Bull. Environm. Contam. Toxicol. 26, 213-218 (1981)

A Laboratory Investigation of Heavy Metal Adsorption on Marine Dredge Spoils

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Despite extensive operations worldwide, there has been considerable uncertainty regarding the environmental impact of offshore mining of sand and gravel. Dredging and disposal activities probably do not introduce new contaminants but can redistribute the sediments and their contaminants to the water column. These sediments are likely to be contaminated with heavy metals, pesticides, hydrocarbons, and chlorinated biphenyls. The important question is whether dredging and/or disposal operations could shift equilibria of toxic species enough so as to release biologically harmful concentrations.

BRANNON (1978) reported that the presence of contamination in dredged material does not necessarily imply that adverse environmental effects would occur as a result of dredging and disposal activities. For example, it is possible that the species may be present in a chemically immobile, biologically unavailable form. In other words, water quality is related to the concentration of mobile, bioavailable species rather than total sediment concentration. In support of this HIRSH et al. (1978) have found that there is little or no correlation between bulk sediment analysis for heavy metals and their environmental impact.

The studies of NEFF et al. (1978) showed that the accumulation potential of toxics can be affected by duration of exposure, salinity, water hardness, exposure concentration, temperature, and of course, the particular organism under study. They also found that the chemical form of metals (speciation) had important effects on their bioavailability.

The investigation reported here was designed to provide information for the sand and gravel mining of Massachusetts Bay. In particular, information was required as to the extent and rates of heavy metal adsorption onto dredged spoils as a function of temperature, light levels, and dissolved oxygen content. The levels of these three parameters are known to be different at the surface where spoils are discharged and at depths of 30 meters where the spoils would finally settle.

In order to properly assess these parameters, a 2^3 factorial experiment was designed. In a factorial experiment, all

0007-4861/81/0026-0213 $01.20

variables from high to low levels are simultaneously changed. An analysis of variance (ANOVA) of the results allows for the complete evaluation of important variables. The major advantages of this experimental design are the amount of information that can be obtained from a limited number of experiments and the unique ability to discover synergistic interactions among parameters. Experiments which vary one parameter at a time ignore possible interactions and are therefore strictly invalid.

Briefly, a 10 liter suspension of typical dredge spoils in sea water was spiked with 100 mg/L of Cu, Pb, Zn, Cd, Ni, and Co under conditions of the factorial design. Concentrations of heavy metals remaining in the sea water were determined as a function of time.

MATERIALS AND METHODS

A bulk sample from Massachusetts Bay representing the top 10 cm of sediment was delivered to the laboratory within a few hours of sampling. The silt and clay materials (less than 20 μm diameter particles), which was thought to be typical dredge spoils, was isolated by wet screening using sea water (32.5°/00 salinity). The silt and clay suspensions were suction filtered, homogenized, and stored moist at 4°C. Moisture determinations were used to correct sample weights to a dry weight basis.

This sample was analyzed to generate baseline data to aid in the interpretation of adsorption experiments. Mineralogical composition, based on X-ray diffraction analysis, showed α quartz to be the predominant mineral. Organic carbon was determined by wet oxidation with dichromate (GAUDETTE 1974) and by combustion techniques. The values agreed very well, giving an average of 1.61% organic carbon. The cation exchange capacity, according to the method of JACKSON (1958), was estimated to be 9.0 meq/100 g. Since the organic carbon content was quite low and the quartz content high, this modest exchange capacity is reasonable. The six trace metals of interest were determined by the solvent extraction-atomic absorption spectrophotometric (AAS) procedure of BROOKS et al. (1967). It was desired to minimize sample pretreatment because of contamination hazards, so no filtration or acid digestion was used. To determine if this procedure would provide accurate results, a series of "spike" recovery experiments were conducted using additions of up to 100 μg/L. The average of triplicate recoveries varied from 97-101% and showed no trend toward low recoveries for the small concentration "spikes".

To aid in the establishment of a sampling regimen for the main experiment, preliminary studies were conducted at room temperature, and with no attempt to control oxygen or light levels. At the start of each experiment, a suspension of screened material in sea water was spiked with 100 μg/L of each of the six elements. Samples were withdrawn after 30 min and then every hour on the hour for 7 h. Very strong adsorption was observed for Cu, Pb, and Cd; moderately strong adsorption for Zn; and significantly weaker adsorption for Co and Ni.

It is certain that the adsorption process was incomplete for the less strongly adsorbed metals. Therefore, duplicate six-day equilibrations were conducted. It was concluded from these experiments that several days were required to reach equilibrium for Co and Ni. Since the most rapid adsorption for all these metals was completed during the first hour, a 3-h equilibration was deemed sufficient time to study the effects of environmental variables. To obtain information on the rate of adsorption, it was decided that sampling should be conducted at 3, 7, 13, 20, 30, 50, 70, 90, 120, and 180 min.

FACTORIAL EXPERIMENT

A 2^3 factorial experiment was used to investigate the effects of oxygen, temperature, and light levels on the rate and extent of adsorption of trace metals from "spiked" sea water. Experiments were performed in a carefully cleaned, 15-L polypropylene bucket containing 10 L of unfiltered sea water. Screened material (150 g; approximately 100 g dry weight) was added to the bucket. This was followed by 10 mL of 100 mg/L solution containing Cu, Pb, Zn, Cd, Ni, and Co to give a final added concentration in solution of 100 µg/L for each element.

Eight experiments were conducted corresponding to the appropriate combinations for a 2^3 factorial. The ninth run was a control in which no sediment was present. Temperature was maintained at either 4 or 20°C by immersing the test container in a water bath. Oxygen concentrations were manipulated by saturating the sea water for 2 h before and throughout the experiment by bubbling either air or nitrogen into the suspension through gas dispersing frits while a polyethylene stirrer maintained homogeneity. Dissolved oxygen content was monitored with a dissolved oxygen meter and BOD probe. Saturated values were about 10 mg/L at 4°C and 7 mg/L at 20°C. When nitrogen was being bubbled into the system, the oxygen content was approximately 1.5 mg/L for both temperatures. Light conditions of 4000 Lux (the level used for phytoplankton growth) were maintained with a "Daylight" 40-watt fluorescent tube (Sylvania Corporation). Dark conditions were produced by covering the bucket with black paper. Light levels in the suspension were measured with a light meter.

At ten predetermined times over a 3-h period, 500 mL aliquots of suspension were siphoned with Tygon tubing into an acid-cleaned, graduated cylinder. Suspensions were immediately filtered through acid-washed Whatman No. 40 paper in Buchner funnels and transferred to polypropylene flasks for trace metal analysis. Acid washing of the filter paper was essential to reduce Zn blanks to an acceptable value. Each filtrate was analyzed for the six metals of interest by the solvent extraction AAS procedure.

After the experiments had been completed, it was discovered that the pH of the air-saturated system (7.9) was much lower than the nitrogen-saturated system (8.6) due to the exclusion of CO_2 during nitrogen purging. It thus became apparent that the variable originally intended to be oxygen concentration was actually confounded with a change in pH. Consequently it was necessary to perform a second 2^2 factorial experiment involving oxygen level and pH before the 2^3 factorial experiment data could be properly interpreted. Here it was learned that the effect of varying oxygen level from 1.5 to 7.0 mg/L was not statistically significant, while a pH change from 7.9 to 8.6 produced changes significant at the 99% probability level with no interaction between variables. Thereafter, the oxygen variable was designated a pH variable.

RESULTS

An analysis of variance (ANOVA) was not conducted on the data for Cu and Pb because the concentrations for both of these elements approached the background level of sea water in the first few minutes and showed only random variations throughout the complete 3-h equilibrations. This finding agrees with the observations of KRAUSKOPF (1956) working with much higher concentrations in sea water systems and is compatible with SCHNITZER (1969) who reported that the highest stability constants for complexes in soils were found for Cu and Pb. CRAIG (1974) and SCRUDATO & ESTES (1975) have reported that these two elements are rapidly and strongly adsorbed on particles in sea water.

For Zn, Cd, Ni, and Co, the concentrations remaining in solution after 3 h were subjected to ANOVA. In Table 1 the F ratios are tabulated for the various independent parameters.

The temperature parameter was significant at the 99.9% probability level and its effect ("effects" are not shown in Table) indicated greater adsorption of the four metals at 20°C than at 4°C. This is important for this study because metals released to surface water during dredging or by other mechanisms would be readsorbed rapidly during the summer months by particulates and thus eliminate potential toxic pollutants.

The effect of changing pH from 7.9 to 8.6 resulted in greater adsorption at the 8.6 value. This difference is statistically significant at the 99.9% level for Ni, Cd, and Zn and at the 99% probability level for Co. Thus, re-adsorption of toxic metals would not be expected to be great in acid waters. This is probably due to the competition between the proton and metal for the exchange/adsorption sites on the particulates.

TABLE 1. ANOVA for Residual Solution Concentrations After a Three-Hour Equilibration.

Variable	Zinc	Cadmium	Nickel	Cobalt
	F	F	F	F
Temperature	3009.***	423.***	744.***	306.***
pH	101.***	37.***	32.***	17.**
Light	14.**	4.5	4.9	25.***
Temp-pH	33.***	21.**	0.2	0.01
Temp-Light	0.1	0.3	4.9	2.7
pH-Light	20.**	26.***	47.***	42.***
Temp-pH-Light	1.3	21.**	5.9*	4.9

F.95(1,8) = 5.32 F.99(1,8) = 11.26 F.999(1,8) = 25.42

*Significant at 95% probability level.
**Significant at 99% probability level.
***Significant at 99.9% probability level.

The effect of light levels was that metal adsorption was always greater in the dark than in the light. However, this effect was only significant for Co (99.9% probability level) and Zn (99% level). The F ratios for both Ni and Cd were just slightly below the required tabular values at the 95% probability level. No explanation for this phenomenon can be offered. The significant interaction (the synergistic effect) between pH and temperature for Zn and Cd is caused by the greater effect of pH at 4°C than at 20°C.

The significant interaction of pH and light for Co, Ni, Zn, and Cd is due to the large pH effect in light compared with the pH effect in the dark. At present, no physical or chemical rationale for these interactions can be suggested, but obviously they deserve greater investigation.

Extent of Adsorption. In all equilibrium experiments the order of trace metal adsorption was the same, i.e., Cu = Pb > Cd > Zn > Ni > Co.. The least adsorbed metals, Co and Ni, may be significantly affected by biological mechanisms which are very slow and would not be observed in this work. Clearly, Ni and Co would have a greater potential for aquatic toxicity than would Cu, Pb, Zn, and Cd.

DISCUSSION

For the purposes of the field study, prior investigations have shown that dredge spoils acting alone by simple desorption mechanisms will not introduce significant heavy metals into the water column. In addition, the work reported here proves that any re-distribution of toxic metals caused by dredging and/or disposal methods would be minimal. The rapid and fairly complete adsorption of Pb, Cu, Zn, and Cd on natural sediment for most environmental conditions, indicates that the concentrations of these metals in the water column will be very small. However, it is possible that Ni and Co concentrations could be increased because of their slow rate and incomplete degree of adsorption. Even here the sediment can be expected to adsorb substantial amounts of these elements, especially during the summer when the water is warm. Unless very large amounts of these metals were released, there should be no detrimental effect on biological organisms.

The findings have further implications concerning other sources of metal pollution in sea water. It is clear that sediments are very effective in scavenging metals from sea water. However, the toxicity potential to the marine environment is not eliminated because filter feeding organisms may find substantial fractions of these metals to be bioavailable. Furthermore, any chemical spill or the development of anoxic conditions could produce a rapid release of those metals to the water column.

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