

Chronological Variations in Concentrations of Heavy Metals in Sediments of the  
Tivoli South Bay: *A Study Using  $^{210}\text{Pb}$  Dating Methodology*

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## ABSTRACT

Heavy metals pose a threat to aquatic organisms and public health via food chain accumulation and direct drinking water contamination. There is little information about historic patterns of input to the Hudson River watershed, rate of loss through sediment burial, or the availability (via resuspension) of metals bound to surficial sediments. Studying the chronology of sediments is an ideal way to approach this issue, because historical information can be extracted once mixing has been taken into account. The research was conducted using  $^{210}\text{Pb}$  dating techniques to gather information on heavy metal pollutants (Pb, Cu, and Zn) in Tivoli South Bay of the Hudson River National Estuarine Reserve ecosystem with emphasis on their historical variations and residence time in surficial sediments. The most recent 20 years of sediments were dated to examine their pollution histories. A sedimentation rate range of 1-3 cm/yr was determined, with possible rapid accumulation during the time period. The concentrations of metals Pb, Cu and Zn were found to be well-correlated with each other in individual cores. This implies a common source for the three metals at these sites. The information provided by  $^{210}\text{Pb}$  dating is very useful in interpreting process such as soil erosion and suspended sediment loading in this area.

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## INTRODUCTION

Heavy metals are among the most toxic, ubiquitous, and persistent contaminants in freshwater systems. Despite recent promulgation of stricter controls, they remain among the most abundant hazardous materials released to the environment. In terms of sheer quantity, lead, for example, ranks fourth of 17 chemical targeted by the EPA for reduced release. But even if further heavy metal pollution were drastically curtailed, those that have been released to the environment and that are present in soils, sediments and other environmental components will continue to pose a threat, because they are not degraded to a harmless form by physical, chemical, or biological processes. Changing physical and geochemical conditions can cause their release from sediments, or their mobility in soil solutions and ground waters that supply streams and rivers. In particular, sediment resuspension coupled with reversible partitioning can lead to release of dissolved metals and availability to aquatic organisms (Benoit et al. 1993).

The heavy metals contained in sediments of estuarine ecosystems can be directly harmful to benthic aquatic organisms, and these impacts may eventually cause human health problems by food chain accumulation. Also, the remobilization of heavy metals in sediments can cause water quality problems. Therefore, the study of the behavior of heavy metals in sediments is important in terms of public health and aquatic ecosystem protection. Studying the history of heavy metals in sediments can provide a record to reveal baseline levels of pollution, to delineate pollution histories, and to explain their fate in terms of physical, chemical, and biological processes after they are disposed into waters (e.g., Bruland et al. 1974, Heit et al. 1981, Wang et al. 1986, Ridgway and Price 1987, McKee et al. 1989).

$^{210}\text{Pb}$  is the final long-lived daughter in the  $^{238}\text{U}$  decay series. Since the source function of this radionuclide is known or easily measurable, it can serve as a useful tracer of metal cycling in aquatic systems. Being radioactive ( $t_{1/2} = 22$  years), it can be used to provide time information, such as removal rates or ages. In particular,

$^{210}\text{Pb}$  has great utility in providing sedimentation rates and histories, and in supplying information about sediment mixing (e.g., Carpenter et al. 1985, Stordal et al. 1985). The distribution of  $^{210}\text{Pb}$  in sediment cores can be used as a geochronometer of recent sedimentation, and comparison with stable lead can elucidate its behavior in terms of inputs and outputs (Evans and Dillon 1982, Evans et al. 1986), scavenging to sediments, redox conditions (Benoit and Hemond 1990), transport processes, and the cycles of other elements (i.e., heavy metals and more abundant chemical components). The data will help to reconstruct the history of contaminant loading and elucidate their behavior in aquatic ecosystems.

The purpose of this study was to establish a time profile of sediment and associated metal pollutants deposited in Tivoli South Bay, the part of Hudson River National Estuarine Research Reserve, using the  $^{210}\text{Pb}$  dating technique. Since the Hudson River watershed is a crucial water resource, our results have implications concerning the presence of metal contaminants in drinking water, fish, and shellfish. Some preliminary research on the pollutants in Hudson River sediments (Peller and Bopp 1986; Stevenson 1986) have indicated that concentrations of trace metal have declined in recent years, but are still significantly above pre-industrial levels. Hudson River freshwater tidal marshes are excellent sites for determining the chronological deposition of certain pollutants. Although a few cores have already been examined in this way, the heterogeneity of this site suggested that more cores should be collected to evaluate spatial variability and to shed light on the extent to which general conclusions can be drawn.

Beyond confirming past research on the Tivoli South Bay, this study aims to derive the sedimentation accumulation rate and mixing processes at this site. Transport and deposition of suspended solids plays a key role in the cycling of environmental contaminants. It has a direct influence on biological communities (for example via turbidity) and reflects erosion rates on the watershed. All of these factors can contribute to suitability of the river ecosystem as a habitat for particular species.

Sediment resuspension can lead to remobilization of metals from bottom sediments to the water column, and consequent increase in bioavailability. This can occur through the process of metal desorption in the course of reversible solid-aqueous partitioning. Knowledge of heavy metal concentrations along with sediment accumulation and mixing rates can thus provide key information about potential hazards to aquatic organisms.

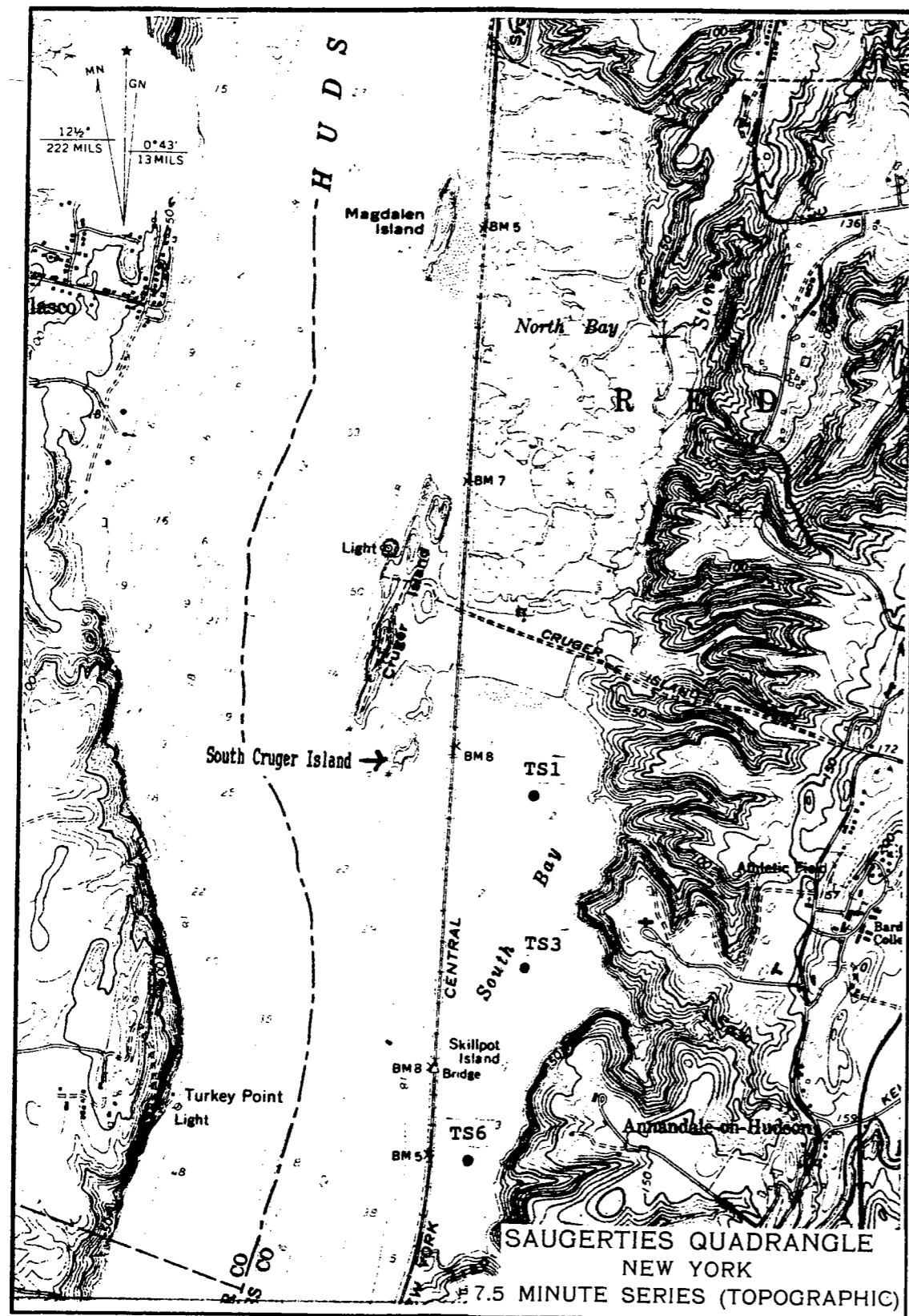
#### METHODS

In order to assign dates to the deposition intervals of the sediment samples, the sedimentation of study sites should have been continuous and only systematic disturbances of the sediment should have occurred (e.g., bioturbation). Thus, sampling was conducted in a relatively undisturbed area of Tivoli South Bay (Figure 1).

A total of six hand-driven cores were collected at three locations in Tivoli South Bay on August 5, 1992. Two cores were taken at each site by a SCUBA diver using plastic core tubes. The collected cores were sectioned immediately at 1 cm intervals to a depth of 5 cm, every 2 cm from 5 to 15 cm, and every 3 cm thereafter. The outside of each section of the cores was removed to prevent possible artifacts due to mixing during coring.

Sediments were dried, ground, and completely dissolved by strong acids in sealed Teflon microwave vessels. In the digestion procedure, 0.50 g of sediment was digested in 10 ml of a 50:50 mixture of  $\text{HNO}_3$  and HF. Pressure reached approximately 800 psi and temperature was about 250 °C for the 2-minute digestions. Aliquots of the digest were then analyzed for Cu, Zn, and Pb by flame atomic absorption spectrophotometry (AAS). The radionuclide  $^{210}\text{Pb}$  was measured via its daughter  $^{210}\text{Po}$  by alpha spectrometry after self-deposition on silver planchets following a room-temperature procedure developed by Benoit and Hemond (1988). In the low-temperature plating procedure,  $^{208}\text{Po}$  yield monitor is added and the sediments completely dissolved by microwave-digestion. The resulting solution is then converted

Figure 1. Study Area: Tivoli Bays, Hudson River



from the  $\text{HNO}_3/\text{HF}$  to  $\text{HCl}$  form in sequential evaporation steps. The residual material is transferred to a 125-ml, large-mouthed polyethylene jar using two 5-ml portions of concentrated  $\text{HCl}$ . To this are added 5 ml of 20% hydroxylamine hydrochloride and 2 ml of 25% sodium citrate, and the pH adjusted to between 1.0 and 2.0 with concentrated ammonium hydroxide. One surface of a silver disk is polished, the other surface coated with electrical tape, and the jar sealed and stored inverted for 7-10 days. The plated silver disks then are counted for their  $^{210}\text{Po}$  by alpha spectrometry.

In addition to six cores collected for this project, two cores (CN2133 TSC and CN2131 TSA) taken by Prof. Richard Bopp on May 13, 1992 in Tivoli South Bay were also analyzed for metal distributions. Locations of cores TS1-6 are indicated in Figure 1, while TSA and TSC were collected along a transect line running east-west in South Tivoli Bay.

## RESULTS AND DISCUSSION

### Metal Distributions in Sediments

High data quality is indicated by the smooth depth distributions and correlations between the various metals. In addition, standard reference sediment was measured in parallel with the sample sediments to test for total recovery. Both Pb and Cu were recovered quantitatively, while Zn recovery was consistently low compared to the certified value. Possible explanations are that Zn was lost during digestion (unlikely in the sealed vessel), that there was a negative interference during the analysis, or that the certified value was in error. The last possibility cannot be ruled out, since our method (microwave digestion in sealed bombs) is an improvement over methods used to establish the certification. In any event, we believe that the difference was consistent and reproducible, since all three metals showed good correlations relative to each other. Nevertheless, it is possible that our Zn data are biased low. They should thus be considered a lower limit to Zn levels in these sediments.

Pairs of cores TS1/TS2, TS3/TS4, and TS5/TS6 were taken from northern, middle and southern parts of the Tivoli South Bay (see Figure 1), respectively. Of these, cores TS2, TS4, and TS5 were considered to be back-ups or duplicates of TS1, TS3, and TS6, respectively. Core TS2 contained numbers of water chestnut seeds below 15 cm that made it unsuitable for comparison below that depth. Comparison of the distributions of Pb, Cu and Zn at sites TS1, TS3, TS6, TSA and TSC reveals important both similar patterns and significant differences. In TS1, the concentrations of all the three metals increases from the surface and reach their highest values at depth 13-15 cm (Figure 2). In TS3, there is little change in the concentrations of the three metals in the core profiles. A small peak can be found between 13-15 cm for the three metals (Figure 3). In TS6, except lead, metals are almost evenly distributed in the core profile (Figure 4). In TSA (Figure 5), the concentrations of the metals are constant or decrease slightly from the surface to about 18 cm. Below 16-20 cm the concentrations decrease dramatically, then level off below 40 cm. In TSC (Figure 6), the concentrations of all three metals have minima near 8-12 cm and maxima at a depth of about 30 cm.

In general, we see great variations of metal distribution patterns among the cores in different locations. Also the absolute concentration values of the metals are different in these cores. For instance, comparison of north, middle, and south metal distributions show that TS1 has higher levels of all three metals compared to TS3 and TS6 (Figure 7). Notably, at the same site, duplicate cores gave similar patterns, but were not identical. (Duplicates were collected approximately 2 m apart.) Thus, some variability exists even on a scale of a few meters. The differing metal concentration distribution patterns from site to site indicates that the Tivoli South Bay has very heterogeneous sedimentation rates despite its small size. Mixing of sediments may also exist in certain areas of the bay.

However, while the metal distributions vary from core to core at different sites, they are very similar for all the three metals for an individual core. This

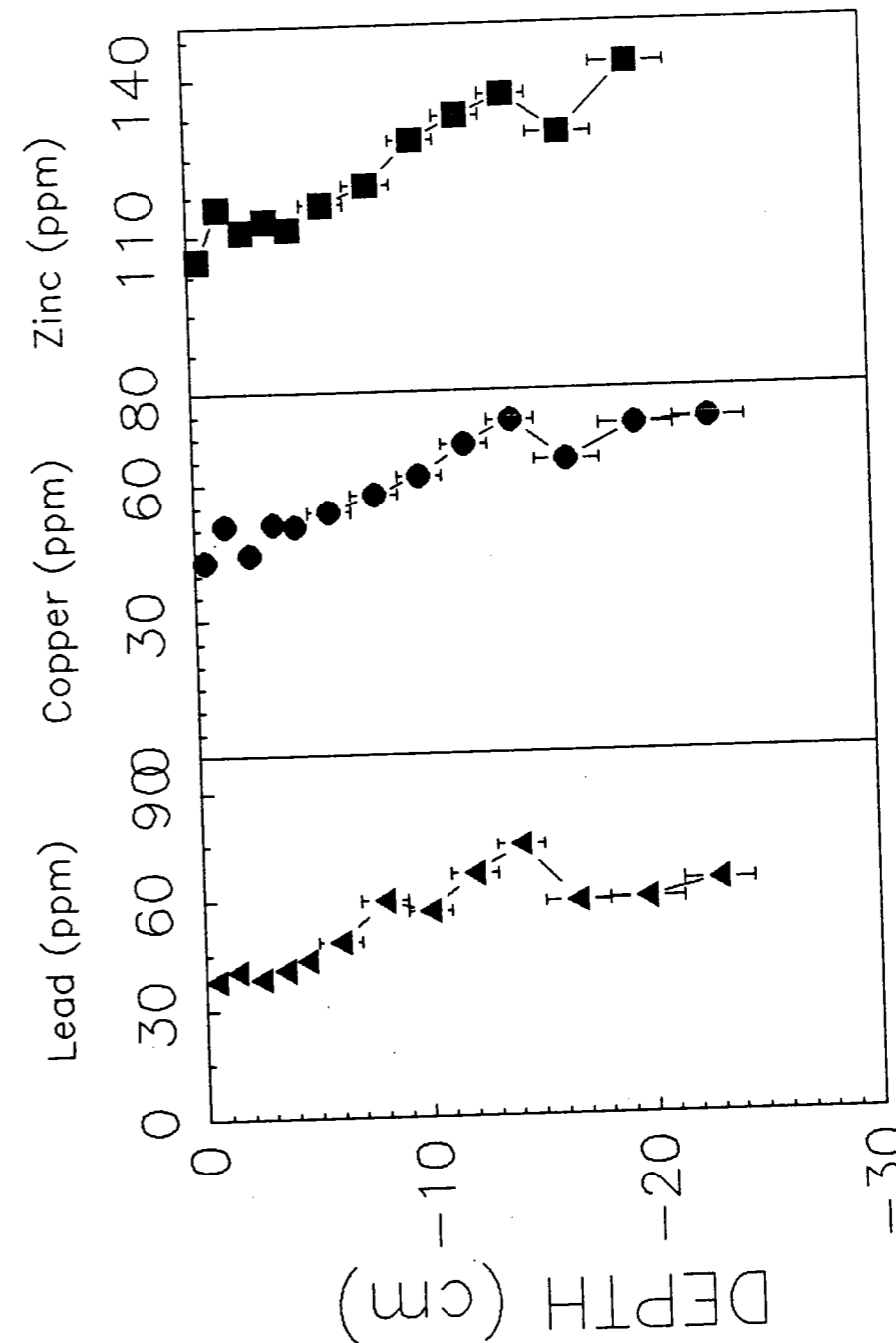


Figure 2. The distributions of Pb, Cu and Zn in TS1

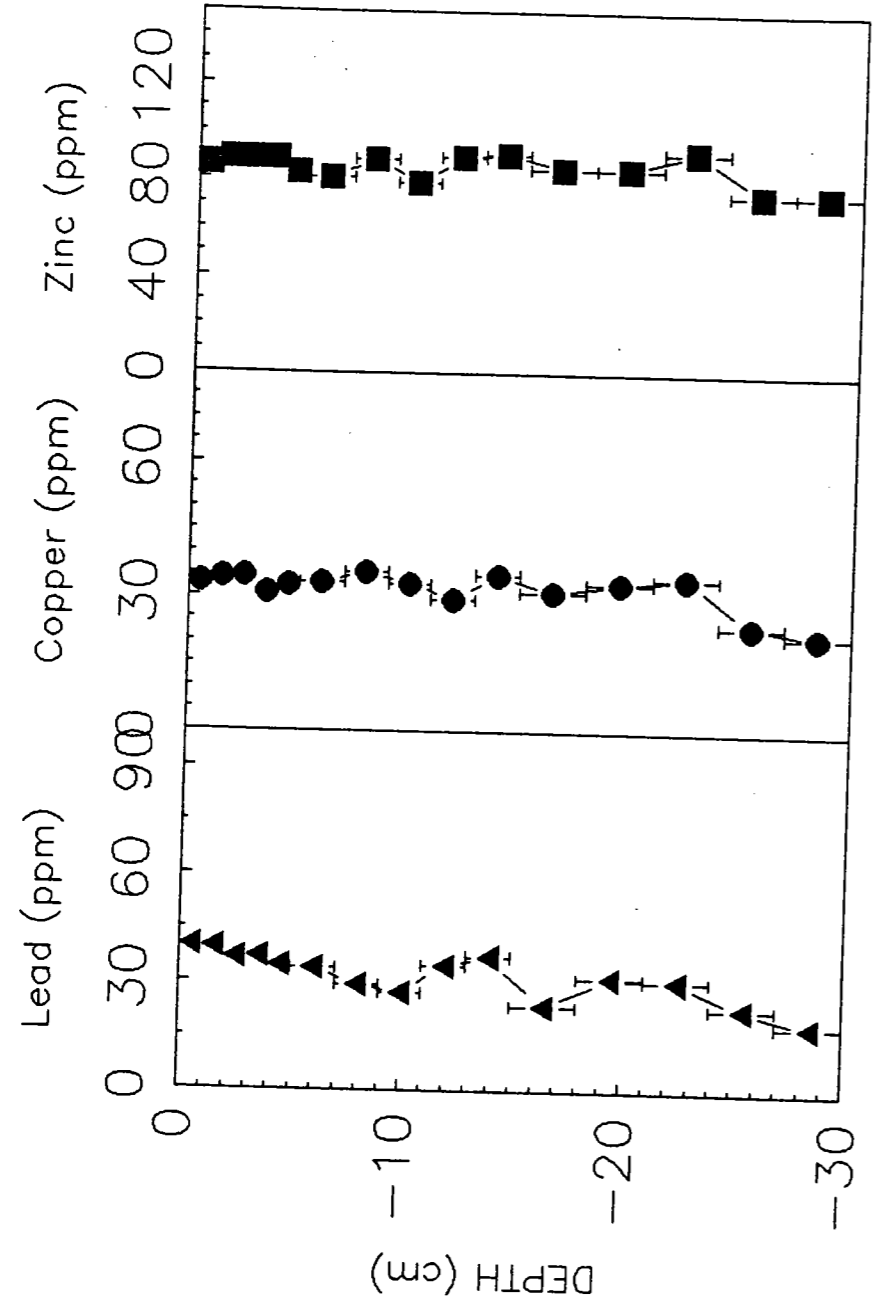


Figure 3. The distributions of Pb, Cu and Zn in TS3

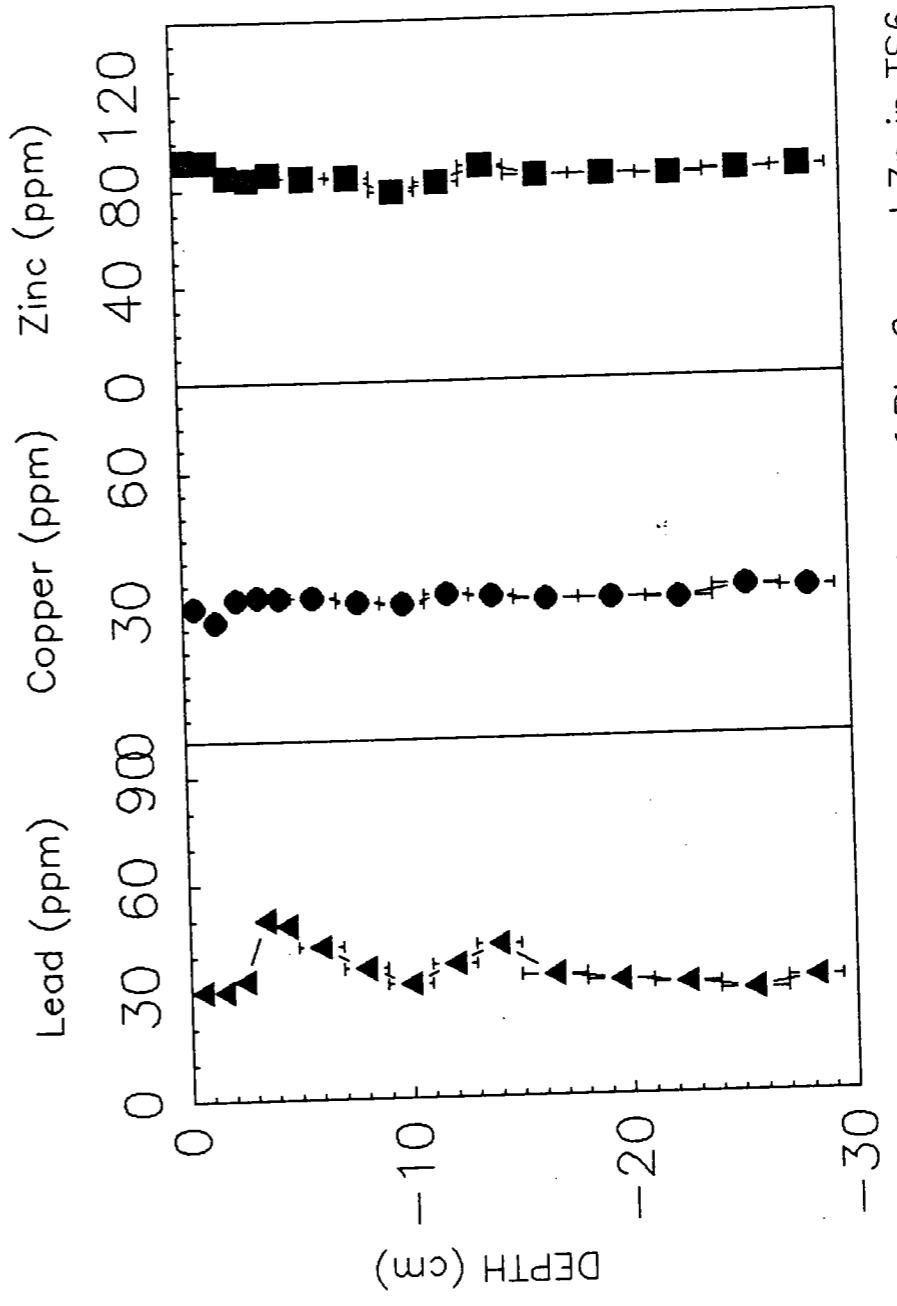


Figure 4. The distributions of Pb, Cu and Zn in TS6

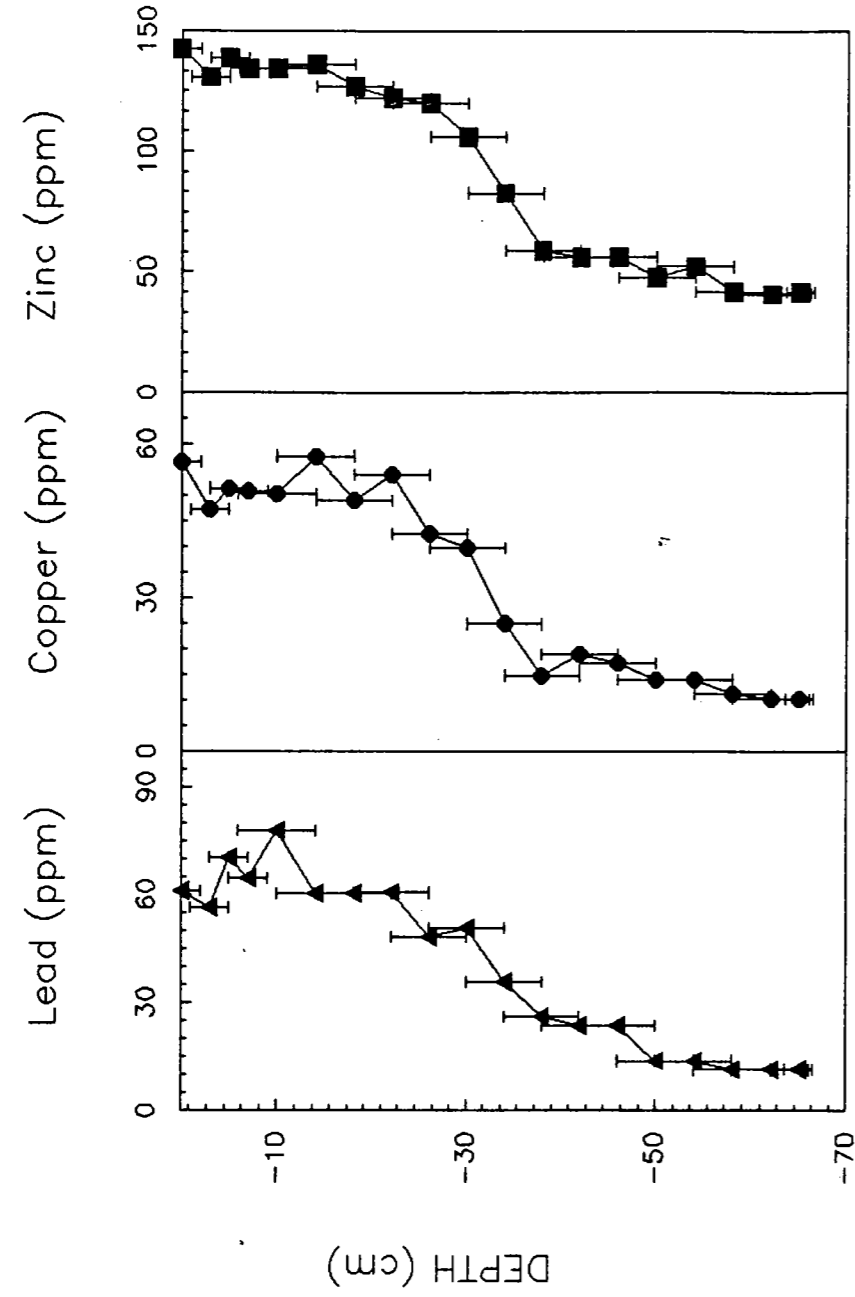


Figure 5. The distributions of Pb, Cu and Zn in TSA

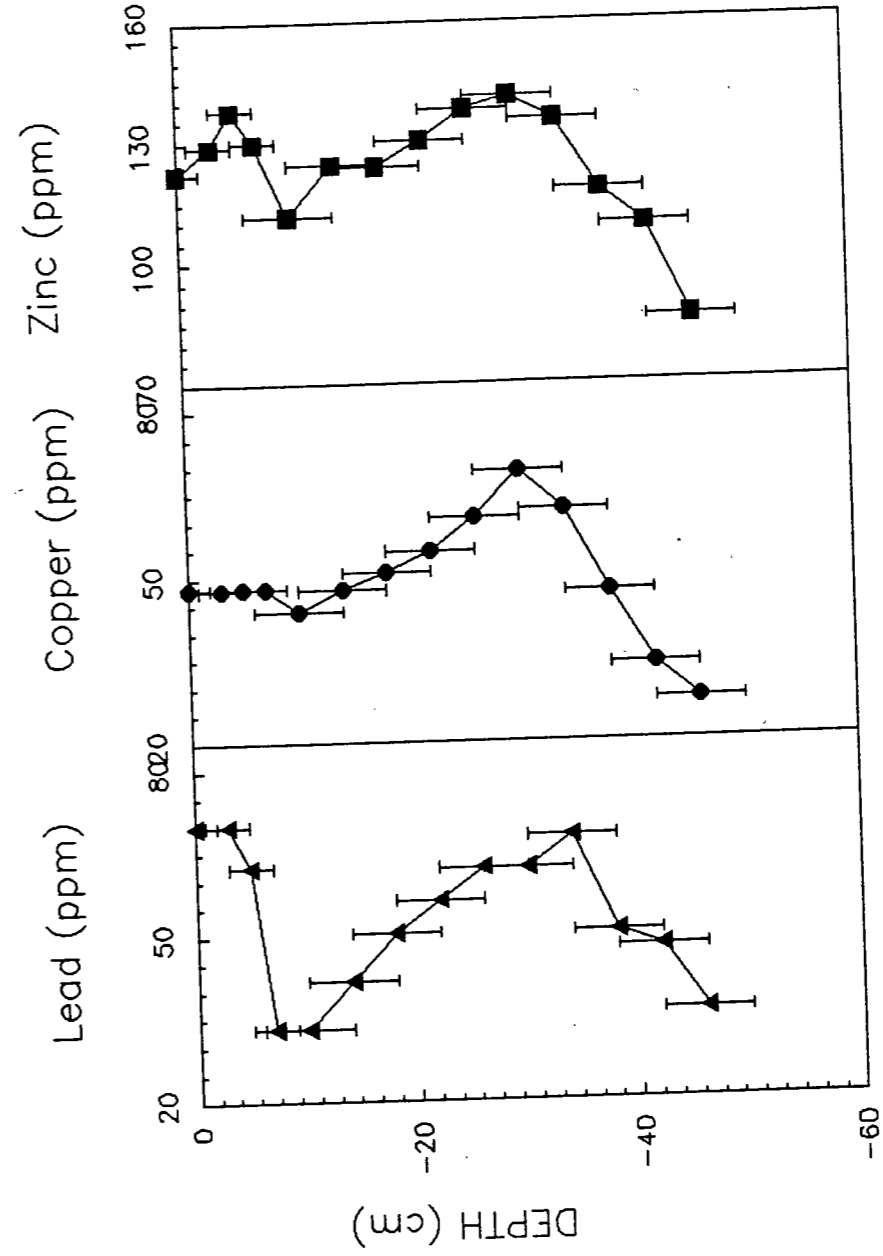


Figure 6. The distributions of Pb, Cu and Zn in TSC

phenomenon is true for all the cores (Figures 2 to 8) including TSA and TSC. To quantify and confirm this observation, we computed the correlations between Pb, Cu and Zn for each core. The result is shown in table 1 below:

Table 1. The Pearson correlation coefficients between Pb, Cu and Zn						
	TS1 Pb	Cu	Zn	TS2 Pb	Cu	Zn
Pb	1.00			1.00		
Cu	0.93	1.00		0.966	1.00	
Zn	0.827	0.978	1.00	0.915	0.996	1.00
	TS3 Pb	Cu	Zn	TS4 Pb	Cu	Zn
Pb	1.00			1.00		
Cu	0.683	1.00		0.941	1.00	
Zn	0.710	0.742	1.00	0.772	0.859	1.00
	TS5 Pb	Cu	Zn	TS6 Pb	Cu	Zn
Pb	1.00			1.00		
Cu	0.386	1.00		0.415	1.00	
Zn	0.442	0.745	1.00	-0.399	-0.067	1.00
	TSA Pb	Cu	Zn	TSC Pb	Cu	Zn
Pb	1.00			1.00		
Cu	0.965	1.00		0.562	1.00	
Zn	0.976	0.988	1.00	0.603	0.885	1.00

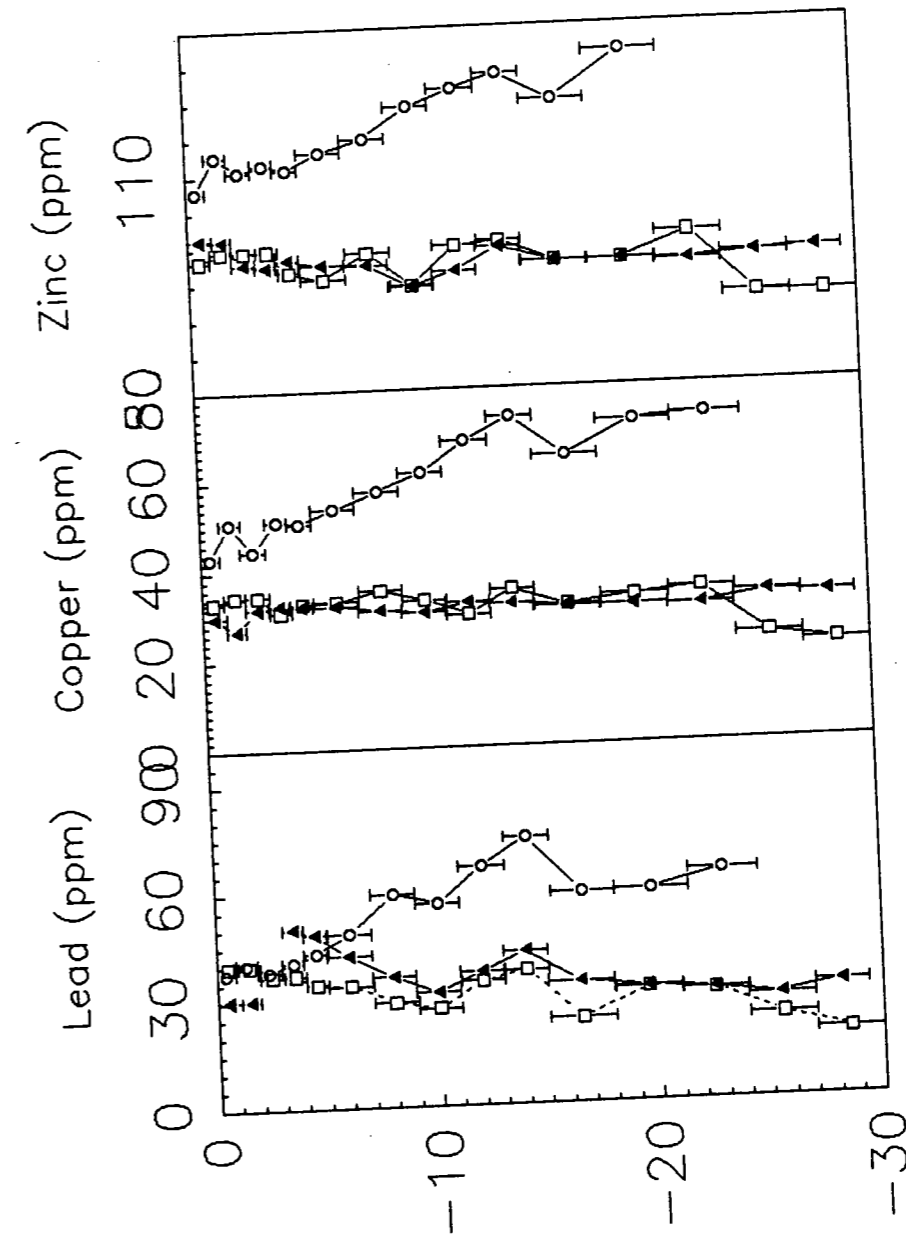


Figure 7. The comparisons of metal distributions in TS1, TS3 and TS6 (circle: TS1, square: TS3 and triangle: TS6)

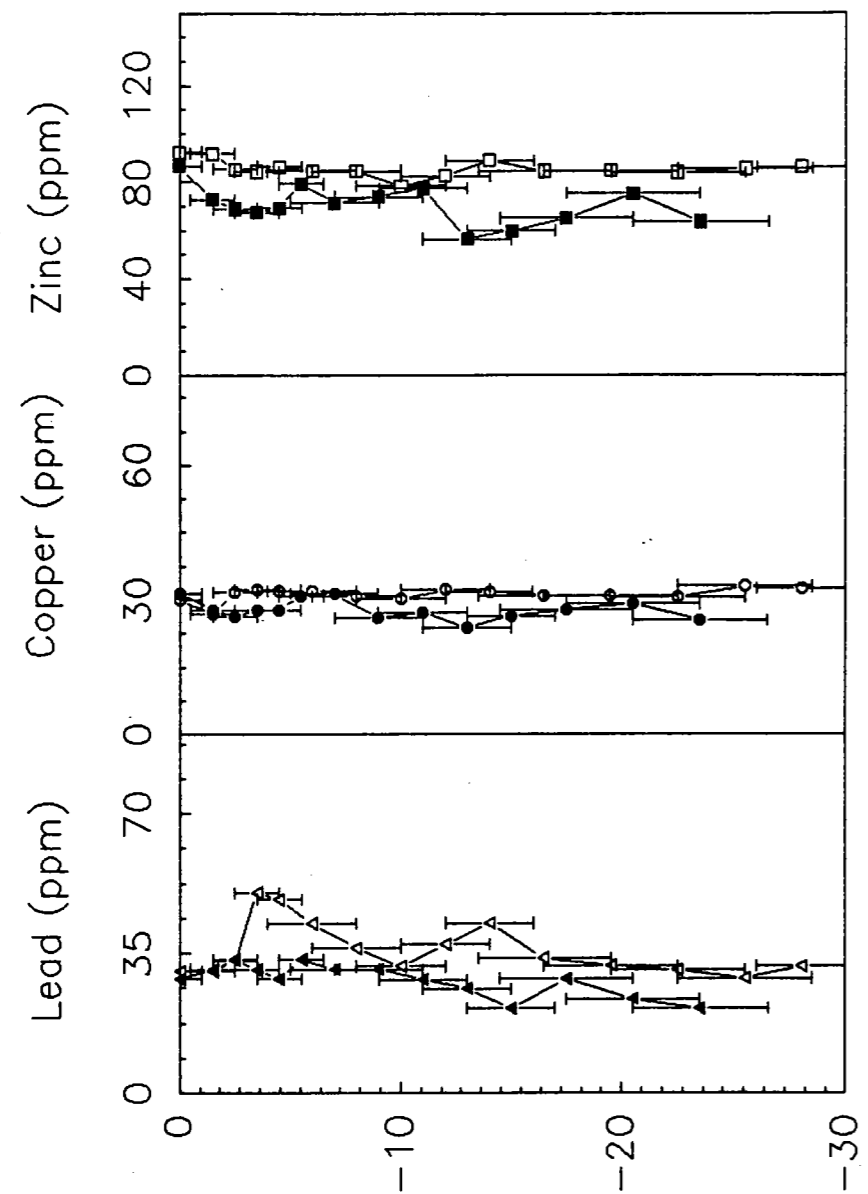


Figure 8. The comparisons of metal distributions in TS5 and TS6 (open symbol: TS6 and filled symbol: TS5)

The three metals are well-correlated in each core except TS6. In TS6, the range of concentrations was so limited that the small amount of noise in the data was as great as the true variability. The correlation between metals implies that they are supplied by a common source. Historically, lead has come mostly from atmospheric deposition of anti-knock compounds in gasoline (Murozumi et al. 1969; Ng and Patterson, 1981; Schaule and Patterson, 1981). Copper and zinc, however, are derived either from pollution discharges or natural sources in soils, and are transported via streams and rivers. Based on our finding in this research, a model of the metal transportation in the Southern Tivoli Bay can be formulated as shown in Figure 9.

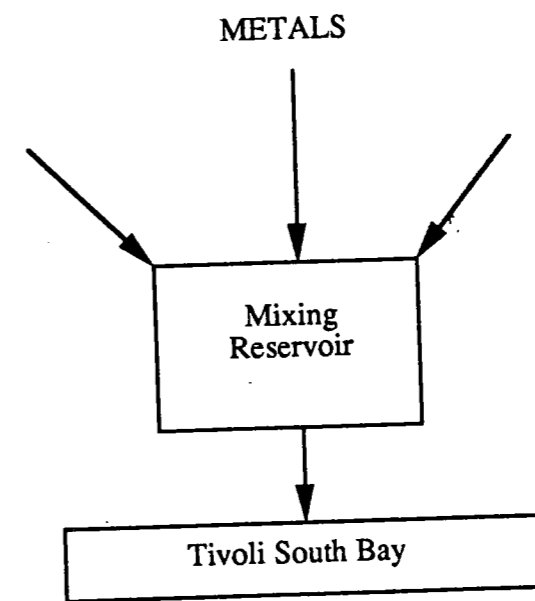


Figure 9. The path of metals transported into the sediments of the Tivoli South Bay

Rather than being incorporated directly into the bay from their original sources, the metals are mixed in a reservoir before they are delivered to the sediments of the bay. The reservoir could not be the bay water itself, since the residence time is much too short compared to the time scale of input processes. A more likely reservoir is watershed soils. If so, our results suggest that metal residence time in the soils is long compared to processes that would cause changes in the metal ratios, such as

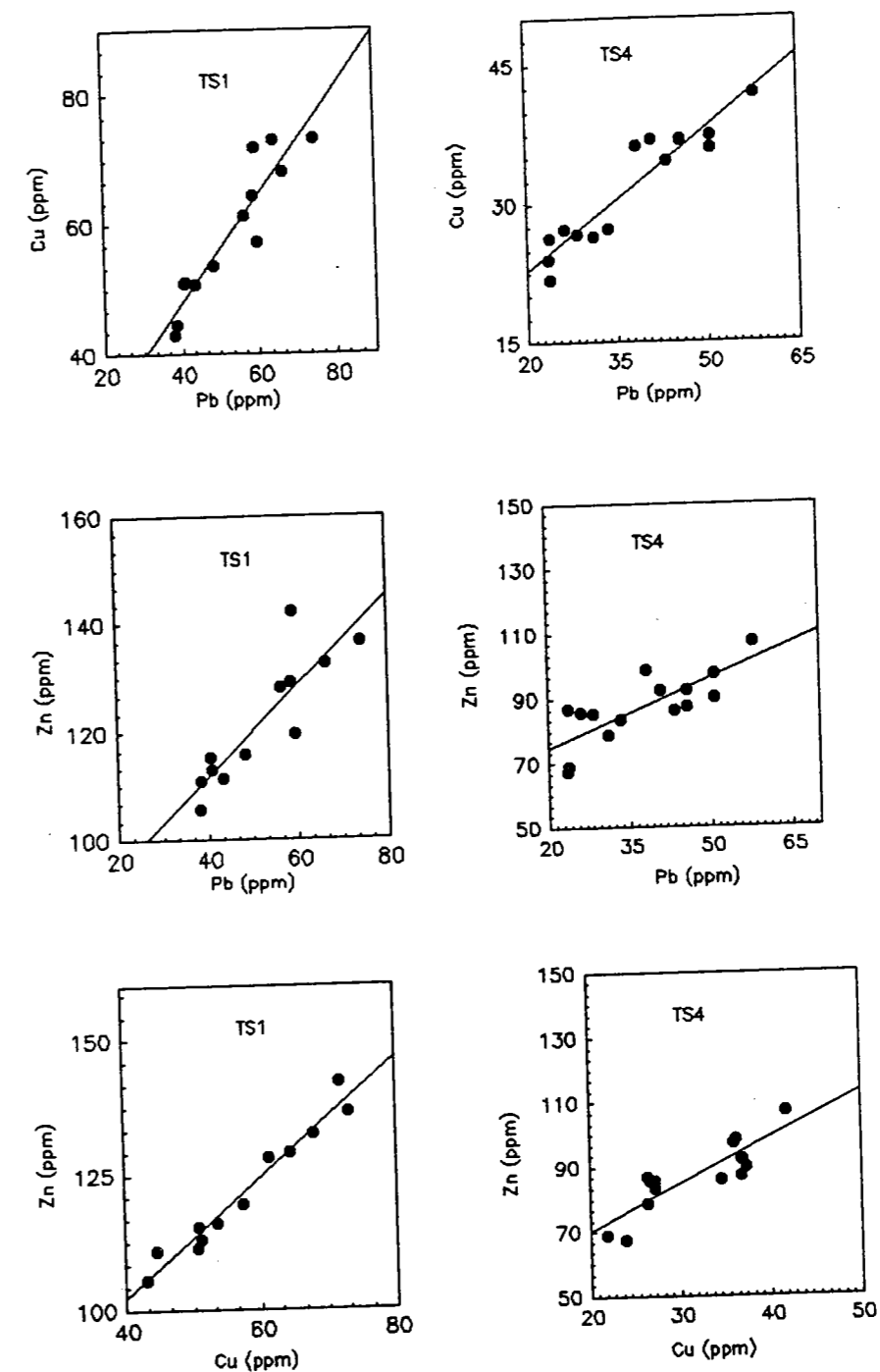
changes in the amount of lead burned in gasoline. In other words, the metals mix in soils over a period of time longer than decades. The soils thus buffer any short term signal imposed on it by the atmosphere, such as the measured change in Pb deposition over the past few decades. In addition, it is clear that a non-point source is indicated.

Another issue concerns the differences in absolute concentrations of the metals from north to south. The level of all three metals in TS1 is significantly greater than in TS3, TS4, TS5, and TS6. One possible explanation is that sediments in the north have a greater amount of fine-grained sediments, which are known to preferentially sequester metals. Another, is that the sediments at the two more southern sites come from different sources, such as the Saw Kill versus tidal exchange with the main stem of the Hudson River. To test these two alternatives, we took advantage of the correlation of the three metals with each other at each site. The ratio is consistent and highly significant (Figure 10). TS1 is compared to TS4 since these had the greatest range of metal concentrations and the most statistically significant correlations, i.e., they represent the "best" data with the smallest uncertainties. For all three possible permutations (Pb:Cu, Pb:Zn, and Cu:Zn), the metal ratios were significantly different at the two sites. This further evidence supports the hypothesis that the sedimentary metals at the various sites are derived from different sources rather than the result of a particle size effect acting to differentiate a uniform source. Furthermore, physical characteristics (porosity, bulk density, solids density) of the various cores are similar. Analysis also shows that TS1, TS3 and TS6 have similar particle size distributions (Table 2).

Table 2. Distributions of particle size for sediments in TS1, TS3 and TS6

	TS1	TS3	TS6
Sand	19%	11%	12%
Silt and Clay	81%	89%	88%

Figure 10. The correlations of metal concentrations in TS1 and TS4



A key conclusion is that even in a small system like Tivoli South Bay, it appears that geomorphical variations have caused heterogeneous sedimentation on both short and longer scale lengths (meters to hundreds of meters). The alternate effects of estuarine tidal exchanges and stream flows leave their mark on the bay sediments. The complex sedimentation leads to highly varied metal concentrations and distributions in the sediments.

### Sediment Chronology

Sedimentation in small lakes, in contrast to that in large lakes and estuaries, is extremely sensitive to events occurring within the water system. In large lake systems, constant rates of sediment accumulation are assumed. In small lakes the sediment accumulation rate and the sediment sources can be expected to change more rapidly and more markedly than in larger systems. Nevertheless, many researchers have been able to unravel the complex sedimentation history (e.g., Brugam 1975, Linsley Pond, Connecticut, and Von Damm et al. 1979, Mirror Lake, New Hampshire). In our analysis we have used the Constant Initial Concentration model (Krishnaswamy et al. 1971).

In this research, three primary cores (TS1, TS3 and TS6) have been dated. In order to avoid the problems caused by compaction of the sediment through time (Robbins 1978), depth of the cores is expressed as cumulative dry mass. Also, we assume that supported  $^{210}\text{Pb}$  (detrital  $^{210}\text{Pb}$  supported by  $^{226}\text{Ra}$  in sediments) is constant or relatively low in sediment profiles, so that measured total  $^{210}\text{Pb}$  activity is nearly used to construct chronology of sediments as unsupported  $^{210}\text{Pb}$  (excess  $^{210}\text{Pb}$  from atmospheric deposition). In general, ignoring supported  $^{210}\text{Pb}$  activity causes sedimentation rate estimates to appear lower than they actually are, though the effect should be slight.

Overall, the  $^{210}\text{Pb}$  distributions reveal complex depositional patterns marked

by: 1) periods of steady deposition, 2) periodic changes in sedimentation rate, and 3) possible sediment reworking. In TS1 (Figure 11), the core can be divided into two distinct segments. The segment 0 to 5 g/cm<sup>2</sup> (0 - 7 cm) shows a relatively rapid decrease in  $^{210}\text{Pb}$  with depth. A single line through the top six data points yields a sediment accumulation rate of 0.8 cm/yr. In the depth interval 5-16 g/cm<sup>2</sup> (7 - 24 cm), the decrease in  $^{210}\text{Pb}$  shows a sediment accumulative rate of 2.0 cm/yr. The lack of a significant offset between the two straight line segments is indirect evidence that the change was not due to a change in mixing, i.e., that it reflects a real change in sediment accumulation processes. Calculated dates assigned to this core are included in Figure 11 and should be considered approximate. The total amount of  $^{210}\text{Pb}$  present in this core is 41.9 dpm/cm<sup>2</sup> which requires an extrapolated flux near 4.2 dpm/cm<sup>2</sup>.yr to this site in the bay. This value is considerably larger than the expected atmospheric flux of about 1 dpm/cm<sup>2</sup>.yr for the northeastern U.S. (Turekian et al. 1977). The implication is that  $^{210}\text{Pb}$  or sediment carrying  $^{210}\text{Pb}$  is preferentially accumulated to this site either from stream inputs or from other locations in the bay basin. Direct atmospheric deposition alone cannot account for the entire inventory.

TS3 (Figure 12) shows a relative steady rate of sediment accumulation near 3.0 cm/yr, although the scatter in the data is relatively large. Considering that one year of sedimentation is sampled by three separate core sections, some of the variability may actually reflect annual or even seasonal changes in  $^{210}\text{Pb}$  deposition. Truly, the variability between sections seems to be regular and periodic. The whole core represents deposition since 1985. The total amount of  $^{210}\text{Pb}$  in this core is 46.8 dpm/cm<sup>2</sup>, indicating an annual flux near 7.4 dpm/yr at this site.

TS6 (Figure 13) does not display a log-linear decrease of  $^{210}\text{Pb}$  with depth. This implies some possible mixing processes occurred during the sedimentation or changing  $^{210}\text{Pb}$  input. The latter explanation seems unlikely, considering the well-behaved profiles observed for the other two cores. Notably, TS6 had the most uniform distribution of stable trace metals (Figure 4), consistent with a mixing

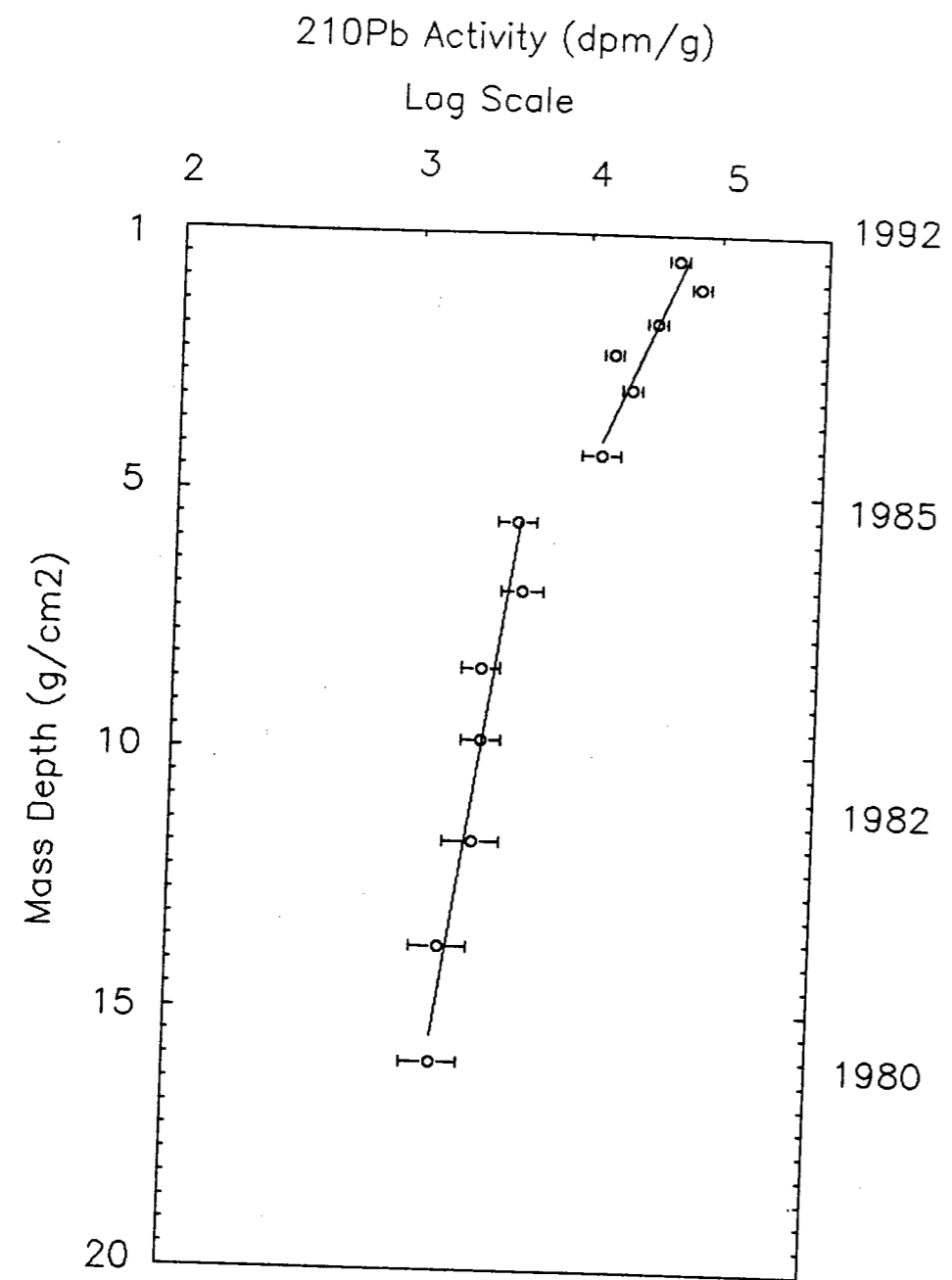


Figure 11. Activity of 210Pb versus depth in TS1

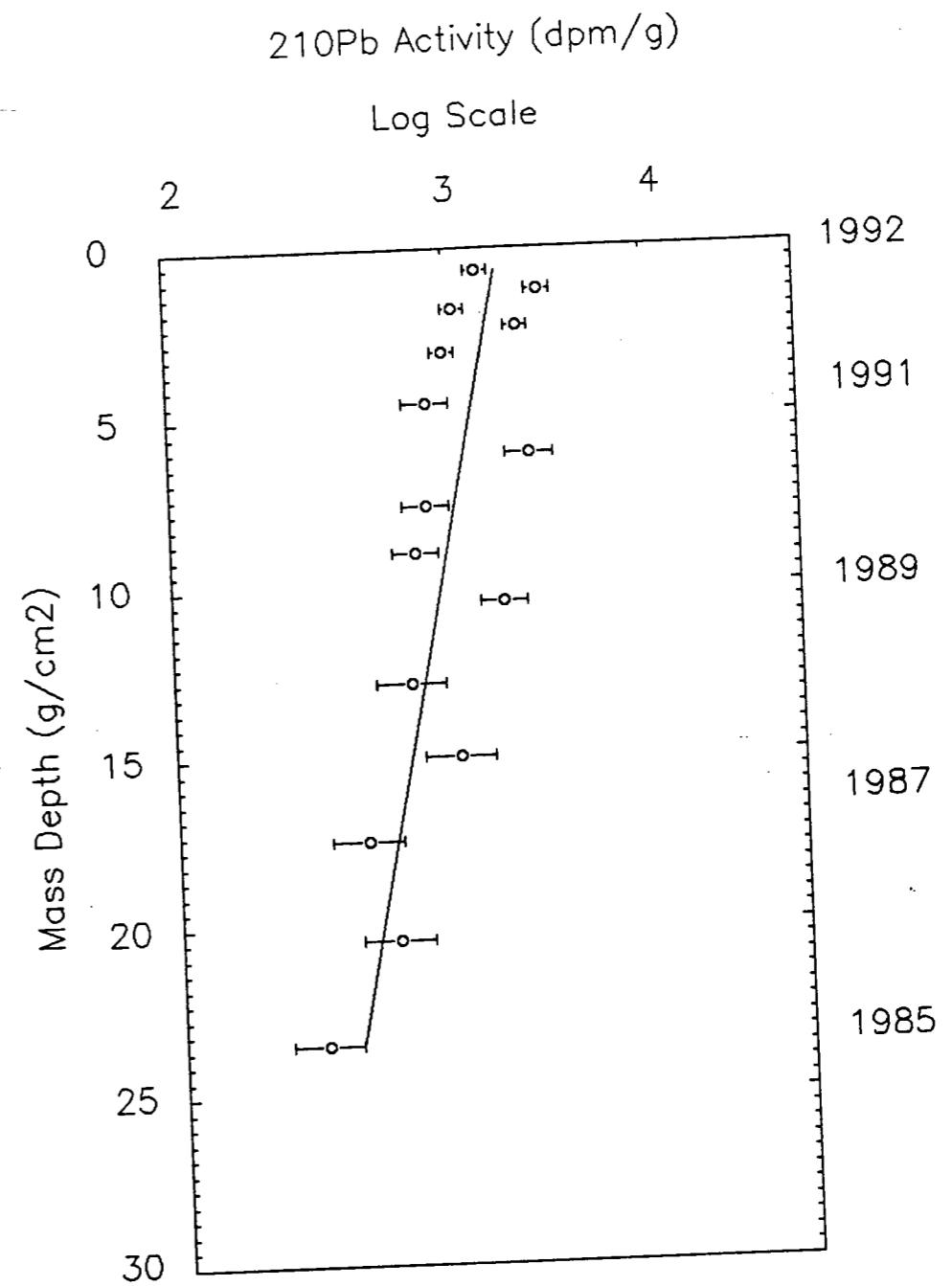


Figure 12. Activity of 210Pb versus depth in TS3

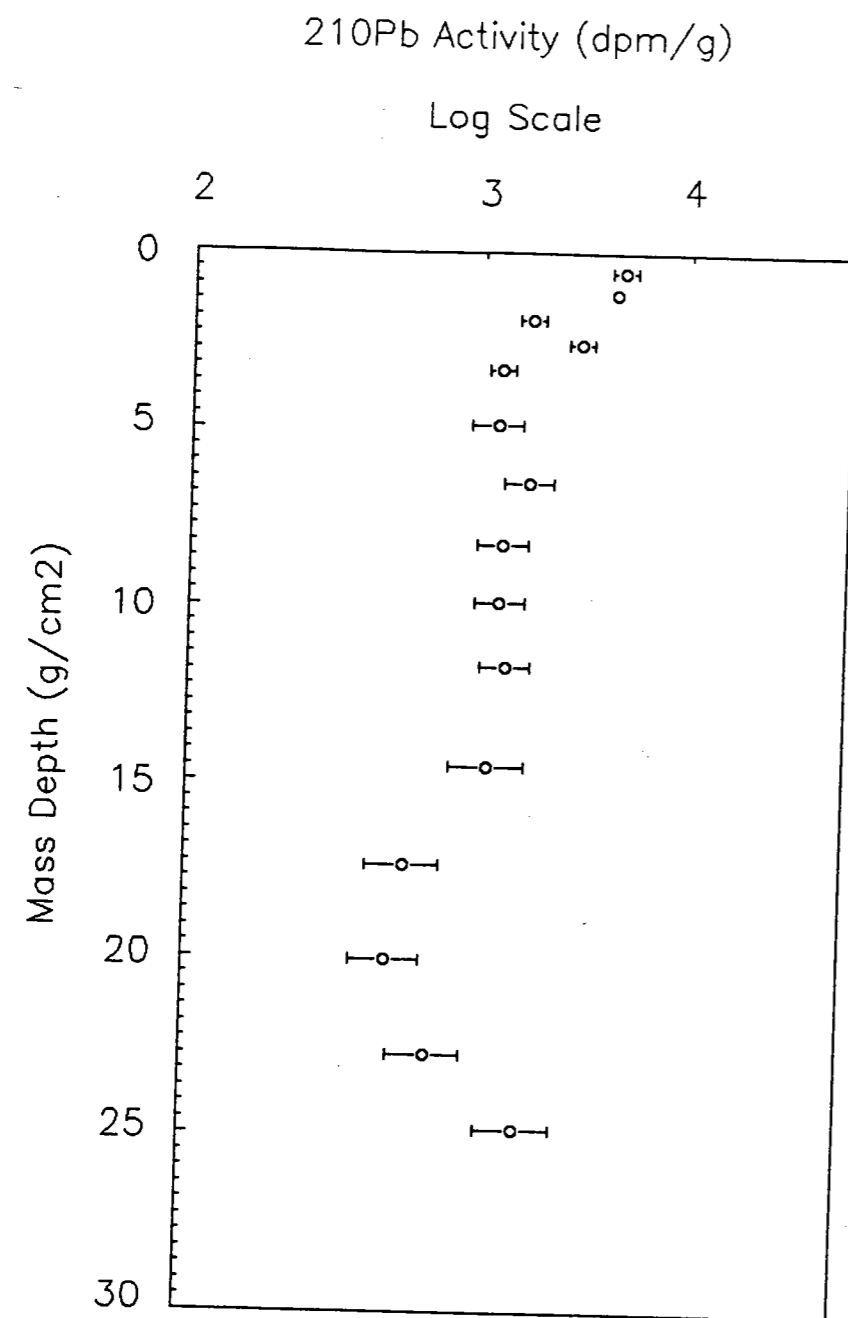


Figure 13. Activity of 210Pb versus depth in TS6

hypothesis. All of this information suggests that mixing processes have obscured the chronological information retained in sediments. Therefore, it is inappropriate to assign dates to this core on the basis of <sup>210</sup>Pb data. To the extent that mixing is active at the other sites, <sup>210</sup>Pb will be transported downward more rapidly than in unmixed sediments, and the quoted sediment accumulation rates are upper limits to the true values.

The dissimilar log-linear relationships between <sup>210</sup>Pb activity and depth for the three different cores is further evidence of heterogeneous sedimentation processes within Tivoli South Bay. The sediment accumulation rates vary with locations.

#### CONCLUSIONS

Several important conclusions can be drawn from this study:

- 1) Pb, Cu and Zn are closely correlated with each other in individual cores. This implies a common source for the three metals at any site. Since lead is expected to have come from leaded fuel, and to be unrelated to copper and zinc, their correlation suggests that they are mixed in some reservoir, such as soils, before delivery to the bay. This also suggests that the metals come from a non-point source.
- 2) Sedimentation is probably not by simple steady state deposition alone. Sedimentation rates change dramatically, and mixing processes exist. It is likely that sediments were scoured and filled in some places.
- 3) Sedimentation rates are in the range from 1-3 cm/yr. This is an upper limit if profiles have been subject to particle reworking processes.
- 4) Within channels, deposition processes are fairly consistent over a short distance. In shallows, no duplicate cores exist to test this hypothesis.
- 5) There is significant variability on a distance scale of 10's to 100's of meters, both in channels and on the flats. The core variability that we found in our research is real because data quality is high.
- 6) Based on absolute concentrations and metal-to-metal ratios, Pb, Cu, and Zn are

derived from different sources in the northern and southern parts of Tivoli South Bay. One possibility is that the two sources are tidal exchange with the Hudson and inflow from the Saw Kill.

7) Even for a small bay like the Tivoli South Bay, the construction of a  $^{210}\text{Pb}$  chronology based on a very limited number of measurements may lead to false interpretation if we do not consider the heterogeneity of sediment accumulation and possible mixing.

#### RECOMMENDATIONS

To better evaluate the the sedimentation rates and pollutant load for the whole bay, more cores should be systematically collected taking into account the geomorphical variations in Tivoli South Bay. The mixing process should be studied by examining a variety of radionuclides, e.g.,  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$ . For the coring technique, effort should be made to get deeper cores for the calculating of unsupported  $^{210}\text{Pb}$  and to avoid possible mixing and contamination during collecting. Information about pollutant discharge, soil erosion and hydrology of watersheds should be gathered to explain the chronological data obtained from  $^{210}\text{Pb}$  dating.

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