mercury with chloride, are strong yet quite labile given their electrochemical activity. Possibly cyanide, the conjugate of a relatively weak acid, promotes adsorption by neutralizing a displaced surface proton. Using the SCF model:

$$-M\text{-}OH + Cd(CN)_3^- \rightarrow -M\text{-}O\text{-}Cd(CN)_2^- + HCN$$

4.2.5 Adsorption/Desorption in SFW' and in Sea Water

A series of experiments was performed to determine the extent to which either competition from alkaline earth cations or complexation with anions such as chloride can inhibit or reverse adsorption. As discussed in Section II, metals adsorbed on suspended particulates may be released into the estuarine environment because of displacement by the calcium and magnesium in sea water. Desorption would be anticipated if the heavy metals were physically absorbed on the suspended load and therefore susceptible to ion exchange with the major cations in sea water. Chemisorbed metals would not be displaced on mixing with sea water, a property which has been used to define "specific" adsorption (Johnson, et al., 1967).

To measure any decrease in adsorption due to the presence of the major ions found in environmental waters, Cd, Cr(III), Cr(VI), and Ag were added to suspensions of HMO, HFO, kaolin, kaolinite, and montmorillonite in SFW' with the same concentrations of metals and particulates as were used in the tests run in distilled water. The results of the SFW' study are listed in Table 21. When compared with the data in Table 19, they show that in almost all cases, adsorption was diminished on the suspensions in SFW'. The only exception involved the adsorption of trivalent chromium on HFO. This reaction was previously shown to contain a large negative chemical free energy, so adsorption was not expected to be influenced by the presence of the other cationic species.

The results of adsorption from distilled-deionized water on 1000 ppm suspensions of montmorillonite and kaolin and on 10^{-4} M HMO, followed by resuspension of the particulate phase in SFW' and in sea water, are given in Table 22. The data show that relatively little desorption took place upon resuspension in synthetic fresh water, although about half the cadmium and silver initially adsorbed on kaolin was released in SFW'. About the same proportion of these two metals was released when kaolin was resuspended in sea water; a smaller proportion of the cadmium on HMO was released. That chromium was not significantly released from any of the particulates in sea water and only

slightly from montmorillonite in SFW' is in agreement with the chemical nature of Cr(III) adsorption evident in the pH dependence of the adsorption isotherms. It should be noted that a second factor could tend to keep the dissolved trivalent chromium concentration in sea water low, namely, the insolubility of chromic hydroxide. Using Ringbom's (1963) thermodynamic data for the equations:

$$\frac{Cr(OH)_2^+}{(Cr^{+3}) \cdot (OH^-)^3} = 10^{18.3}$$

and

$$(Cr^{+3}) \cdot (OH^-)^3 = 10^{-31}$$

one can calculate the solubility of $Cr(OH)_2^+$ in pH 7.5 sea water to be 45 ppb, assuming an activity coefficient for monovalent species of 0.74 (Zirino and Yamamoto, 1972). Clearly, precipitation is not the factor causing the low dissolved levels observed in the experimental data.

4.3 Characterization of Environmental Samples

4.3.1 Water Chemistry

The results of water quality analyses are given in Table 23. They show the river to be typical of most eastern streams: neutral to slightly acidic pH, well oxygenated, and with a slight elevation in chlorinity at the station furthest downstream, indicating salt water intrusion from Boston Harbor. The river water has a perpetual dark brown cast, indicating the presence of the dissolved and colloidal organic matter known as humic substances.

The results of complexation capacity measurements varied significantly depending on the metal used. With Cu(II), complexing capacities of 0.4 and 0.7 $\mu\underline{M}$ were measured. More than 90% of this capacity was lost after 24 hours irradiation with ultraviolet light. These same samples did not significantly decrease the electrochemical activity of 9×10^{-8} $\underline{M}$ Cd. Given the much higher affinity of copper for many organic chelators (Ringbom, 1963), the experimental results indicate that, despite the presence of organic complexing agents in the river water, the association of cadmium with these substances may be minimal.

Dissolved concentrations of the three metals in samples of river water are listed in Table 24. Cadmium and silver levels exhibited considerable variability, while chromium levels were found to be relatively constant. Pooling the data from all samples, the average dissolved chromium concentration is 1.7 ± 0.6 ppb. The cause of the variability in cadmium and silver levels is not clear. One logical source of variability could be the intermittent discharge of sources of pollution into the river basin. Comparable variability in silver

concentrations was found in samples along 400 km of the Neuse River, North Carolina (Turekian, et al., 1967). The authors concluded that the observed variation (total range = 0.18 - 0.86 ppb; standard deviation among 25 samples = 47%) was due to total analytical uncertainty, due mostly to sampling and processing inconsistencies.

4.3.2 Suspended Solids

Results of the analysis of the suspended matter in the large volume river water samples are listed in Table 25. Sequential extraction of the material indicated that approximately half the total load was not dissolved by any of the reagents. This residual matter was assumed to consist mostly of clay minerals for the purpose of the phase equilibrium model described below. That most of the weight lost during the aqua regia and peroxide digestions was due to volatilization of organic matter agrees with results of sample combustion. Portions of the four suspended solids samples lost an average of 51% of their initial dry weight after heating to 550° C for 4 hours.

The distribution of heavy metals between the extracted phases (Table 26) showed that most of the cadmium and usually over half the silver was associated with iron and manganese hydrous oxides or is adsorbed on acid exchangeable sites. The chloroform extracts contained substantial quantities of silver in only two of the four samples. Given the bright green color of the organic phase after the first few cycles of the soxhlet extractor, it is assumed that some portion of the metals associated with viable phytoplankton would have been extracted in this step. The substantial release of chromium in the aqua regia digestion (73%-78% for 3 of the 4 samples) may have been due to the release of metal sequestered within clay layers or polar organic matrices. Metal release by hydrogen peroxide was probably due to dissolution of organic matter. Since the loss in sample weight during aqua regia and peroxide digestions approaches the average total organic content of these samples, most of the metal released in these steps was likely associated with organic matter.

A comparison of the dissolved and particulate concentrations shows that all three metals are concentrated in the suspended solids by factors of between 10^3 to 10^4. These factors resemble those observed in the adsorption of the metals from SFW' on clay particles and in their uptake by phytoplankton. A more quantitative comparison of natural and simulated phase distribution equilibria is presented in paragraph 4.3.4.

4.3.3 Sediments

The results of physical and chemical characterization of the sediment phases are presented in Tables 27 and 28. The data

showed that the texture of the sediments changes appreciably between stations 2 and 3, from 90% silt and clay downstream to 85% sand and larger material at station 3. The sediments were anoxic, as indicated by the presence of free sulfide, and the dissolved solid levels and pH of the interstitial waters were higher in the downstream stations. The cation exchange capacity (CEC) of samples from stations 1 and 2 was much higher than commonly found in the clay sediments of streams in the eastern United States (Kennedy, 1965). The large CEC values in the Charles River sediments presumably reflect the presence of numerous metal-binding functional groups in the organic silt fraction.

The distribution of cadmium, chromium and silver among several sedimentary phases is presented in Table 29. A comparison of these data with the geochemical associations found in suspended particulate samples indicates several similarities. For example, cadmium was extracted almost completely from both phases by hydroxylamine hydrochloride in acetic acid. The chloroform extracts contained negligible metal levels. In the case of chromium and silver, a higher proportion of the total sediment concentration was present as basic salts, adsorbed on acid exchangeable sites, or associated with hydrous iron and manganese oxides.

The ratios of total metal concentrations in the solid phases with those in the interstitial water indicate that the sediment solids have a stronger affinity for all three metals. To compare the dissolved/particulate metal distributions in the suspended particulate and sediment phases, naturally occurring concentration factors for both were calculated for samples from stations 1 and 2 (Table 30). The data from these two stations are well suited for such comparisons since the sediments were mostly silt and clay and so more likely to resemble the suspended solids in size and adsorptive capacity. Concentration factors in the sediments of 10^4-10^5 for cadmium and chromium are an order of magnitude higher than those calculated for suspended solids. Since no silver was detected in the interstitial water, a sedimentary concentration factor cannot be enumerated, but it must exceed a value of 10^5.

Given the insolubility of silver sulfide (pKsp = 49), the lack of detectable dissolved silver in reducing sediments was to be expected. In the reducing environment of these sediments, any dissolved chromium would be in the trivalent state and susceptible to precipitation as the hydroxide. Using the pH and salinity values for stations 1 and 2 from Table 28 and the equations in paragraph 4.2.5, the chromium concentrations in equilibrium with solid $Cr(OH)_3$ would be 42 and 85 ppb for stations 1 and 2 respectively. For station 1 this value approximates that measured in the interstitial water. The presence of the hydroxide precipitate would help explain the large proportion of the chromium dissolved in the first sediment extraction step. The concentrations of cadmium in the interstitial waters of all three samples were above those at which sulfide precipitation should have occurred. However, due to the

formation of polysulfide complexes, the extent of sulfide precipitation is not easily quantified in natural water systems.

To better characterize the availability of sediment metals to the water column, freeze dried samples from each station were resuspended in SFW' at pH 6.5, 4.0 and 2.5. The concentration of metal released at each pH is listed in Table 31. Since the suspension loading was 1 g/l, a 1 ppb increase in dissolved metal concentration corresponds to a release from the solid phase of 1 ppm. Thus, the release of cadmium observed in pH 2.5 SFW' approximates the total sediment concentration extracted by the procedures listed in Table 29. However, there was no detectable release of silver at pH 2.5 from any of the samples and less than 5% of the total chromium was extracted. Since $Cr(OH)_3$ should have dissolved with the lowering of pH, the maintenance of the low dissolved levels listed in Table 31 may have been due to the readsorption of the hydrolyzed chromic ion on the suspended particulate phase.

To measure the residual metal-binding capacity of fine-grained river sediments, the silt and clay fraction of the sample from station 2 was used to prepare 100 and 1000 ppm suspensions to which were added variable concentrations of Cd, Cr(III), and Ag. The results of the tests were used to calculate the concentration factors listed in Table 32. The relative uniformity of these data reflect a residual binding capacity that is not significantly diminished by the adsorption of dissolved cadmium, chromium and silver several orders of magnitude above natural levels.

The geochemical associations of the metals adsorbed by resuspended sediment were determined using the usual three-stage extraction technique. The results showed that after 24 hours' contact time with SFW', the metals adsorbed on the sediment were extracted in a pattern that fell between those of suspended solids and bottom sediment. Thus, 90% of the cadmium, 80% of the chromium, and 79% of the silver adsorbed during resuspension was extracted with hydroxylamine hydrochloride in acetic acid. The remainder was released by aqua regia digestion. Compared with natural metal distributions, these results more closely resemble the pattern found initially in the anoxic sediments, although a smaller proportion of all three metals was released in the aqua regia digestion of the non-suspended sediments.

4.3.4 Computer Model

Computer modeling calculations were used initially to predict the distribution of dissolved metal species. Given specific ligand concentrations and such water quality parameters as pH, oxidation potential, and salinity, the concentrations of metal species in model fresh water and sea water systems were calculated using principally the thermodynamic data of Martell and Sillen (1964) and Ringbom (1963). In the present study the computer program was expanded to include metal distributions between dissolved and solid phases. This portion of the program made use of the concentration factors determined experi-

mentally on the model particulate phases.

As a model fresh water system, Charles River station 3 was selected. Water quality, suspended solids loading, and total metal concentrations used were those average values measured during May of 1976. For the purposes of these computations, the suspended organic loading (51% of the total) was considered to be mostly viable or detrital phytoplankton. Concentration factors for the metals in the organic phase was the unweighted average of the factors of the three algae used in this study. The inorganic suspended loading was assigned the adsorptive properties of kaolin, the most common clay mineral in eastern U.S. streams. The concentrations of iron and manganese in the suspended particulates were measured, and these concentrations were converted to the corresponding loading of HFO and HMO.

The results of the model computation are given in Tables 33-35. According to the model, of the total metal content of the water samples, 31% of the chromium, 11% of the silver, and 8% of the cadmium should have been present in a particulate form. The corresponding values actually measured were 2%, 3% and 5% for Cr, Ag and Cd, respectively.

There are at least three reasons why the model consistently predicted a higher degree of association of all three metals with the particulate phases.

1. The natural suspended load had a lower affinity for these metals than the model particulates.
2. A significant portion of the suspended load was of such small size that it was not removed by centrifugation.
3. The dissolved metals were stabilized in solution by complexation with naturally occurring organic ligands.

Of these factors, the latter two are probably the more important. As recently reported by Florence and Batley (1976), some trace metals in sea water are apt to be stabilized in the water column by adsorption on or occlusion with colloidal matter or complexation with organic chelators. Given the turbidity and perpetual brownish cast of the waters of the Charles River, the presence of organic colloids and chelators, as yet uncharacterized, seems assured, and the interaction of the metals of interest with these substances would be expected.

An additional factor further confuses modeling: the selection of "effective," as opposed to thermodynamically derived, oxidation potentials. Based somewhat arbitrarily on the observation by Elderfield (1970) that measured redox potentials for sea water are usually around +300 mV vs SHE while the theoretical value is +750 mV, a value of +300 mV was used to calculate the distribution of trivalent and hexavalent chromium in the model instead of the theoretical value of +813 mV. Had an effective oxidation potential $>\sim 400$ mV been selected, then

hexavalent chromium would have comprised a significant fraction of the total dissolved chromium concentration and that fraction of the total in the particulate phase would have decreased. Given the lack of reliable oxidation potential values, and the lack of information on the kinetics of redox processes involving chromium and naturally occurring electron acceptors and donors, phase equilibria modeling for this metal seems to have little meaning.

SECTION V

CONCLUSIONS

The principal mechanisms controlling the transport of chromium, cadmium, and silver in natural waters involve adsorption on settling particulate materials. Only chromium is likely to precipitate from solution and then only in alkaline waters following the reduction of the metal to the trivalent state. Adsorption processes are rapid, usually approaching equilibrium within a few minutes. Adsorption reversibility is quite variable and appears to depend on the adsorptive mechanism, i.e., whether coulombic attraction or a chemical interaction is involved.

Chromium entering fresh water systems in the hexavalent state will not be appreciably adsorbed by suspended inorganic particulates such as clay particles and hydrous iron and manganese oxides, and will be only slightly adsorbed by phytoplankton. However, Cr(VI) is apparently reduced to Cr(III) in fresh waters by oxidizing dissolved or particulate organic matter. The trivalent form is strongly adsorbed by most inorganic particulates, with the exception of hydrous manganese oxide, and by phytoplankton. Chromium(III) adsorption involved a significant negative chemical free energy on clay particles and on hydrous ferric oxide. Therefore, desorption of the metal should not take place on mixing with sea water or when stream pH is lowered due to the discharge of acidic wastes.

Cadmium and silver are also strongly adsorbed by clay minerals and by hydrous manganese oxide. However, these processes do not appear to involve a significant chemical component, and should be reversible under the environmental conditions discussed above. Adsorption on phytoplankton may be a significant factor in the removal of all three metals, especially in eastern U.S. streams where the suspended load of inorganic particulates is relatively low.

Once a part of the bottom sediments, these metals undergo other geochemical transformations which further reduce their availability to the aqueous phase. Thus, short-term resuspension of bottom sediments does not release substantial levels of any of the metals at pH 6.5. However, cadmium can be quantitatively extracted from sediments at pH 2.5. These results, taken with those of Chen, et al. (1976) indicate that prolonged resuspension of anoxic sediments in an aerated water system can result in the reintroduction of cadmium to the water column. Chromium and silver, once a part of the sediment layer, are not likely to re-enter the aqueous phase.

Elderfield, H. 1970. "Chromium Speciation in Seawater", Earth and Planetary Science Letters, Vol. 9, pp. 10-16.

Florence, T. M. and Batley, G. E. 1975. "Removal of Trace Metals from Seawater by a Chelating Resin", Talanta, Vol. 22, pp. 201-204.

Florence, T. M. and Batley, G. E. 1976. "Trace Metal Species in Seawater - I. Removal of Trace Metals from Seawater by a Chelating Resin", Talanta, Vol. 23, pp. 179-186.

Fukai, R. 1967. "Valency State of Chromium in Seawater", Nature, Vol. 213, p. 901.

Fukai, R. and Huynh-Ngoc, L. 1968. "Studies on the Chemical Behavior of Radionuclides in Seawater. I. General Considerations and Study of the Precipitation of Trace Amounts of Chromium, Manganese, Iron, Cobalt, Zinc, and Cerium", International Atomic Energy Agency Conference on Radioactivity in the Sea. Number 22.

Fukai, R. and Vas, D. 1967. "A Differential Method of Analysis for Trivalent and Hexavalent Chromium in Sea-water", Journal of the Oceanographical Society of Japan, Vol. 23, pp. 298-305.

Gadde, R. R. and Laitinen, H. A. 1974. "Studies of Heavy Metal Adsorption by Hydrous Iron and Manganese Oxides", Analytical Chemistry, Vol. 46, pp. 2022-2026.

Gardiner, J. 1974. "The Chemistry of Cadmium in Natural Water - II. The Adsorption of Cadmium on River Muds and Naturally Occurring Solids", Water Research, Vol. 8, pp. 157-164.

Gilbert, T. R. 1971. "Electrochemical Studies of Environmental Trace Metals", Ph.D. Thesis, Massachusetts Institute of Technology, 159 pp.

Gilbert, T. R. and Clay, A. M. 1973a. "Determination of Chromium in Sea Water by Atomic Absorption Spectrometry", Analytica Chimica Acta, Vol. 67, pp. 289-295.

Gilbert, T. R. and Clay, A. M. 1973b. "Determination of Ammonia in Aquaria and Sea Water Using the Ammonia Electrode", Analytical Chemistry, Vol. 45, pp. 1757-1759.

Goldschmidt, V. M. 1954. Geochemistry, Oxford University Press.

Harvey, R. S. and Patrick, R. 1967. "Concentration of ^{137}Cs, ^{65}Zn, and ^{90}Sr by Fresh-Water Algae", Biotechnology and Bioengineering, Vol. 9, pp. 449-456.

BIBLIOGRAPHY

Allen, H. E., Matson, W., and Mancy, K. 1970. "Trace Metal Characteristics in Aquatic Environments by Anodic Stripping Voltammetry", Journal Water Pollution Control Federation, Vol. 42, pp. 573-581.

Bostrom, K. 1967. "Some pH-Controlling Redox Reactions in Natural Waters", in Equilibrium Concepts in Natural Water Systems, R. F. Gould [Editor], American Chemical Society Advances in Chemistry Series No. 67, pp. 286-311.

Brooks, R. R., Presley, B. J., and Kaplan, I. R. 1968. "Trace Elements in the Interstitial Waters of Marine Sediments", Geochimica et Cosmochimica Acta, Vol. 32, pp. 397-414.

Chau, Y. K. and Lum-Shue-Chan, K. 1974. "Determination of Labile and Strongly Bound Metals in Lake Water", Water Research, Vol. 8, pp. 383-388.

Chen, K. Y., Gupta, S. K., Sycip, A. Z., Lu, J. C. S., Knezevic, M. and Choi, W. W. 1976. "Research Study on the Effect of Dispersion, Settling, and Resedimentation on Migration of Chemical Constituents During Open-Water Disposal of Dredged Materials", Contract Report D-76-1, U.S. Army Engineer Waterways Experiment Station, Vicksburg, Mississippi.

Chester, R. V. 1965. "Adsorption of Zinc and Cobalt on Illite in Sea Water", Nature, Vol. 206, pp. 884-886.

Chuecas, L. and Riley, J. P. 1966. "The Spectrophotometric Determination of Chromium in Sea Water", Analytica Chimica Acta, Vol. 35, pp. 240-246.

Curl, H., Jr., Cutshall, N. and Osterberg, C. 1965. "Uptake of Chromium(III) by Particles in Sea Water", Nature, Vol. 205, pp. 275-276.

Cutshall, N., Johnson, V., and Osterberg, C. 1966. "Chromium-51 in Seawater: Chemistry", Science, Vol. 152, pp. 202-203.

Duchart, P. Calvert, S. E., and Price, N. B. 1973. "Distribution of Trace Metals in the Pore Waters of Shallow Water Marine Sediments", Limnology and Oceanography, Vol. 18, pp. 605-610.

Dyck, W. 1968. "Adsorption and Coprecipitation of Silver on Hydrous Ferric Oxide", Canadian Journal of Chemistry, Vol. 46, pp. 1441-1444.

Hodgson, J. F. 1960. "Cobalt Reactions with Montmorillonite", Soil Science Society Proccedings, Vol. 24, pp. 165-168.

Holmes, C. W., Slade, E. A., and McLerran, C. J. 1974. "Migration and Redistribution of Zinc and Cadmium in Marine Estuarine System", Environmental Science and Technology, Vol. 8, pp. 255-259.

Horne, R. A. 1969. Marine Chemistry, Wiley-Interscience.

James, R. O. and Healy, T. W. 1972a. "Adsorption of Hydrolyzable Metal Ions at the Oxide-Water Interface. I. Co(II) Adsorption on SiO_2 and TiO_2 as Model Systems", Journal of Colloid and Interface Science, Vol. 40, pp. 42-52.

James, R. O. and Healy, J. W. 1972b. "Adsorption of Hydrolyzable Metal Ions at the Oxide-Water Interface. III. A Thermodynamic Model of Adsorption", Journal of Colloid and Interface Science, Vol. 40, pp. 65-81.

Johnson, V., Cutshall, N., and Osterberg, C. 1967. "Retention of ^{65}Zn by Columbia River Sediment", Water Resources Research, Vol. 3, pp. 99-102.

Kennedy, V. 1965. "Mineralogy and Cation-Exchange Capacity of Sediments from Selected Streams", United States Geological Survey Professional Paper 433-D.

Kharkar, D. P., Turekian, K. K., and Bertine, K. K. 1968. "Stream Supply of Dissolved Silver, Molybdenum, Antimony, Selenium, Chromium, Cobalt, Rubidium, and Cesium to the Oceans", Geochimica et Cosmochimica Acta, Vol. 22, pp. 285-298.

Knauer, G. A. and Martin, J. H. 1973. "Seasonal Variations of Cadmium, Copper, Manganese, Lead, and Zinc in Water and Phytoplankton in Monterey Bay, California", Limnology and Oceanography, Vol. 18, pp. 597-604.

Krauskopf, K. B. 1956. "Factors Controlling the Concentrations of Thirteen Rare Metals in Sea Water", Geochimica et Cosmochimica Acta, Vol. 9, pp. 1-32B.

MacNaughton, M. G. and James, R. O. 1974. "Adsorption of Aqueous Mercury(II) Complexes at the Oxide/Water Interface", Journal of Colloid and Interface Science, Vol. 47, pp. 431-440.

Martell, A. E. and Sillen, L. G. 1964. Stability Constants of Metal-Ion Complexes, 1st Edition, Special Publication No. 17, The Chemical Society, London.

Matson, W. R., Allen, H. E., and Rekshan, P. 1969. "Trace Metal Organic Complexes in the Great Lakes", Paper presented at the 157th National American Chemical Society Meeting, Minneapolis.

Mattraw, H. C. 1973. "Cation Exchange Capacity and Exchangeable Metals in Soils and Sediments of a South Florida Watershed", National Technical Information Service, PB-233,526, 80 pp.

Morel, F. and Morgan, J. 1972. "A Numerical Method for Computing Equilibria in Aqueous Chemical Systems", Environmental Science and Technology, Vol. 6, pp. 58-65.

Morgan, J. J. 1967. "Applications and Limitations of Chemical Thermodynamics in Water Systems", in Equilibrium Concepts in Natural Water Systems, R. F. Gould [Editor], American Chemical Society Advances in Chemistry Series No. 67, pp. 1-29.

Morgan, J. J. and Vuceta, J. 1976. "Complexation, Precipitation and Adsorption of Trace Metals in Water", Paper presented at the Symposium on Nonbiological Transport and Transformation of Pollutants on Land and Water, National Bureau of Standards, Gaithersburg, Maryland.

Murray, D. J., Healy, T. W., and Fuerstenau, D. W. 1968. "The Adsorption of Aqueous Metal on Colloidal Hydrous Manganese Oxide", in Adsorption from Aqueous Solution, R. F. Gould [Editor], American Chemical Society Advances in Chemistry Series No. 79, pp. 74-81.

Parks, G. A. 1965. "Aqueous Surface Chemistry of Oxides and Complex Oxide Minerals. Isoelectronic Point and Zero Point of Charge", in Equilibrium Concepts in Natural Water Systems, R. F. Gould [Editor], American Chemical Society Advances in Chemistry Series No. 67, pp. 121-160.

Peech, M. 1945. "Determination of Exchangeable Cations and Exchange Capacity of Soils - Rapid Micromethods Utilizing Centrifuge and Spectrophotometer", Soil Science, Vol. 59, pp. 25-38.

Perhac, R. M. 1974. "Water Transport of Heavy Metals in Solution and by Different Sizes of Particulate Solids", National Technical Information Service, PB-232-427, 41 pp.

Rice, H. V., Leighty, D. A., and McLeod, G. C. 1973. "The Effects of Some Trace Metals on Marine Phytoplankton", Chemical Rubber Company Critical Reviews in Microbiology, pp. 27-49.

Riley, J. P. and Roth, I. 1971. "The Distribution of Trace Elements in Some Species of Phytoplankton Grown in Culture", Journal of the Marine Biological Association of the United Kingdom, Vol. 51, pp. 63-72.

Ringbom, A. 1963. Complexation in Analytical Chemistry, Interscience.

Sayre, W. W., Guy, H. P., and Chamberlain, A. R. 1963. "Uptake and Transport of Radionuclides by Stream Sediments", United States Geological Survey Professional Paper 433-A, 35 pp.

Sillen, L. G. 1961. "The Physical Chemistry of Sea Water", in Oceanography, M. Sears [Editor], American Association for the Advancement of Science, No. 67, pp. 549-582.

Stolzberg, R. J. 1975. "Ammonium Pyrrolidinecarbodithioate - Methyl Isobutyl Ketone Extraction System for Some Trace Metals in Seawater", in Analytical Methods in Oceanography, T. R. P. Gibb, Jr. [Editor], American Chemical Society Advances in Chemistry Series No. 147, pp. 30-43.

Stolzberg, R. J. and Rosin, D. 1976. "Complexing Capacity Measurements Using the Sodium Form of Chelex 100: General Theory and Application to Seawater-like Matrices", Paper presented at the 172nd National American Chemical Society Meeting, San Francisco.

Tewari, P. H., Campbell, A. B., and Lee, W. 1972. "Adsorption of Co^{+2} by Oxides from Aqueous Solution", Canadian Journal of Chemistry, Vol. 50, pp. 1642-1648.

Turekian, K. K., Harriss, R. C., and Johnson, D. G. 1967. "The Variations of Si, Cl, Na, Ca, Sr, Ba, Co, and Ag in the Neuse River, North Carolina", Limnology and Oceanography, Vol. 12, pp. 702-706.

Turekian, K. K. and Scott, M. R. 1967. "Concentrations of Cr, Ag, Mo, Ni, Co, and Mn in Suspended Material in Streams", Environmental Science and Technology, Vol. 1, pp. 940-942.

Watts, J. R. and Harvey, R. S. 1963. "Uptake and Retention of Cesium-137 by a Blue-green Alga in Continuous Flow and Batch Culture Systems", Limnology and Oceanography, Vol. 8, pp. 45-49.

Zirino, A. and Yamamoto, S. 1972. "A pH-Dependent Model for the Chemical Speciation of Copper, Zinc, Cadmium, and Lead in Seawater", Limnology and Oceanography, Vol. 17, pp. 661-671.

TABLE 1. SYNTHETIC FRESH WATER (SFW)

MAJOR CONSTITUENTS (SFW')	FINAL CONCENTRATION (mg/l)
1. $NaNO_3$	25
2. $NaH_2PO_4 \cdot H_2O$	2
3. $MgSO_4 \cdot 7H_2O$	22.5
4. $CaCl_2 \cdot 2H_2O$	16.65
5. $NaHCO_3$	15
TRACE METAL MIXTURE	**(µg/l)**
1. H_3BO_3	170
2. $MnCl_2 \cdot 4H_2O$	21.6
3. $ZnSO_4 \cdot 7H_2O$	3.12
4. $CoCl_2 \cdot 6H_2O$	6.45
5. $NaMoO_4 \cdot 2H_2O$	0.3
6. $FeCl_3 \cdot 6H_2O$	125
VITAMIN MIXTURE	**(mg/l)**
1. Thiamine HCL	0.1
2. Biotin	0.5
3. B_{12}	0.5

Total Ca^{++} and Mg^{++} concentration = 2.0×10^{-4} M

Ionic strength = 5.0×10^{-2} M

TABLE 2. EXTRACTION PROCEDURE

	Extractant	Geochemical Phase
1.	SFW' (pH 6.5)	Water soluble metal salts
2.	1.0 M ammonium acetate	Exchangeable metals
3.	SFW' (acidified)	Basic salts; acid exchangeable metals
4.	1.0 M hydroxylamine hydrochloride in 25% (v/v) acetic acid	Acid exchangeable metals; iron and manganese oxides
5.	Chloroform	Non-polar organics
6.	Aqua Regia	Hydrophylic organics, sulfides, metals within clay expanded layers

TABLE 3. TOXICITY OF CADMIUM TO CHLORELLA VULGARIS*

Concentration in ppb	Exposure Time (in Days)						
	1	4	5	6	7	8	12
0	5 ± 1	12 ± 3	12 ± 2	22 ± 4	19 ± 2	18 ± 3	17 ± 2
1	4 ± 2	12 ± 3	15 ± 1	20 ± 2	17 ± 2	18 ± 4	18 ± 4
10	2 ± 1	12 ± 3	14 ± 1	18 ± 2	19 ± 2	16 ± 3	19 ± 2
25	2 ± 1	10 ± 2	18 ± 2	16 ± 2	17 ± 2	18 ± 2	18 ± 3
50	4 ± 3	7 ± 2	12 ± 2	22 ± 4	18 ± 3	21 ± 5	18 ± 4
100	3 ± 1	10 ± 2	8 ± 2	10 ± 4	17 ± 4	17 ± 3	21 ± 3

* Cells/ml (x 10^{-4})

Each value represents the mean and standard deviation of four counts.

TABLE 4. TOXICITY OF CHROMIUM(III) TO CHLORELLA VULGARIS*

Concentration in ppb	Exposure Time (in Days)								
	2	3	4	5	6	9	10	11	16
0	4 ± 2	4 ± 2	7 ± 2	11 ± 2	13 ± 2	22 ± 3	24 ± 2	23 ± 2	28 ± 2
50	3 ± 2	4 ± 2	10 ± 2	12 ± 2	18 ± 5	18 ± 1	23 ± 1	20 ± 2	28 ± 2
100	3 ± 3	4 ± 2	11 ± 1	11 ± 3	16 ± 6	21 ± 2	20 ± 1	20 ± 3	26 ± 2
150	3 ± 1	5 ± 1	10 ± 3	9 ± 2	12 ± 3	17 ± 2	18 ± 3	19 ± 2	25 ± 5
200	3 ± 2	4 ± 1	10 ± 2	9 ± 2	13 ± 4	20 ± 5	17 ± 2	18 ± 2	27 ± 3
250	2 ± 1	4 ± 2	6 ± 2	9 ± 3	10 ± 3	17 ± 2	19 ± 2	17 ± 2	22 ± 3

* Cells/ml (x 10^{-4})

Each value represents the mean and standard deviation of four counts.

TABLE 5. TOXICITY OF CHROMIUM(VI) TO CHLORELLA VULGARIS*

Concentration in ppb	Exposure Time (in Days)								
	1	7	8	9	10	11	14	17	21
0	0 ± 1	2 ± 1	3 ± 2	4 ± 2	8 ± 2	10 ± 2	11 ± 2	20 ± 4	27 ± 3
50	0 ± 1	2 ± 2	2 ± 2	3 ± 1	6 ± 1	9 ± 2	8 ± 2	18 ± 2	27 ± 3
100	1 ± 1	1 ± 2	2 ± 3	4 ± 1	5 ± 1	6 ± 1	8 ± 2	18 ± 1	28 ± 2
150	0 ± 1	1 ± 1	2 ± 4	5 ± 3	7 ± 1	8 ± 1	9 ± 2	17 ± 3	26 ± 3
200	1 ± 1	2 ± 1	2 ± 1	4 ± 1	5 ± 3	7 ± 2	9 ± 2	21 ± 3	27 ± 4
250	0 ± 1	2 ± 1	1 ± 1	4 ± 1	6 ± 1	6 ± 2	7 ± 1	18 ± 2	27 ± 3

* Cells/ml ($\times 10^{-4}$)

Each value represents the mean and standard deviation of four counts.

TABLE 6. TOXICITY OF SILVER TO CHLORELLA VULGARIS*

Concentration in ppb	Exposure Time (in Days)								
	1	2	3	7	8	9	10	13	17
0	2 ± 1	2 ± 1	4 ± 1	12 ± 2	18 ± 2	16 ± 2	18 ± 2	19 ± 3	27 ± 2
10	2 ± 2	3 ± 1	4 ± 2	14 ± 3	20 ± 2	20 ± 3	19 ± 2	23 ± 7	29 ± 2
25	2 ± 2	2 ± 1	4 ± 2	10 ± 6	11 ± 8	15 ± 2	15 ± 3	21 ± 2	20 ± 1
50	2 ± 1	2 ± 1	2 ± 2	2 ± 1	2 ± 2	2 ± 1	1 ± 1	4 ± 1	2 ± 2
100	2 ± 2	2 ± 1	3 ± 1	1 ± 1	1 ± 1	4 ± 2	2 ± 2	1 ± 1	2 ± 1
200	2 ± 1	1 ± 1	2 ± 2	1 ± 1	2 ± 1	4 ± 2	2 ± 1	2 ± 1	2 ± 2

* Cells/ml (x 10^{-4})

Each value represents the mean and standard deviation of four counts.

TABLE 7. METAL ADSORPTION ON PYREX GLASS

Contact Time with Pyrex Flask (d.)	Metal Concentration Remaining in SFW (ppb)			
	Cr(III)	Cr(VI)	Ag(I)	Cd(II)
0	10	12	6	9
1	8	11	1	10
2	6	10	2	10
7	3	9	3	8
10	3	10	3	6

TABLE 8. UPTAKE OF CADMIUM BY THREE CONCENTRATIONS OF CHLORELLA

	CHLORELLA - 10^3 cell/ml			CHLORELLA - 10^4 cell/ml			CHLORELLA - 10^5 cell/ml		
TIME	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density ($x10^4$/ml)	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density ($x10^4$/ml)	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density ($x10^4$/ml)
0 hr	10	---	10^{-1}	10	---	1.0	10	---	10^1
24 hr	8.9 ± 0.7	-0.6 ± 0.8	---	7.9 ± 0.8	0.4 ± 0.8	---	7.6 ± 1.4	0.7 ± 1.4	---
40 hr	7.7 ± 0.1	-1.7 ± 0.5	< 1	7.6 ± 0.2	-1.6 ± 0.5	2 ± 2	3.8 ± 0.1	2.2 ± 0.5	17 ± 3
72 hr	8.5 ± 0.7	-0.3 ± 0.7	< 1	8.0 ± 0.6	0.2 ± 0.6	8 ± 2	3.3 ± 0.8	4.9 ± 0.8	20 ± 2
90 hr	8.2 ± 1.3	-1.9 ± 1.6	< 1	8.5 ± 0.1	-2.2 ± 1.0	11 ± 1	3.3 ± 0.9	3.0 ± 1.3	23 ± 5
48 hr (after cell death)	6.7 ± 0.1	4.0 ± 0.3	< 1	8.7 ± 1.2	2.0 ± 1.2	11 ± 1	4.1 ± 0.8	6.5 ± 0.8	23 ± 5

*Corrected for any decrease in metal concentration in the blank samples.

TABLE 9 UPTAKE OF CHROMIUM (III) BY THREE CONCENTRATIONS OF CHLORELLA

	CHLORELLA - 1[illegible] cell/ml			CHLORELLA - 10^4 cell/ml			CHLORELLA - 10^5 cell/ml		
TIME	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density ($x10^4$/ml)	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density (10^4/ml)	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density ($x10^4$/ml)
0 hr	10	---	0.1	10	---	1	10	---	10
24 hr	4.8 ± 0.9	-0.1 ± 1.3	---	5.8 ± 0.6	-1.1 + 1.2	---	5.9 ± 0.1	-1.2 ± 1.0	---
40 hr	3.5 ± 1.7	0.5 ± 1.9	<1	3.1 ± 0.6	0.9 ± 1.1	2 ± 2	2.6 ± 0.3	1.4 ± 0.9	17 ± 3
72 hr	2.0 ± 0.3	0.6 ± 0.7	<1	2.2 ± 0.1	0.4 ± 0.6	8 ± 2	2.2 ± 0.2	0.4 ± 0.6	20 ± 2
90 hr	2.9 ± 0.6	-0.7 ± 1.0	<1	3.3 ± 0.4	-1.1 ± 0.9	11 ± 1	3.0 ± 0.1	-0.8 ± 0.8	23 ± 5
48 hr (after cell death)	4.3 ± 0.1	0 ± 0.7	<1	5.0 ± 0.9	-0.7 ± 1.1	11 ± 1	6.5 ± 0.7	-1.2 ± 1.0	23 ± 5

*Corrected for any decrease in metal concentration in the blank samples.

TABLE 10. UPTAKE OF SILVER BY THREE CONCENTRATIONS OF CHLORELLA

	CHLORELLA - 10^3 cell/ml			CHLORELLA - 10^4 cell/ml			CHLORELLA - 10^5 cell/ml		
TIME	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density ($x10^4$/ml)	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density ($x10^4$/ml)	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density ($x10^4$ ml)
0 hr	10	---	10^{-1}	10	---	1	10	---	10
24 hr	4.2 ± 1.3	0.2 ± 1.4	---	4.6 ± 1.0	-0.6 ± 1.1	---	2.7 ± 0.7	1.3 ± 0.8	---
40 hr	3.4 ± 0.1	0.6 ± 0.2	<1	1.9 ± 1.2	2.1 ± 1.2	2 ± 2	1.8 ± 0.1	2.2 ± 0.2	17 ± 3
72 hr	3.4 ± 0.1	0.5 ± 0.7	<1	3.3 ± 1.5	0.6 ± 1.6	8 ± 2	2.8 ± 1.1	1.1 ± 1.3	20 ± 2
90 hr	3.6 ± 0.3	-0.1 ± 0.9	<1	2.2 ± 0.4	1.3 ± 1.0	11 ± 1	2.2 ± 0.5	1.3 ± 1.0	23 ± 5
48 hr (after cell death)	4.8 ± 0.9	0.2 ± 1.0	<1	2.9 ± 0.7	2.1 ± 0.9	11 ± 1	3.8 ± 1.4	1.2 ± 1.5	23 ± 5

*Corrected for any decrease in metal concentration in the blank samples.

TABLE 11. SHORT-TERM UPTAKE OF CADMIUM BY HIGH-DENSITY CULTURES OF ANABAENA & CHLORELLA

	ANABAENA - 10^6 cell/ml			CHLORELLA - 10^5 cell/ml			CHLORELLA - 10^6 cell/ml		
TIME	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density ($x10^4$/ml)	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density ($x10^4$/ml)	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density ($x10^4$/ml)
0 min	2.0	---	100	2.0	---	10	2.0	---	100
5 min	1.4 ± 0.1	0.2 ± 0.1	---	1.4 ± 0.1	0.2 ± 0.1	---	1.2 ± 0.1	0.4 ± 0.1	---
30 min	1.3 ± 0.1	0.4 ± 0.1	---	1.5 ± 0.1	0.2 ± 0.1	---	1.2 ± 0.1	0.5 ± 0.1	---
60 min	1.3 ± 0.1	0.5 ± 0.1	---	1.4 ± 0.3	0.4 ± 0.3	---	0.8 ± 0.1	1.0 ± 0.1	---
24 hr	1.0 ± 0.1	0.8 ± 0.1	120 ± 10	1.6 ± 0.1	0.2 ± 0.1	13 ± 2	0.9 ± 0.1	0.9 ± 0.1	105 ± 12

*Corrected for any decrease in metal concentration in the blank samples.

TABLE 12. SHORT-TERM UPTAKE OF CHROMIUM (III) BY HIGH-DENSITY CULTURES OF ANABAENA & CHLORELLA

	ANABAENA - 10^6 cell/ml			CHLORELLA - 10^5 cell/ml			CHLORELLA - 10^6 cell/ml		
TIME	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density ($x10^4$/ml)	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density ($x10^4$/ml)	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density ($x10^4$/ml)
0 hr	10	---	100	10	---	10	10	---	100
5 min	2.1 ± 0.3	5.7 ± 0.4	---	6.7 ± 0.1	1.1 ± 0.2	---	2.8 ± 0.2	5.0 ± 0.3	---
30 min	4.0 ± 0.9	1.6 ± 0.9	---	5.6 ± 0.5	0 ± 0.5	---	4.8 ± 1.5	0.8 ± 1.5	---
60 min	4.3 ± 0.6	1.0 ± 1.2	---	5.3 ± 0.1	0 ± 1.1	---	4.8 ± 1.5	0.5 ± 1.9	---
24 hr	2.8 ± 0.4	-0.6 ± 0.4	120 ± 10	3.9 ± 0.1	-1.7 ± 0.1	13 ± 2	3.4 ± 0.4	-1.2 ± 0.4	105 ± 12

*Corrected for any decrease in metal concentration in the blank samples.

TABLE 13. SHORT-TERM UPTAKE OF SILVER BY HIGH-DENSITY CULTURES OF ANABAENA & CHLORELLA

	ANABAENA - 10^6 cell/ml			CHLORELLA - 10^5 cell/ml			CHLORELLA - 10^6 cell/ml		
TIME	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density ($x10^4$/ml)	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density ($x10^4$/ml)	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density ($x10^4$/ml)
0 hr	2.0	---	100	2.0	---	10	2.0	---	100
5 min	0.4 ± 0.1	1.0 ± 0.4	---	0.7 ± 0.2	0.7 ± 0.4	---	0.8 ± 0.1	0.6 ± 0.4	---
30 min	0.5 ± 0.1	0.3 ± 0.1	---	0.6 ± 0.2	0.2 ± 0.2	---	0.8 ± 0.1	0 ± 0.1	---
60 min	0.5 ± 0.1	0.5 ± 0.1	---	0.7 ± 0.1	0.3 ± 0.1	---	0.8 ± 0.1	0.2 ± 0.1	---
24 hr	0.3 ± 0.1	0.1 ± 0.1	120 ± 10	0.5 ± 0.1	-0.1 ± 0.1	13 ± 2	0.7 ± 0.1	-0.3 ± 0.1	105 + 12

*Corrected for any decrease in metal concentration in the blank samples.

TABLE 14. UPTAKE OF CADMIUM BY THREE PHYTOPLANKTON SPECIES

	ANABAENA - 2.6 x 10^5 cell/ml			MELOSIRA - 8.6 x 10^4 cell/ml			CHLORELLA - 2.6 x 10^5 cell/ml		
TIME	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density (x10^4/ml)	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density (x10^4/ml)	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density (x10^4/ml)
0 min	3.0	---	26	10	---	8.6 ± 1.4	3.0	---	26
5 min	2.5 ± 0.4	0.5 ± 0.4	---	6.0 ± 0.7	4.0 ± 1.3	---	2.3 ± 0.1	0.7 ± 0.2	---
30 min	2.4 ± 0.1	0.2 ± 0.2	---	5.8 ± 0.3	4.1 ± 0.8	---	2.2 ± 0.3	0.4 ± 0.4	---
60 min	2.3 ± 0.1	0.0 ± 0.1	---	5.4 ± 0.1	4.6 ± 1.5	---	1.8 ± 0.1	0.5 ± 0.1	---
120 min	ONLY FIRST HOUR		---	6.0 ± 0.1	4.2 ± 0.9	---	ONLY FIRST HOUR		---
73 hr	---	---	66 ± 15	5.2 ± 0.4	4.4 ± 1.3	24 ± 2	---	---	51 ± 8
3 days (after cell death)	---	---	66 ± 15	5.5 ± 1.2	4.4 ± 1.2	24 ± 2	---	---	51 ± 8

*Corrected for any decrease in metal concentration in the blank samples.

TABLE 15. UPTAKE OF CHROMIUM (III) BY THREE PHYTOPLANKTON SPECIES

TIME	ANABAENA - 2.6 x 10^5 cell/ml			MELOSIRA - 2.1 x 10^5 cell/ml			CHLORELLA - 2.6 x 10^5 cell/ml		
	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density ($x10^4$/ml)	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density ($x10^4$/ml)	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density ($x10^4$/ml)
0 min	4.1	---	26	4.7	---	21	4.6	---	26
5 min	4.6 ± 0.1	1.0 ± 0.2	---	3.6 ± 0.4	2.0 ± 0.4	---	3.4 ± 0.4	2.2 ± 0.4	---
30 min	4.0 ± 0.2	2.5 ± 0.2	---	3.4 ± 0.2	3.1 ± 0.2	---	4.3 ± 0.1	2.2 ± 0.1	---
60 min	3.8 ± 0.5	1.6 ± 0.6	---	3.3 ± 0.1	2.1 ± 0.3	---	2.8 ± 0.4	2.6 ± 0.5	---
120 min	2.8 ± 0.5	0.7 ± 0.5	---	2.7 ± 0.1	0.8 ± 0.2	---	1.6 ± 0.2	1.9 ± 0.3	---
480 min	3.5 ± 0.5	0.1 ± 0.5	---	2.5 ± 0.1	1.1 ± 0.2	---	1.0 ± 0.1	2.6 ± 0.2	---
73 hr	3.8 ± 0.4	-1.1 ± 0.4	66 ± 15	1.8 ± 0.2	0.9 ± 0.2	42 ± 4	2.7 ± 0.9	0.0 ± 0.9	51 ± 8
3 days (after cell death)	4.2 ± 0.3	0.4 ± 0.3	66 ± 15	3.8 ± 0.1	0.8 ± 0.1	42 ± 4	5.2 ± 0.1	-0.6 ± 0.1	51 ± 8

*Corrected for any decrease in metal concentration in the blank samples.

TABLE 16. UPTAKE OF CHROMIUM [III] BY THREE PHYTOPLANKTON SPECIES

	MELOSIRA - 1.0 x 10^5 cell/ml			ANABAENA - 1.0 x 10^6 cell/ml			CHLORELLA - 1.0 x 10^5 cell/ml		
TIME	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density (x10^4/ml)	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density (x10^4/ml)	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density (x10^4/ml)
0 min	19.8	---	10.0 ± 3	19.8	---	102 ± 9	11.6	---	10 ± 2
5 min	18.8 ± 0.3	0.2 ± 0.4	---	18.2 ± 0.1	0.8 ± 0.3	---	---	---	---
30 min	17.9 ± 0.1	1.4 ± 0.1	---	18.2 ± 0.1	1.1 ± 0.1	---	---	---	---
120 min	17.2 ± 0.1	2.5 ± 0.3	---	17.1 ± 1.0	2.6 ± 1.0	---	---	---	---
24 hr	14.8 ± 0.2	4.5 ± 1.4	---	19.9 ± 1.6	-0.6 ± 2.1	---	9.2 ± 0.8	2.2 ± 1.1	---
55 hr	19.8 ± 1.1	0.9 ± 1.7	---	17.5 ± 2.6	3.2 ± 2.9	---	9.8 ± 0.2	0.4 ± 0.5	21 ± 4
6 days	17.4 ± 0.8	1.4 ± 0.9	26 ± 2	16.5 ± 0.5	2.3 ± 0.7	221 ± 19	7.1 ± 0.3	2.2 ± 0.6	54 ± 6
1 day (after cell death)	18.0 ± 0.2	1.5 ± 0.2	26 ± 2	16.6 ± 0.1	2.9 ± 0.1	221 ± 19	---	---	---
4 days (after cell death)	19.2 ± 1.5	0.5 ± 1.6	26 ± 2	18.5 ± 0.6	1.2 ± 0.8	221 ± 19	1.3 ± 0.3	8.6 ± 0.3	54 ± 6

*Corrected for any decrease in metal concentration in the blank samples.

TABLE 17. UPTAKE OF SILVER BY THREE PHYTOPLANKTON SPECIES

TIME	ANABAENA - 2.6 x 10^5 cell/ml			MELOSIRA - 2.1 x 10^5 cell/ml			CHLORELLA - 2.6 x 10^5 cell/ml		
	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density (x10^4/ml)	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density (x10^4/ml)	Dissolved Metal Concentration (ppb)	Adsorbed* Metal Concentration (ppb)	Cell Density (x10^4/ml)
0 min	2.4	---	26	2.6	---	21	2.5	---	26
5 min	1.5 ± 0.1	0.8 ± 0.1	---	1.1 ± 0.1	1.2 ± 0.1	---	1.2 ± 0.1	1.1 ± 0.1	---
30 min	1.2 ± 0.1	1.0 ± 0.1	---	1.1 ± 0.1	1.1 ± 0.1	---	1.1 ± 0.1	1.1 ± 0.1	---
60 min	0.8 ± 0.1	1.2 ± 0.1	---	1.1 ± 0.4	0.9 ± 0.4	---	1.2 ± 0.3	0.8 ± 0.3	---
120 min	0.4 ± 0.1	0.8 ± 0.2	---	0.9 ± 0.1	0.3 ± 0.2	---	0.8 ± 0.1	0.4 ± 0.2	---
25 hr	0.6 ± 0.2	0.9 ± 0.2	---	1.0 ± 0.1	0.5 ± 0.1	---	0.7 ± 0.3	0.8 ± 0.2	---
73 hr	1.0 ± 0.2	0.4 ± 0.4	66 ± 15	1.3 ± 0.2	0.1 ± 0.4	42 ± 4	1.2 ± 0.6	0.2 ± 0.7	51 ± 8
3 days (after cell death)	2.8 ± 0.8	-1.9 ± 0.8	66 ± 15	2.8 ± 0.3	-1.9 ± 0.4	42 ± 4	2.7 ± 2.2	-1.8 ± 2.2	51 ± 8

*Corrected for any decrease in metal concentration in the blank samples.

TABLE 18. CONCENTRATION FACTORS IN FRESH WATER PHYTOPLANKTON

PHYTOPLANKTON SPECIES	CELL DENSITY	EXPOSURE TIME	Cd	Cr(III)	Cr(VI)	Ag
Chlorella vulgaris	2.6×10^5	30 mins	$(2.3 \pm 1.7) \times 10^3$	$(6.3 \pm 0.6) \times 10^3$		$(1.2 \pm 0.2) \times 10^4$
	5.4×10^5	6 days			$(1.8 \pm 0.4) \times 10^3$	
Anabaena constricta	2.6×10^5	30 mins	$< 5 \times 10^3$	$(3.6 \pm 0.5) \times 10^4$		$(4.8 \pm 1.0) \times 10^4$
	2.2×10^6	6 days			$(9.4 \pm 2.6) \times 10^2$	
Melosira varians	8.6×10^5	5 mins	$(9.9 \pm 3.3) \times 10^4$			
	2.1×10^5	30 mins		$(5.6 \pm 0.7) \times 10^4$		$(6.1 \pm 1.2) \times 10^4$
	2.6×10^5	6 days			$(4.0 \pm 2.6) \times 10^3$	

TABLE 19. CONCENTRATION FACTORS IN DISTILLED WATER (pH 6, 20°C)

	Cd	Cr(III)	Ag
HMO (10^{-5} M)	$(7.1 \pm 1.8) \times 10^6$	$(5.0 \pm 1.0) \times 10^5$	$(9 \pm 3) \times 10^6$
HFO (10^{-5} M)	$(4.6 \pm 0.5) \times 10^5$	$(2.1 \pm 0.2) \times 10^6$	5×10^4
KAOLIN (100 ppm)	$(8 \pm 1) \times 10^3$	$(1.6 \pm 0.3) \times 10^5$	$(1.1 \pm 0.3) \times 10^4$
MONTMORILLONITE (100 ppm)	$(2.4 \pm 1.3) \times 10^5$	$(1.23 \pm 0.09) \times 10^5$	$(1.7 \pm 0.2) \times 10^4$
FULLER'S EARTH (100 ppm)	$(1.6 \pm 0.1) \times 10^5$		

TABLE 20. ADSORPTION OF CADMIUM IN THE PRESENCE OF CYANIDE

	CONCENTRATION FACTOR	
PARTICULATE PHASE	3.3×10^{-4} M CN^-	DISTILLED WATER
KAOLIN (110 ppm)	$(6 \pm 3) \times 10^3$	$(8 \pm 1) \times 10^3$
MONTMORILLONITE (100 ppm)	$(2.0 \pm 0.6) \times 10^4$	$(2.4 \pm 1.3) \times 10^4$
HYDROUS MANGANESE OXIDE (10^{-4} M)	$(1.1 \pm 0.2) \times 10^6$	$(5 \pm 2) \times 10^5$

TABLE 21. CONCENTRATION FACTORS IN SFW' (pH 6.5, 20° C)

	Cd	Cr(III)	Cr(VI)	Ag
HMO (10^{-} M)	$(7\pm3) \times 10^{5}$	$<1 \times 10^{5}$	$<4 \times 10^{4}$	$(6\pm1) \times 10^{5}$
HFO (10^{-} M)	$<2 \times 10^{5}$	$(2.3\pm0.4) \times 10^{6}$	$<6 \times 10^{4}$	$<1 \times 10^{5}$
KAOLIN (100 ppm)	$<7 \times 10^{2}$	$(4.0\pm1.2) \times 10^{4}$	$<6 \times 10^{2}$	$(5\pm2) \times 10^{3}$
KAOLINITE (100 ppm)	$<8 \times 10^{2}$	$(2.5\pm0.9) \times 10^{4}$	$<7 \times 10^{2}$	$(8\pm2) \times 10^{3}$
MONTMORILLONITE (100 ppm)	$(5\pm2) \times 10^{4}$	$(4.4\pm0.6) \times 10^{4}$	$<1 \times 10^{3}$	$<3 \times 10^{3}$

TABLE 22. DESORPTION OF METALS IN SYNTHETIC FRESH WATER AND SEA WATER

	HMO	KAOLIN	MONTMORILLONITE
% ADSORBED			
Ag	96	7	43
Cd	91	61	47
Cr	<5	94	89
% DESORBED IN SFW			
Ag	3	3	5
Cd	2	34	4
Cr	<5	<5	14
% DESORBED IN SEA WATER			
Ag	53	3	15
Cd	16	31	23
Cr	<5	<5	<5

TABLE 23. CHARLES RIVER WATER QUALITY PARAMETERS

Range of Values: October 21, 1975 to June 2, 1976

STATION	pH	DISSOLVED OXYGEN (% satn)	ALKALINITY (10^{-4}M)	CHLORIDE (10^{-3}M)	COMPLEXATION CAPACITY (Cu) (10^{-7}M)	Ca (ppm)	Mg (ppm)
1	6.4-7.0	81-89	6.4	(3.2-3.3)		27-29	2.8-3.0
2	6.7-7.0	84-93	5.5	(1.1-1.7)	4	29-32	2.2-2.6
3	6.5-7.6	85-95	(4.8-5.1)	(1.1-1.2)	6	16	3.0

TABLE 24. DISSOLVED METAL CONCENTRATIONS IN CHARLES RIVER WATER

STATION	DATE	Cd (ppb)	Cr (ppb)	Ag (ppb)
1	3/5	0.18 ± 0.02		
	4/1	0.24 ± 0.06	1.4 ± 0.3	0.13 ± 0.02
	6/2	0.57 ± 0.06	1.4 ± 0.1	
2	4/29	0.33 ± 0.02	1.4 ± 0.1	0.043 ± 0.005
	6/2	0.19 ± 0.002	2.2 ± 0.3	0.19 ± 0.04
3	5/6	0.19 ± 0.06	1.23 ± 0.09	0.3 ± 0.1
	5/17	0.16 ± 0.05	1.29 ± 0.04	0.12 ± 0.06
	6/2	0.43 ± 0.02	2.9 ± 0.2	0.04 ± 0.02

TABLE 25. DISTRIBUTION OF GEOCHEMICAL PHASES IN CHARLES RIVER SUSPENDED PARTICULATES

STATION	TOTAL SUSPENDED LOAD (mg/l)	% OF TOTAL WEIGHT in NH_2OH-HOAc EXTRACT	in $CHCl_3$ EXTRACT	in AQUA REGIA DIGESTATE	in PEROXIDE EXTRACT	RESIDUAL
1	7.8	22.0	12.0	42.5	5.4	38.4
2	7.5	12.8	9.6	41.6	15.8	40.2
3 (5/6/76)	14.3	6.5	8.1	38.2	8.7	47.4
3 (5/17/76)	12.3	6.3	11.2	50.3	14.3	36.0

TABLE 26. DISTRIBUTION OF METALS IN CHARLES RIVER SUSPENDED PARTICULATES

STATION	METAL	TOTAL CONC. (ppm)*	CONCENTRATION EXTRACTED (% of total in sample) NH_2OH-HOAc EXTRACT	$CHCl_3$ EXTRACT	AQUA REGIA EXTRACT	PEROXIDE EXTRACT
1	Cd	0.58	72	-	21	7
	Cr	11.9	42	-	42	16
	Ag	0.56	46	36	-	18
	Mn	63.0				
	Fe	2.0×10^3				
2	Cd	0.44	84	-	16	-
	Cr	6.5	26	1	73	-
	Ag	0.39	66	15	19	-
	Mn	136.0				
	Fe	1.45×10^3				
3 (5/6/76)	Cd	0.38	87	-	13	-
	Cr	5.8	22	-	78	-
	Ag	0.25	67	-	33	-
	Mn	136.0				
	Fe	7.5×10^2				
3 (5/17/76)	Cd	0.53	89	-	11	-
	Cr	4.9	24	1	75	-
	Ag	0.39	59	-	15	25
	Mn	270.0				
	Fe	7.5×10^2				

* Iron and manganese concentrations were measured in NH_2OH-HOAc extracts only

TABLE 27. CHARLES RIVER SEDIMENT GRAIN SIZE DISTRIBUTION

STATION	% OF TOTAL WEIGHT			
	PEBBLES & LARGER MATERIALS (>4mm)	GRANULES (2-4mm)	SAND (2-.063mm)	SILT & CLAY (<0.063mm)
1	0	0	8.70	91.30
2	0	0.07	7.97	91.96
3	0.74	1.34	85.07	12.85

TABLE 28. CHEMICAL CHARACTERIZATION OF CHARLES RIVER SEDIMENTS

STATION	INTERSTITIAL WATER pH	INTERSTITIAL WATER SALINITY ($^0/_{00}$)	INTERSTITIAL WATER FREE SULFIDE (ppb)	CATION EXCHANGE CAPACITY (meg/100g)
1	7.51	14.5	72 ± 8	136 ± 0.7
2	7.09	3.0	28 ± 1.4	124 ± 2.1
3	5.65	0.6	96 ± 15	21.2 ± 0.3

TABLE 29. METAL CONTENT OF SEQUENTIAL SEDIMENT EXTRACTIONS

STATION	METAL	INTERSTITIAL WATER (ppb)	CONCENTRATION EXTRACTED (ppm of total sample weight) NH_2OH - HOAc (ppm)	$CHCl_3$ (ppm)	AQUA REGIA (ppm)	TOTAL (ppm)
1	Cd	4.1 ± 0.6	52.6 ± 6.8	0.7 ± 0.2	3.24 ± 0.64	56.6 ± 6.8
	Cr	42 ± 8.0	538 ± 19.4	1.4 ± 0.3	61 ± 11	420 ± 22
	Ag	0.05	6.62 ± 0.4	<0.06	3.12 ± 0.6	9.7 ± 0.7
2	Cd	3.2 ± 0.6	35 ± 2.4	0.16 ± 0.04	0.834 ± 0.033	36 ± 2.4
	Cr	40 ± 3.0	178 ± 9.2	<0.1	29 ± 2.0	207 ± 9.4
	Ag	0.05	5.22 ± 0.62	<0.03	0.885 ± 0.096	6.1 ± 0.63
3	Cd	5 ± 3.0	1.71 ± 0.04	<0.03	0.24 ± 0.11	1.97 ± 0.11
	Cr	2.3 ± 0.9	17 ± 1.0	<0.1	7.5 ± 0.6	24.6 ± 0.4
	Ag	0.4 ± 0.1	0.97 ± 0.11	<0.03	0.07 ± 0.01	1.04 ± 0.11

TABLE 30. NATURALLY OCCURRING CONCENTRATION FACTORS

STATION	METAL	CONCENTRATION FACTORS	
		SUSPENDED SOLIDS*	SEDIMENTS
1	Cd	1.8×10^3	1.4×10^4
	Cr	8.0×10^3	1.0×10^4
	Ag	4.3×10^3	1.9×10^5
2	Cd	1.7×10^3	1.1×10^4
	Cr	3.6×10^3	5.2×10^3
	Ag	3.3×10^3	1.2×10^5

* Based on the average of dissolved metal concentrations in 2 (station 2) or 3 (station 1) samples.

TABLE 31. DESORPTION OF METALS FROM SEDIMENTS IN SFW'

STATION	METAL	METAL CONCENTRATION IN SFW' (ppb)			
		pH 6.5	pH 4.0	pH 2.5 (24 hr)	pH 2.5 (7 days)
1	Cd	1.0 ± 0.2	6.6 ± 0.8	60 ± 15	63 ± 3
	Cr	1.0 ± 0.2	9.3 ± 5.1	12.4 ± 0.6	-
	Ag	0.11 ± 0.06	0.17 ± 0.02	<0.05	-
2	Cd	0.3 ± 0.1	2.8 ± 0.9	32 ± 8.0	38 ± 0.8
	Cr	0.8 ± 0.3	1.4 ± 0.8	7 ± 1.0	-
	Ag	<0.05	<0.05	<0.05	-
3	Cd	<0.04	0.5 ± 0.4	1.2 ± 0.2	2.2 ± 0.6
	Cr	<0.4	<0.4	1.1 ± 0.1	-
	Ag	<0.05	<0.05	<0.05	-

TABLE 32. METAL ADSORPTION ON RESUSPENDED SEDIMENTS

PARTICULATE CONCENTRATION*	Cd		Cr(III)		Ag	
	CONC. ADDED (ppb)	CONC. FACTOR ($\times 10^{-3}$)	CONC. ADDED (ppb)	CONC. FACTOR ($\times 10^{-3}$)	CONC. FACTOR (ppb)	CONC. FACTOR ($\times 10^{-3}$)
100 ppm	5	32 ± 4.0	20	3.2 ± 0.3	5	24 ± 4.0
1000 ppm	50	99 ± 21	50	5.3 ± 0.4	10	34 ± 10
	500	11 ± 3.0	500	5.4 ± 0.5	25	33 ± 2.0
	5000	12 ± 1.0	-	-	50	24 ± 8.0

* Particulate phase consisted of a silt and clay (<10μm) fraction of station 2 sediments.

TABLE 33. CHARLES RIVER WATER MODEL 6/ 4/ 1976

T= 11.0°C; Salinity = 0.07°/oo; Dissolved Oxygen = 10.00 mg/l; pH = 7.00; Eh = 0.813; pS = 43.687;

γ_0 = 1.000; γ_1 = 0.948; γ_2 = 0.809; γ_3 = 0.621; γ_4 = 0.429; γ_5 = 0.226;

CHROMIUM = 3.1000000000-08M

SPECIES	LIGAND CONC.	LIGAND ACT. COEFF.	FORMATION CONSTANT	SPECIES CONC.
CrHMO	3.000000000-08	1.000	8.600000000e03	3.986644550-12
CrHFO	1.100000000-06	1.000	2.000000000e05	3.399473630-09
CrKaolinite	6.600000000e00	1.000	2.500000000-02	2.549605222-09
CrPhytoplankton	6.700000000e00	1.000	3.600000000-02	3.727059271-09
CrCl	1.100000000-03	0.948	3.981071705e00	1.680897567-15
$CrCl_2$			7.765471166-01	2.918509145-19
Cr(OH)	1.000000000-07		1.584983192e10	6.413451019-10
$Cr(OH)_2$			1.995262314e18	6.890680695-09
$Cr(OH)_3$			3.162277660e25	1.035902561-08
Cr^{+3}				1.117217648-17
$HCrO_4^-$				1.301430708-13

TABLE 34. CHARLES RIVER WATER MODEL 6/ 4/ 1976

CADMIUM = 2.3000000000-09M

SPECIES	LIGAND CONC.	LIGAND ACT. COEFF.	FORMATION CONSTANT	SPECIES CONC.
CdHMO	3.0000000000-08	1.000	6.0000000000e04	2.6505175537-12
CdHFO	1.1000000000-06	1.000	1.7000000000e04	2.0787226472-11
CdKaolinite	6.6000000000e00	1.000	8.0000000000-02	5.8693345331-10
CdPhytoplankton	6.7000000000e00	1.000	1.1000000000-02	8.1926127857-11
CdCl	1.1000000000-03	.948	9.5499258602e01	1.1677439510-10
$CdCl_2$			4.0738027780e02	4.9300789457-13
$CdCl_3$			1.7378008287e02	2.3133777745-16
$CdCl_4$			3.4673685045e01	5.6432031110-20
$CdCO_3$	2.1000000000-07	.809	2.5118864315e05	4.7467046654-11
$Cd(CO_3)_3^{3}$			1.7378008287e06	2.2099665515-23
$CdHCO_3$	5.0000000000-04	.948	1.2589254117e02	6.9972106018-11
Cd^{+2}				1.8 -09

TABLE 35. CHARLES RIVER WATER MODEL 6/ 4/ 1976

SILVER = 9.2000000000-10M

SPECIES	LIGAND CONC.	LIGAND ACT. COEFF.	FORMATION CONSTANT	SPECIES CONC.
AgHMO	3.0000000000-08	1.000	5.2000000000e04	4.4193252610-13
AgHFO	1.1000000000-06	1.000	8.0000000000e03	2.4929527111-12
AgKaolinite	6.6000000000e00	1.000	8.0000000000-03	1.4957716265-11
AgPhytoplankton	6.7000000000e00	1.000	4.8000000000-02	9.1106089981-11
AgCl	1.1000000000-03	.948	1.5135612484e03	4.4738439813-10
$AgCl_2$			1.9952623149e05	6.4874424718-11
$AgCl_3$			1.9952623149e05	7.9314509447-14
$AgCl_4$			7.0794578438e05	3.8240028130-16
AgOH	1.0000000000-07		1.5848931924e02	4.4898452051-15
$Ag(OH)_2$			8.1283051616e03	2.4275857923-20
$Ag(OH)_3$			1.3489628825e05	4.7206765384-26
Ag^+				2.98 -10

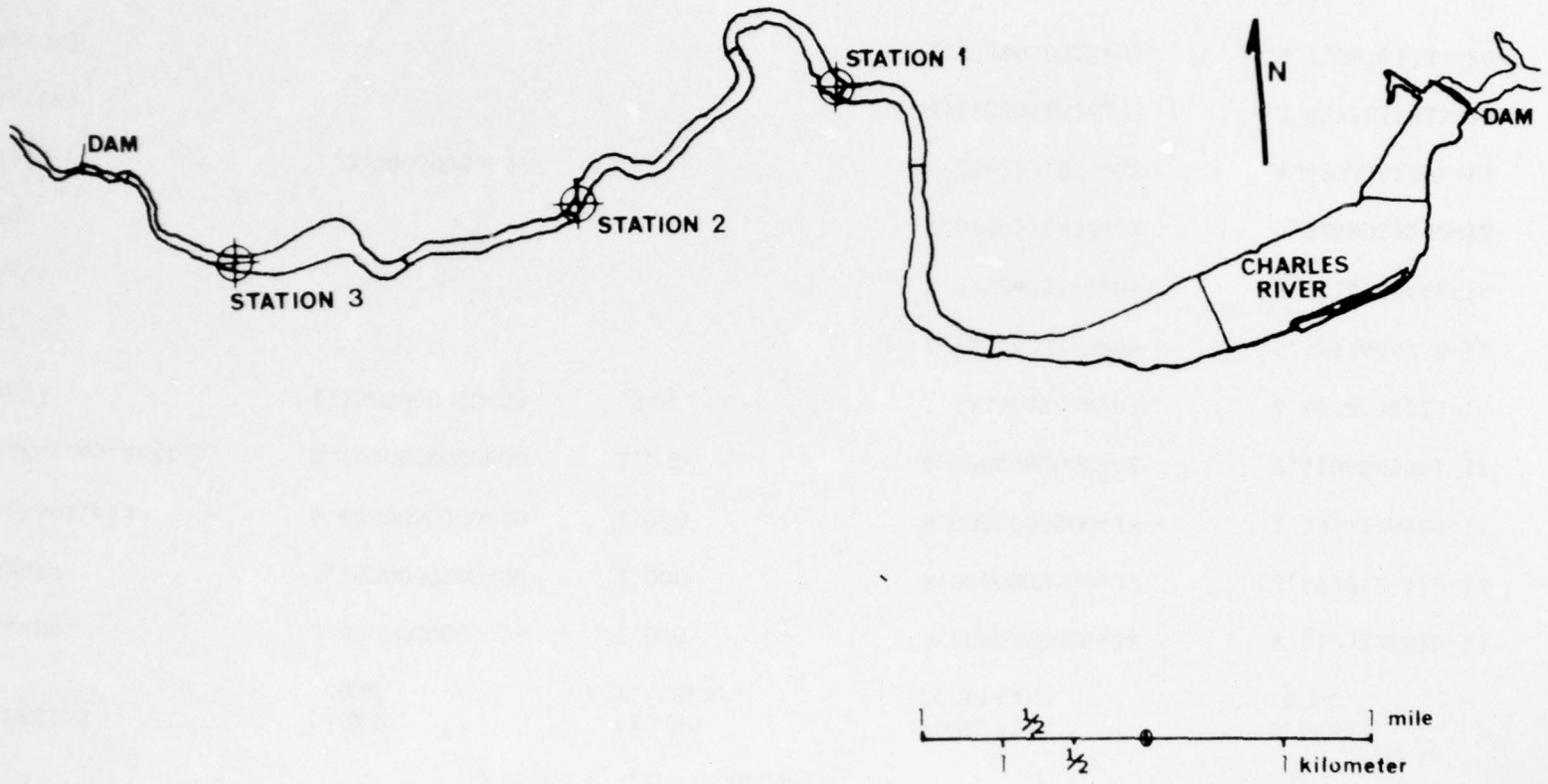


Figure 1. Map of Sampling Locations

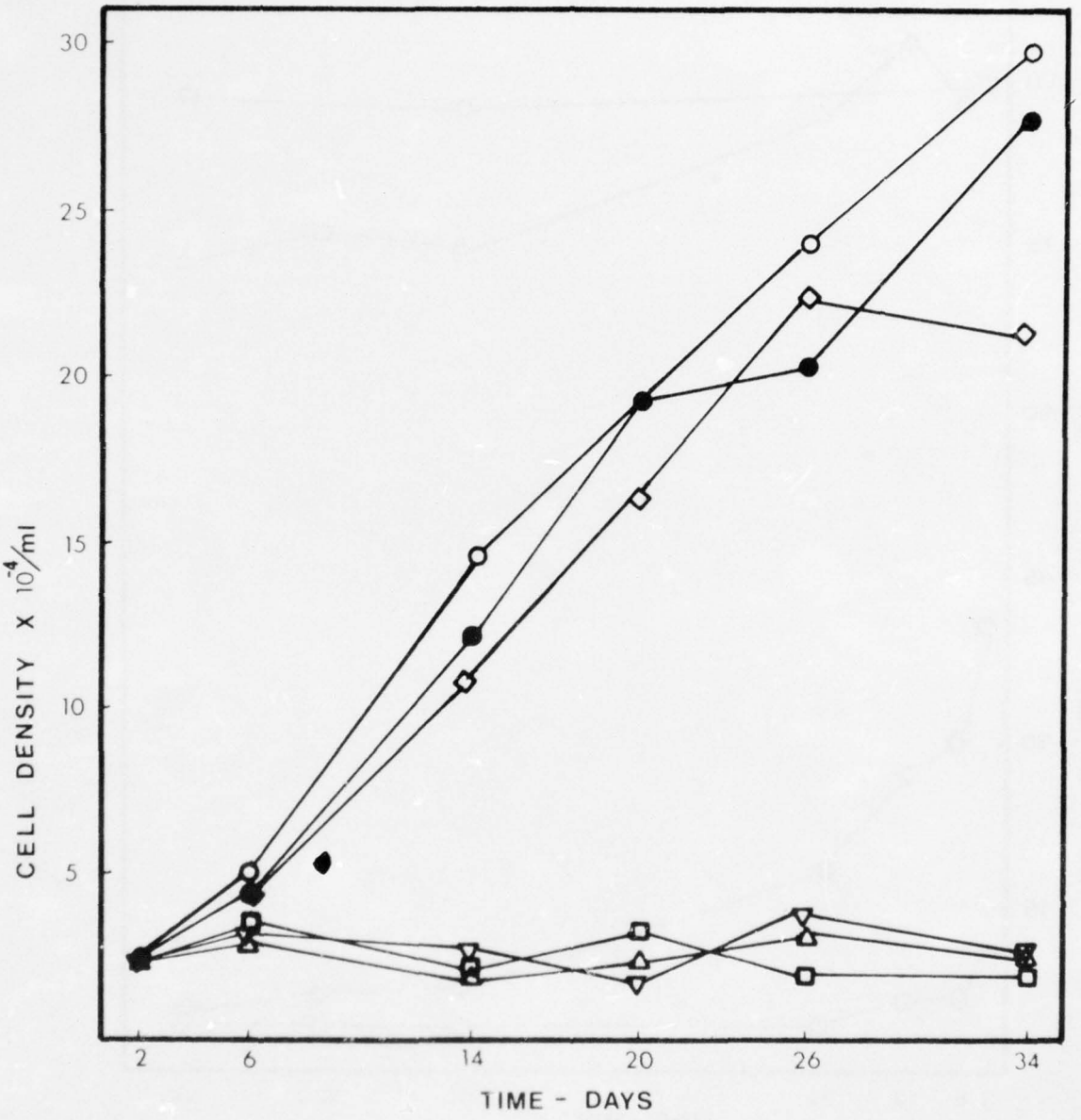


Figure 2. Effect of silver on growth rate of Chlorella vulgaris

Ag(I): ●- none added, ○- 10 ppb, ◇- 25 ppb, ▽- 50 ppb, □- 100 ppb, △- 200 ppb.

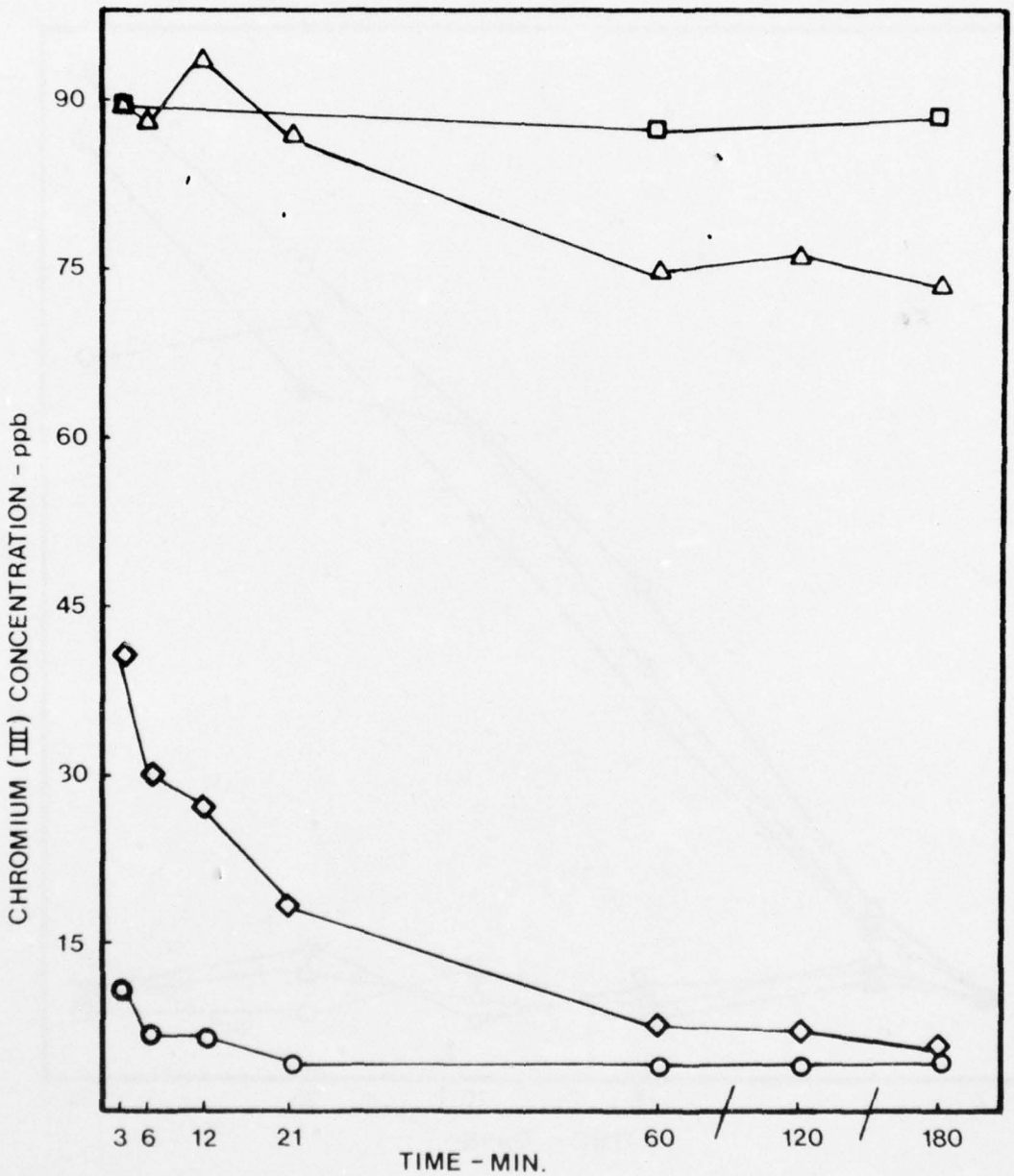


Figure 3. Chromium adsorption on kaolin

Cr (III) : 100 ppb; kaolin : □ - none added, △ - 10 ppm, ◇ - 100 ppm, ○ - 1000 ppm; pH 6; 20°C.

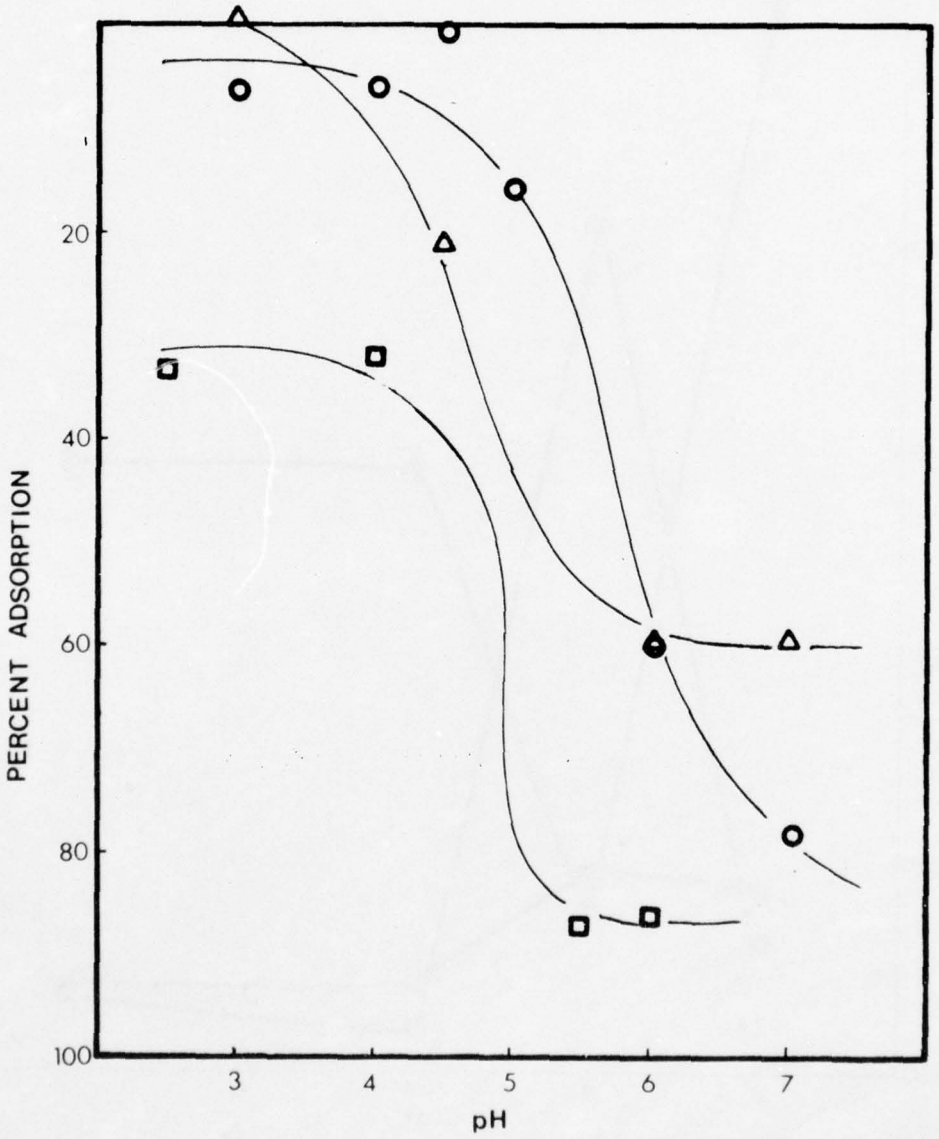


Figure 4. Effect of pH on the adsorption of metals on kaolin

△- silver, 10 ppb; ○ - cadmium, 10 ppb; □ - chromium, 20 ppb: kaolin, 100 ppm.

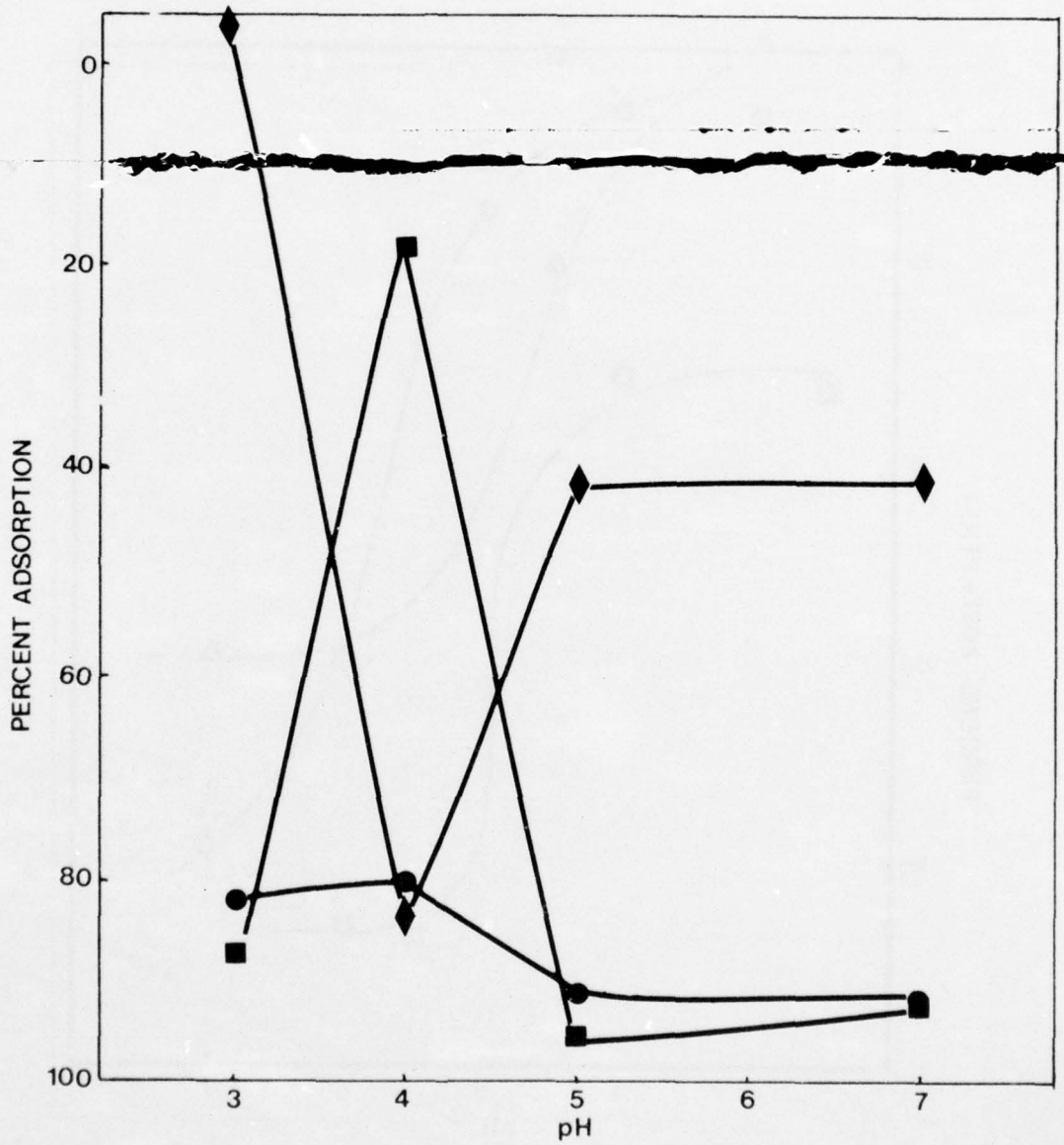


Figure 5. Effect of pH on the adsorption of metal on Montmorillonite

●– chromium, 20 ppb; ■– cadmium, 5 ppb; ♦–silver, 5 ppb;

Montmorillonite, 100 ppm.

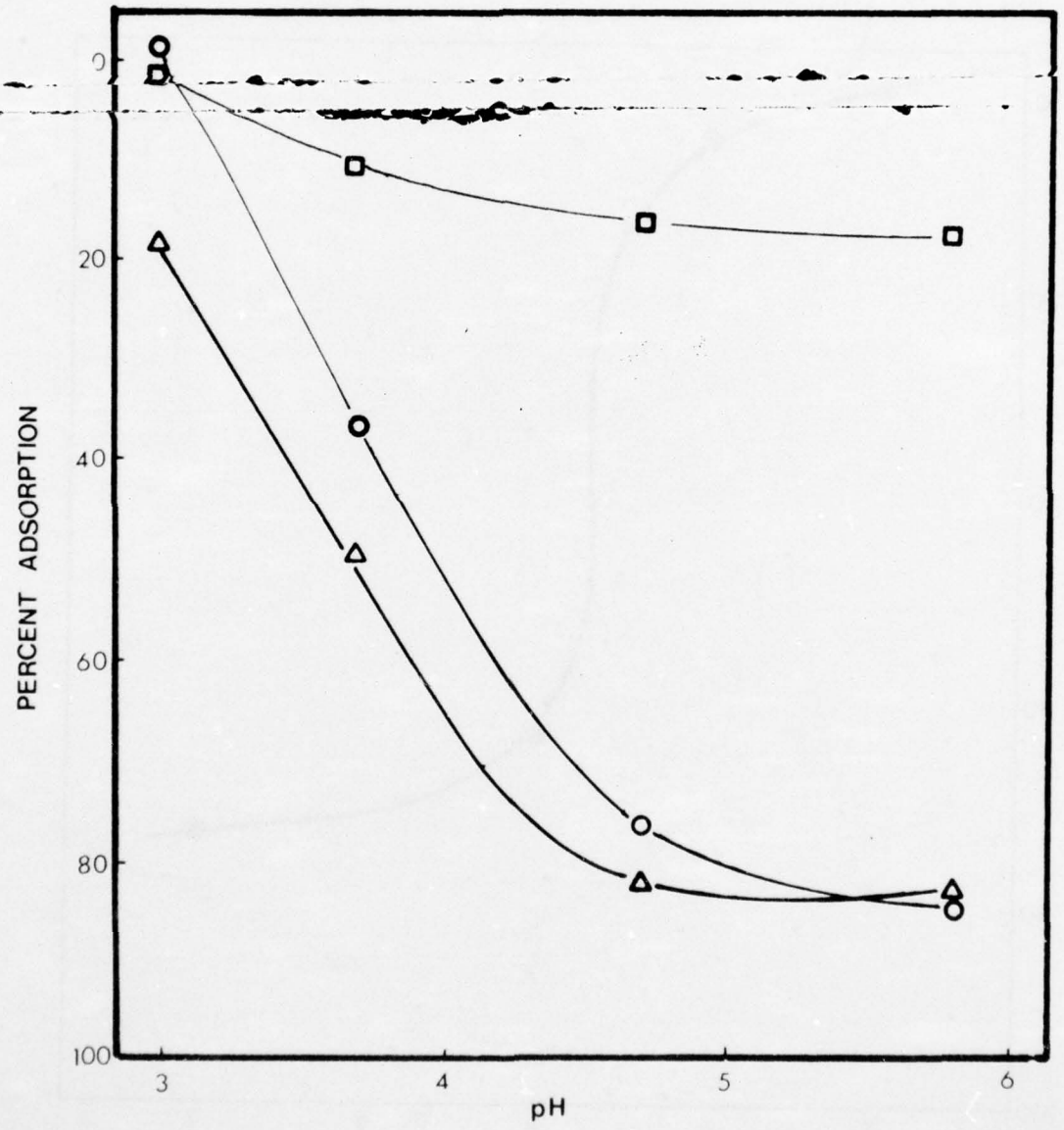


Figure 6. Effect of pH on the adsorption of metals on HMO

△–silver, 10 ppb; ○–cadmium, 10 ppb; □–chromium, 10 ppb; HMO, 0·01 mM.

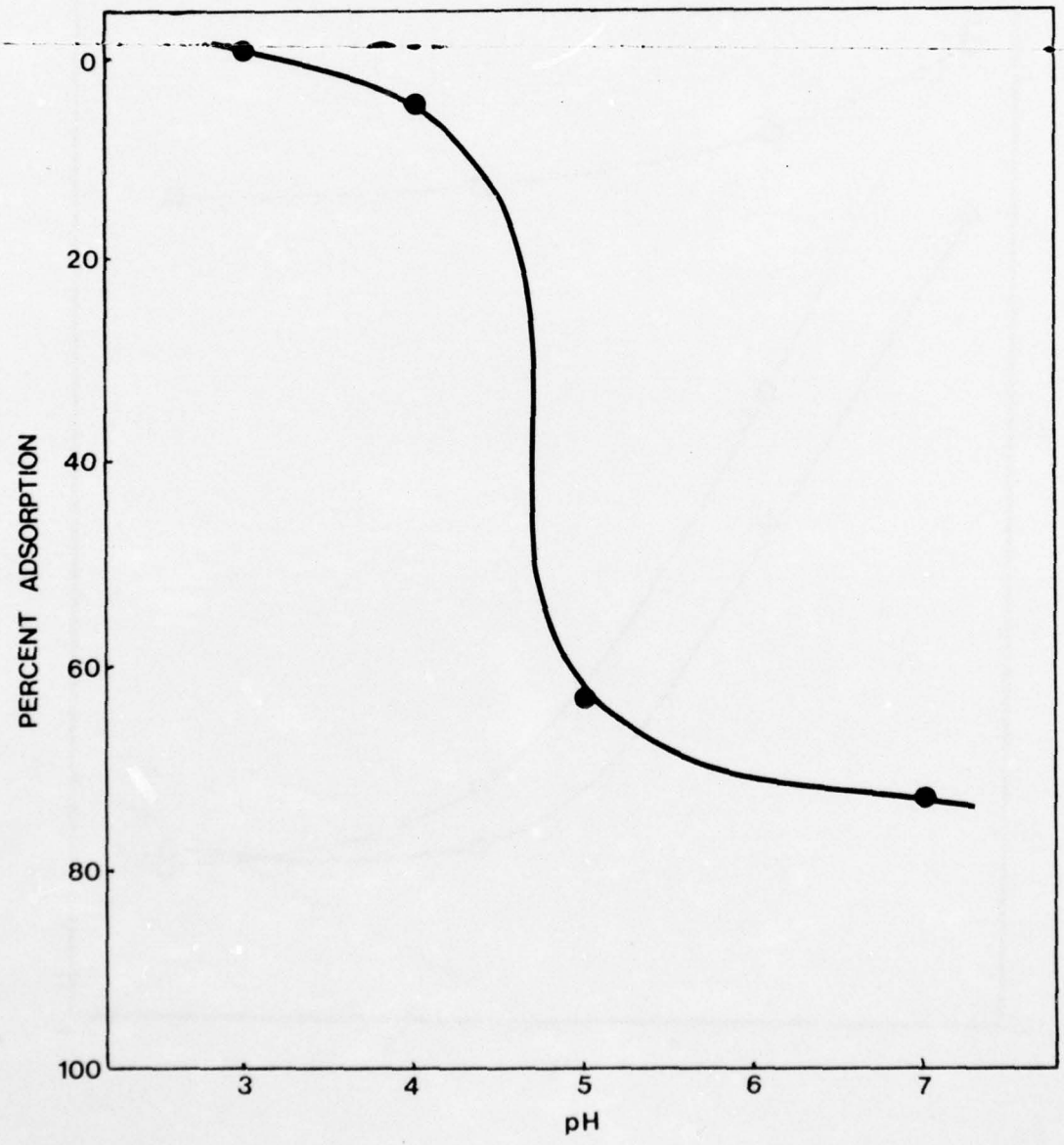


Figure 7. Effect of pH on the adsorption of 20 ppb chromium (III) on 0.01 mM HFO.

APPENDIX

CALCULATION OF CONCENTRATION FACTORS

As described in Section II, the concentration factor is essentially the Freundlich Isotherm constant K. In its application to adsorption experiment data, the equation was modified slightly to account for losses in dissolved metal concentration due to adsorption on container walls. Blank samples containing metal additions but no particulates were processed with the test samples. The concentration of metal species adsorbed by the particulates was considered to be the blank dissolved metal concentration (Mb) minus the dissolved metal concentration in the sample (Ms). This modification yields the following equation for the concentration factor:

$$K = \frac{(Mb) - (Ms)}{\frac{(Ms)}{(P)}}$$

where (P) is the concentration of the particulate in suspension.

The variance of any derived quantity W, which is a function of the independently variable experimental quantities a, b, c,... etc., may be found by the following equation:

$$W = f(a,b,c,\ldots)$$

$$Sw^2 = \frac{dW^2}{da} \cdot Sa^2 + \frac{dW^2}{db} \cdot Sb^2 + \frac{dW^2}{dc} \cdot Sc^2 + \ldots$$

This expression is exact for linear functions of the variables, and is not limited to Gaussian distributions. In the case of the derivation of the concentration factor, the following expression for the total analytical uncertainty was derived:

$$S_k^2 = \frac{1}{(\bar{M}s)\ (\bar{P})}^2 \cdot S_{(\bar{M}b)}^2 + \frac{[(\bar{M}b) - (\bar{M}s)]^2}{(\bar{M}s) \cdot (\bar{P})^2} \cdot S_{(\bar{P})}^2 + \frac{(\bar{M}b)^2}{(\bar{P}) \cdot (\bar{M}s)^2} \cdot S_{(\bar{M}s)}^2$$

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Hq USAF/PREE	1	OEHL/CC	3
Hq USAF/RDPS	2	OEHL/OL-AA	1
Hq USAF/SAFOI	1	OEHL/OL-AB	1
Hq USAF/SGPA	2	AFWL/SUL (Tech Library)	1
Hq USAF/PREV-P	1	AFGL/XOP	1
Hq USAF/PREV-X	1	USAFSAM/EDE	2
Hq Comd USAF/DEE	1	AFRPL/Library	1
CINCAD/DEEV	2	FTD/LGM	1
CINCAD/DEECV	1	SAMTEC/SEH	1
CINCAD/SGPAP	1	SAMSO/DEC	1
AFCS/DEEE	1	SAMSO/SG	1
AFLC/SGB	1	AMD/RDU	1
AFLC/DEPV	1	ADTC/CSV	1
AFLC/MAUT	1	ADTC/DLOSL	1
AFLC/MMRF	1	AFFTC/DE	1
AFSC/DE	1	AFETR/DER	1
AFSC/SD	1	1035 USAF Technical Ops Gp	1
AFSC/DEV	1	SAALC/MAGCB	1
AFSC/SGB	1	1 Med Service Wg/SGB	1
AFSC/SGPE	1	DDC/TCA	12
AFSC/DASR	1	ARPA	1
AFSC/DLCAM	2	Defense Rsch & Engr/AD (E&LS)	1
ATC/DEPV	1	OASD/(I&L)ES	1
ATC/SGPAP	1	USA Environ Hygn Agcy	1
AAC/DEV	1	Dir, USA WW Exp Stn	1
AAC/SGB	1	USA CERL	1
MAC/SGPE	1	Dir, USA Eng R&D Lab/MERDC	1
MAC/DEEE	1	Dept of the Army/DARD-ARE-E	1
CINCPACAF/DEMU	2	NCEL, Code 25111	1
CINCPACAF/SGPE	1	Naval Ship R&D Ctr (Code 3021)	1
CINCSAC/DEPV	1	Technology Transfer Staff (EPA)	1
CINCSAC/SGPA	1	Office of Rsch & Development	
TAC/DEEV	1	(EPA)	1
TAC/SGPB	1	National Science Foundation	1
USAFSS/DEMM	1	US Army Med Bioengr R&D Lab	
CINCUSAFE/Surgeon	1	SGRD-UBG	1
CINCUSAFE/DEPV	2	Dept for Civil Engr/Stanford	
AFISC/SGMS	1	Univ	1
AFISC/SES	2	Dept of Earth Sciences/	
AFRES/DEEE	1	Stanford Univ	1
USAFA/DEV	1	Dept of Environmental Sciences/	
AFIT/DEM	1	Cal Inst of Tech	1
AUL	1	Mass Inst of Technology	1
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AFOSR	1	AFRCE/Eastern Region	1
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