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Covariation of Selected Trace Elements with Binding Substrates in Cores Collected from Two Contaminated Sediments

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Sediments serve as a final sink for many trace elements in the aquatic environment. Successive deposition of various elements to sediments year after year creates a historical record of trace element influx. The vertical distribution of many trace elements often reflects changes in anthropogenic loadings to the aquatic system (LeLand et al., 1974; Christensen et al., 1978 McIntosh and Bishop, 1976). It is well documented that upon sedimentation elements partition themselves among various binding substrates within the sediments, e.g., oxides of iron and manganese (Jenne, 1977; Helsinger and Friedman, 1982; Gadde and Laitinen, 1974; and organics (Slavek and Pickering, 1981; Saar and Weber, 1982; Nriagu and Coker, 1980). Diagenesis may alter the postdepositional distribution of various trace elements due to chemical and/or biological reactions occurring within surficial and deeper sediments (Cornwell, 1986; Reuther et al., 1984; Viel et al., 1984). This study examines the vertical distribution of various trace elements and their covariance with certain binding substrates within two contaminated sediments.

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MATERIALS AND METHODS

Weston's Mill Pond is the last in a series of impoundments in a series of three on Lawrence Brook and lies approximately 1.0 km upstream from the brook's confluence with the Raritan River, in New Brunswick, NJ. The impoundment was formed after construction of a dam in the mid-1800's. Weston's Mill Pond can be classified as a eutrophic system with a total phosphorus loading of 4153 kg/yr (Middlesex County 208 Study, 1977). The system is characterized by heavy sedimentation, erosion, summer algal blooms, and excessive aquatic macrophyte production. The reservoir is surrounded by a network of heavily-travelled highways and suburban developments. The site of sediment core collection was upstream approximately 200 m from a heavily travelled two-lane bridge.

The Delaware and Raritan Canal is a 71 km long water conduit linking Bordentown, NJ, on the Delaware River to New Brunswick, NJ, to the northeast at the head of navigation on the Raritan River. The canal was constructed in 1834. Several industrial, residential, and agricultural districts contribute to the point and non-point source influx of metals to the canal. The site on the canal where sediment cores were collected was located approximately 50 m downstream from the Alexander Road bridge near Princeton, NJ.

Sediment cores were collected from each site by SCUBA divers. PCV tubing measuring 40 cm in length (5.1 cm I.D.) were used to collect sediment samples. Four cores were collected at random from the deepest location in each water body. The cores were gently pressed into the sediments, capped on the top, slowly withdrawn from the sediments, and then capped on the bottom. Cores were transported to the laboratory in the vertical position. All cores contained some overlying water, which was permitted to settle for 24 hr in a 4°C constant temperature room prior to freezing the cores in the upright position.

Frozen sediment cores were thawed, extruded, and sectioned into 5-cm portions. The sections were dried overnight at 106°C. After drying, the sediments were cooled for 24 hr in a desiccator. The sections were then crushed in a mortar and pestal and passed through a 100-μm stainless steel sieve. Each 5-cm section was split into four replicates for trace metal analysis. Each replicate consisted of approximately 0.5 g of sediment which was weighed into a 150-mL beaker and digested in concentrated nitric acid on a hot plate for 6 hr at 75°C. The sediment slurry was poured into a polycarbonate centrifuge tube and spun at 2700 g for 10 min. The supernatant was carefully decanted into a 25-mL volumetric flask and diluted to mark with distilled/deionized water. Samples were stored in 30-mL Nalgene bottles until analyses. Seven elements were determined by flame A.A.: Pb, Zn, Cr, Cu, Ni, Fe, and Mn. Element analyses were performed on a Perkin-Elmer 603 flame atomic absorption spectrophotometer.

The means and standard deviations for each element at each depth were determined using the Statistical Analysis System (SAS, 1981). Simple pair-wise linear correlations were calculated for each possible combination of elements.

RESULTS AND DISCUSSION

Lead concentrations in WMP ranged from 49.2 to 392.6 μg/g (dry weight basis). The maximum concentration occurred at a depth of 10 to 15 cm in the sediment cores (Figure I). The minimum concentration occurred at 30 to 35 cm. Generally, Pb exhibited an overall decrease in concentration with increasing sediment depth. The range of Pb concentrations in DRC was 152.3 to 668.6 μg/g. The maximum concentration corresponed to a sediment depth of 15-20 cm. The minimum average concentration occurred in the surficial layer of sediments (0-5 cm).
Chromium levels ranged from 21.2 to 64.6 μg/g in WMP. The maximum concentration was observed at 15 to 20 cm in the sediment cores (Figure I). The minimum concentration was found at a depth of 30 to 35 cm within the sediments. The range of Cr concentrations in DRC was similar to WMP (25.5 to 60.8 μg/g). The maximum level occured at a slightly greater depth, 15 to 20 cm, in DRC than in WMP sediments. The minimum Cr content in DRC sediments was similar to WMP.

Copper concentrations in the four replicate cores collected from WMP ranged from 20.9 to 138.7 μg/g. The maximum average concentration was observed at a depth of 20 to 25 cm (Figure I). The minimum concentration was noted at the deepest portion of the core (30 to 35 cm). Probably lower concentrations would be found at still greater depths within the sediments. The range of Cu levels in DRC sediments was 45.4 to 101.5 μg/g. The maximum level was noted at a 15 to 20 cm depth in the sediment cores. The lowest concentrations of Cu were observed in the surficial sediments. The decrease in Cu concentration with sediment depth was more pronounced in WMP than DRC. In WMP, Cu levels declined 110 μg/g within a 15 cm increment, from the maximum at 20 to 25 cm.

Nickel concentrations ranged from 17.5 to 169.1 μg/g in WMP sediments. The maximum level occurred at the 20 to 25 cm depth. The minimum was observed at the greatest depth to which the core was inserted (30 to 35 cm) (Figure I). The range of Ni levels in DRC was below detection to 95.9 μg/g. The maximum concentration was found at 5 to 10 cm in the sediments. The minimum Ni concentration was observed at the greatest core depth (30 to 35 cm). Nickel levels in DRC sediment cores were quite variable. A slight decrease in concentration over depth was noted, however, given the large standard deviations at each depth, no definite trends were discerned.

The range of Zn values in WMP cores was 156.8 to 929.3 μg/g. The average maximum concentration was located at 15 to 20 cm within the cores. The minimum level was observed at the greatest core depth (30 to 35 cm) (Figure 1). Zinc levels ranged from 245.0 to 1675.0 μg/g in DRC cores. The average maximum concentration was noted at a greater depth than in WMP sediment cores (25 to 30 cm). The minimum Zn concentration occurred in the surficial layer of sediments (0 to 5 cm). An abrupt decrease in Zn concentration was noted below the maximum; Zn decreased approximately 400 μg/g with a 5 cm increase in depth in DRC sediments.

WMP is characterized by very high levels of Fe. The Raritan-Magothy geologic formation, which comprises a large portion of WMP's drainage basin, is rich in iron-containing minerals (Middlesex County 208 Study, 1977). Iron concentrations ranged from 23287 to 55330 μg/g. The maximum concentration occurred in the surficial layer (0 to 5 cm). Below the maximum, Fe concentrations decreased slightly, leveling off at approximately 45000 μg/g. At 20 to 25 cm, Fe levels sharply declined, attaining a minimum at 30 to 35 cm (Figure 1). In DRC sediments, Fe ranged in concentration from 15670 to 45392 μg/g. The maximum level occurred much deeper within the DRC sediments (25 to 30 cm). The minimum concentration occurred above the maximum (15 to 20 cm).

The range of Mn concentrations in WMP sediment cores was 199.8 to 697.5 μg/g. The maximum Mn level was observed in the surficial layer, similar to Fe. The minimum concentration occurred at the greatest sediment core depth (30 to 35 cm) (Figure 1). Manganese levels ranged from 193.4 to 502.4 μg/g in DRC sediments. The maximum value was also noted in the surficial layer for this element, as noted in WMP cores. The minimum concentration occurred at a depth of 30 to 35 cm.

Simple linear correlations were performed on all possible combinations of elements at each site using data from all replicate core analyses. In WMP sediment cores, all elements exhibited significant positive correlations ($p < 0.0001$) with one another over depth except Ni, which correlated only with Cu. Negative correlations between Ni/Pb and Ni/Mn were observed, but were not significant. Significant positive correlations were observed between trace elements and the possible binding substrate elements Fe and Mn in WMP sediments (Table 1).

Generally, most elements in DRC sediment cores showed poor correlations between one another. There were negative correlations between Ni/Pb, Ni/Zn, and Pb/Mn, but these were not significant. In DRC sediment cores, only Zn and Cu, and Ni correlated with the possible binding substrate, Fe and Mn, respectively (Table 2).

The vertical distributions of trace elements in WMP and DRC serve as historic records of past anthropogenic activities in the surrounding watershed. Unfortunately, sediment core dating was not performed on the sediments; therefore, no estimate of sedimentation rates could be derived. In lakes of northern Wisconsin, concentrations of trace elements in sediments at depths greater than 50 cm corresponded to sediments deposited circa 300 to 400 years ago (Iskandar and Keeney, 1974). Concentrations of metals at this depth were 44, 16, <0.1, 0.3, and 20 μg/g for Cu, Zn, Pb, Cr, and Ni, respectively. Concentrations of these elements at the 30 to 35 cm depth in WMP and DRC sediments were substantially greater than those observed in Wisconsin lake sediments. It is most likely that sediments deposited in precultural times were not collected in the present study.

Vertical distributions similar to those observed for trace elements examined in the present study have been observed in Lake Washington (Crecelius and Coker, 1973), Lake Ontario (Nriagu and Coker, 1980), various Wisconsin lakes (Iskandar and Keeney, 1974), two Maine lakes (Kahl and Norton, 1983), Adirondack lakes (Davis et al., 1982), and other sediment systems (Reuther et al., 1979; Viel et al., 1979). Generally, Pb concentration decreased with increasing sediment depth, below a maximum which normally occurred several centimeters below the sediment/water interface; concentrations decreased from the maximum upwards to the interface. In contrast, in acidified Lake Gardsjoh (Sweden) maxima for Zn, Cd, and Pb were observed at the 2 to 3 cm sediment depth (Reuther et al., 1979).

Inputs of Pb into many aquatic systems have been attributed primarily to the deposition of atmospheric Pb from automobile exhaust. Ninety-five percent of the Pb in Lake Michigan sediments was attributed to atmospheric sources (Goldberg et al., 1981). The decrease in Pb concentration in recently deposited sediments is most likely related to a reduction in the use of leaded gasoline. The maxima for Pb concentrations in WMP and DRC may serve as chronological markers for the time at which conversion to unleaded fuel began (circa 1974). An estimate of sedimentation rate was calculated from the observed Pb maximum in each system; 7.5 mm/yr for WMP and 17.5 mm/yr for DRC. These estimates are very crude, as sediment mixing processes and diagenesis are not considered. However, the rates are comparable to those observed in other

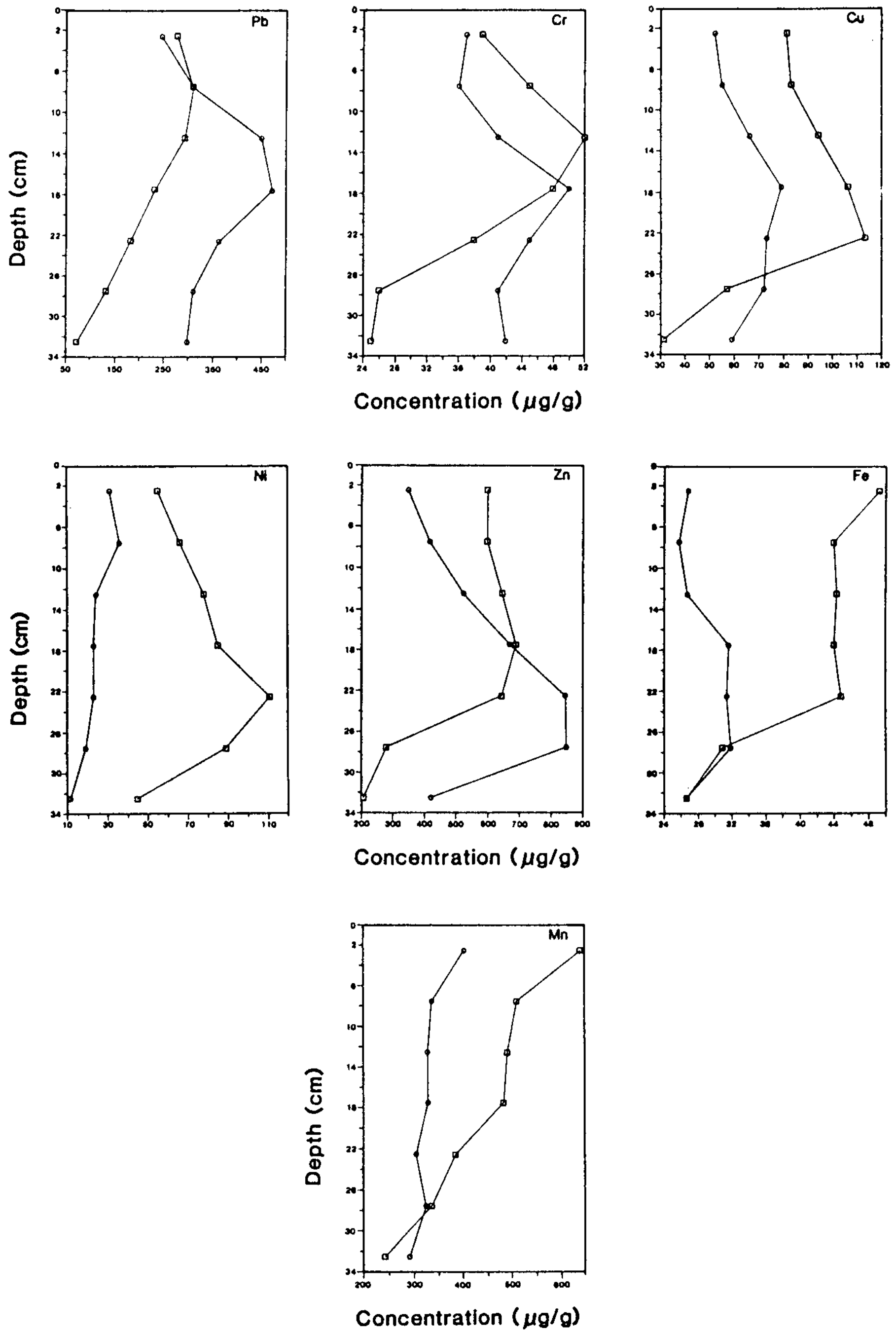

Figure 1. Vertical distribution of trace elements in WMP (□) and DRC (○) sediments.

Table 1. Pearson product-moment correlation matrix of elements in Weston's Mill Pond sediment cores. The upper number is the correlation coefficient and the lower number is the probability that the observed correlation is due to chance.

	Pb	Zn	Cu	Cr	Ni	Fe	Mn
Pb							
Zn	0.7211 0.0001						
Cu	0.5419 0.0001	0.8689 0.0001					
Cr	0.7717 0.0001	0.7853 0.0001	0.6739 0.0001				
Ni	-0.0511 0.6208	0.2098 0.0402	0.4560 0.0001	0.0714 0.4891			
Fe	0.7567 0.0001	0.8849 0.0001	0.7909 0.0001	0.6873 0.0001	0.1172 0.2553		
Mn	0.8015 0.0001	0.6228 0.0001	0.4237 0.0001	0.0583 0.0001	-0.0557 0.5901	0.7735 0.0001	

Table 2. Pearson product-moment correlation matrix of elements in Delaware and Raritan Canal sediment cores. The upper number is the correlation coefficient and the lower number is the probability that the observed correlation is due to chance.

	Pb	Zn	Cu	Cr	Ni	Fe	Mn
Pb							
Zn	0.2969 0.0041						
Cu	0.5087 0.0001	0.5872 0.0001					
Cr	0.5173 0.0001	0.4656 0.0001	0.7794 0.0001				
Ni	-0.0344 0.7448	-0.1933 0.0649	0.0374 0.7235	0.1342 0.2022			
Fe	0.1816 0.0831	0.7462 0.0001	0.4229 0.0001	0.3253 0.0016	-0.0785 0.4572		
Mn	-0.0255 0.8090	-0.0684 0.5171	0.1342 0.2022	0.1757 0.0938	0.2990 0.0038	0.1042 0.3230	

aquatic systems: 4 mm/yr in Lake Michigan (Goldberg et al., 1981), 2-5 mm/yr in select Wisconsin lakes (Iskandar and Keeney, 1974), and 20 mm/yr in Newport Bay Christensen et al., 1978).

The correlation between various trace elements in WMP and DRC sediments may indicate the same or related sources of elements in each system. Significant correlations between various trace elements in sediment cores collected from select Wisconsin lakes were observed (Iskandar and Keeney, 1974). The weak correlations between Ni and most metals in both WMP and DRC has also been observed in Lake Michigan (Leland et al., 1974) and Hudson River sediments (Helsinger and Friedman, 1982). Nickel was found to be associated ith fine-grained particles (< 13 um) in Lake Erie (Mudroch, 1984) and Detroit River (Mudroch, 1985) sediments. Of the elements assessed in this study, nickel may be the only one associated with fine-grained particles, hence the lack of correlation with other elements. The lack of correlation may also be partly due to dissimilar deposition patterns. Nickel has been shown to have a tendency to migrate downwards into deeper, sulfide-rich sediments (Carignan and Nriagu, 1985), further disrupting possible correlation with elements which tend to remain stationary upon burial or migrate upwards.

There was a general lack of strong correlations between most metals in DRC sediments, as compared to WMP. This finding may be due, in part, to the wide diversity of metal sources in the canal. WMP receives its metal loadings primarily from stormwater runoff (Middlesex County 208 Study, 1977), while DRC receives metal loadings from over 67 major industries, institutions, and commercial establishments. Thus, metal ratios in WMP would tend to be more constant over time as compared to DRC.

The vertical distribution of trace elements may be strongly dependent upon the vertical distribution of certain binding substrates (e.g., Fe and Mn oxides, organics, sulfides, carbonates). Significant correlations between Pb, Zn, Cu, and Cr, and the oxide substrate elements Fe and Mn were noted in WMP sediments, and to a lesser degree in DRC sediments over depth. In Hudson River sediments strong correlations between trace elements and Fe and Mn oxides were observed (Helsinger and Friedman, 1982). In Detroit River sediments mobility of Cd, Zn, Co, Pb, Cr, Ni, and P were controlled largely by Fe oxides (Lum and Gammon, 1985). In Lake Michigan sediments a significant relationship was found between the vertical distribution of trace elements and total organic carbon (Leland et al., 1974) while poor correlation was observed in Detroit River sediments (Mudroch, 1985). Unfortunately, organic carbon analyses were not performed on sediment cores collected in WMP and DRC. Lead and zinc were found to be associated with Fe oxides in extractions of WMP surficial sediments (Lewis and McIntosh, 1985). This observation is consonant with results of scanning electron microscopic analyses of WMP surficial sediments, where Pb was shown to be associated almost entirely with an amorphous matrix of Fe and Mn oxides (Newman et al., 1983). Chemical extractions of DRC surficial sediments did not provide evidence of Pb and Zn association with Fe and Mn oxides (Lewis and McIntosh, 1985). Given the abundant concentration of Fe in WMP sediments, Fe oxides would be favored as the predominant binding substrate, whereas in DRC sediments, with its lower concentration of Fe, alternate sinks for trace element deposition would be favored, e.g., organics.

In deep sediments Fe and Mn oxides are reduced, allowing them to migrate upwards, where they are oxidized and redeposited in surficial layers (Sundby et al., 1981; Gobeil et al., 1981). The fate of trace elements associated with these binding substrates is unclear. Given the strong correlations between Pb, Zn, Cu, and Cr, and Fe and Mn over depth in WMP sediments, it appears that these trace elements may migrate together. Cornwell (1986) observed similar metal behavior in Toolik Lake sediments. The author normalized elemental concentrations with respect to Al, to eliminate the effect of sediment dilution by Fe and Mn oxides. Thus, the observed correlations between trace elements and Fe and Mn were due to co-migration and not simply coprecipitation. Tsunogai et al. (1979) postulated co-migration of Co, Cu, Zn, Ni, Pb, and Ba with Mn in ocean sediments.

Often associated with Fe and Mn oxides is an organic layer which also competes with metal oxides for trace metal binding (Jenne, 1977). It is not fully understood whether oxide-associated organics migrate upwards with reduced Fe and Mn, including trace metals associated with the organic phase. In DRC sediments, organics may serve as an alternate binding substrate, given the lack of oxide-associated trace elements over depth. It is proposed that organically-bound trace elements do not migrate to the extent of oxide-associated elements. It is indeed likely that trace elements deposited in association with oxides of Fe and Mn may redistribute to alternate binding substrates (e.g., organics, carbonates, sulfides) in deep, reduced sediments, provided sufficient available binding sites are available on these alternate substrates. Also, pH and redox conditions must be conducive for binding sites on other substrates to be active. The complex chemical and biological interactions involved in sediment diagenesis has yet to be thoroughly understood.

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