HEAVY METAL INPUTS TO MISSISSIPPI DELTA SEDIMENTS

A Historical View

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Abstract. Heavy metal concentrations were determined in suspended particulates, filtered water and sediment collected in the Mississippi River and from its marine delta. More than 90% of the metal load of the river is associated with particulate matter, which is relatively constant in chemical composition with time and place. The Mississippi River suspended material is similar to average crystal rocks in Fe, Al, V, Cr, Cu, Co, Mn, and Ni concentration but is generally enriched in Zn, Cd and Pb. Sediment cores dated by the Pb-210 method show that the Cd and Pb enrichments are recent phenomenon and are most likely due to the activities of man. About 6000 tonne of Pb and 300 tonne of Cd are being added to the delta sediments by man each year, more than 30 times the amount added to the Southern California Bight.

River particulate matter is essentially identical to deltaic sediments in Al, Fe, Cr, V, Cd and Pb concentration, but the sediments are depleted in Co, Cu, Mn, Ni and Zn by 20 to 40%. Chemical leaching of the solids show the metal losses to be primarily from the oxide phase, suggesting diagenetic reduction and mobilization as a mechanism.

Trace metal concentrations in filtered Mississippi River water were below the limits for safe drinking water and were similar to world average river values. The abundant river suspended matter and high pH combine to keep dissolved trace metal concentrations low.

1. Introduction

Rivers are the major pathway by which both the products of natural geological processes and the pollutants of man reach the sea. Garrels and Mackenzie (1971) estimate that rivers carry 90% of the total seaward transport of dissolved and suspended solids. The major United States river, the Mississippi, drains more than 40% of the coterminous U.S., including numerous municipalities and scores of industrial facilities. Its drainage basin stretches from New York to Montana and from Canada to the Gulf of Mexico (Figure 1). The river carries about 60% of the total dissolved solids (Leifeste, 1974) and 66% of the total suspended solids (Curtis *et al.*, 1973) transported to the oceans from the continental United States. The massive sediment input of the river (280 Mtonne yr^{-1}) has built a series of deltaic complexes over the past 6000 yr (Fisk *et al.*, 1954; Coleman and Gagliano, 1964) culminating in the modern birdfoot (or Balize) delta, an 1800 km^2 platform on which 113 km^3 of sediment has been deposited since the early 1500s (Fisk *et al.*, 1954).
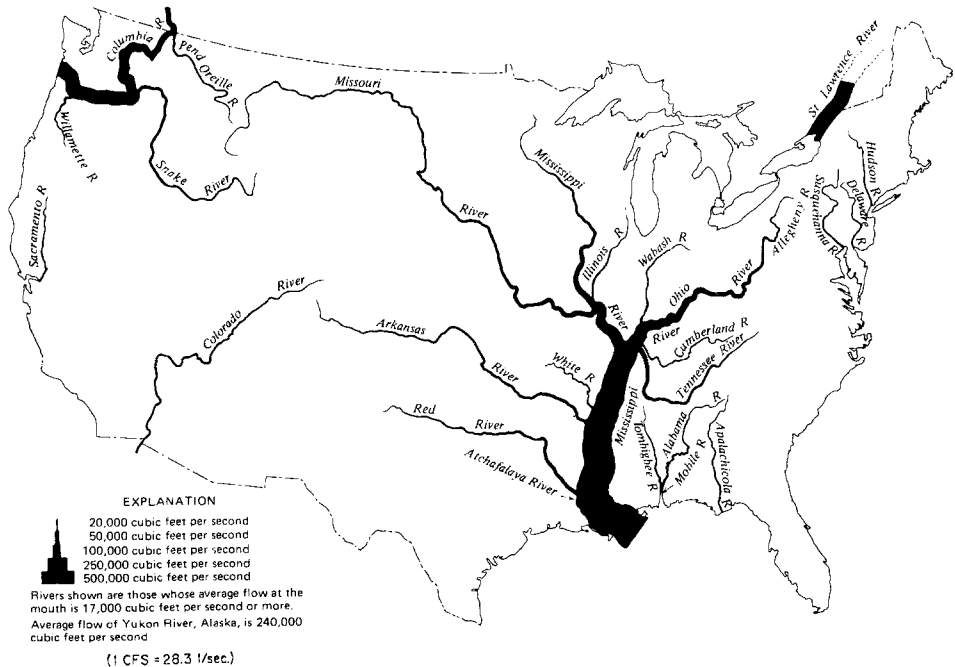
EXPLANATION

20,000 cubic feet per second
50,000 cubic feet per second
100,000 cubic feet per second
250,000 cubic feet per second
500,000 cubic feet per second

Rivers shown are those whose average flow at the
mouth is 17,000 cubic feet per second or more.
Average flow of Yukon River, Alaska, is 240,000
cubic feet per second

(1 CFS = 28.3 l/sec.)

Fig. 1.   Relative sizes of major rivers in the United States. Note the size and extensive drainage area of the
Mississippi River System (from Iseri and Langbein, 1974).

Estimates of industrial, municipal and agricultural waste inputs to the Mississippi
River (Everett, 1971) suggest that the river pollutant load is large and diverse. Organic
contaminants have been cited as troublesome since the 1950s fish kills from the
insecticides endrin and heptachlor (Louisiana Wildlife and Fisheries Commission, 1958–
1959). Recent data show that river phenol concentrations frequently exceed public water
supply criteria (U.S. Army Corps of Engineers, 1975) and that the river has a significant
anthropogenic burden of light hydrocarbons (Brooks, 1976) and phthalic acid esters,
DDT, and PCB's (Giam *et al.,* 1976). Added to this load is the domestic sewage from
almost 2 million people in the lower Mississippi area alone. Because many of the
organics use oxygen as they degrade in the river, a progressive decrease in dissolved
oxygen has been measured downstream from Baton Rouge to the Gulf (Everett, 1971).

   In addition to organic substances, an estimated 18 million kilograms of inorganic
wastes are discharged into the lower Mississippi River daily (Everett, 1971). This flux is
equivalent to 7% of the total dissolved load at average river flow and 21% of the total at
low flow. Much of this discharge is composed of industrial acids which are known to
contain various heavy metals (National Academy of Science, 1975). Trefry and Presley
(1976a,b) found evidence of Pb and Cd pollution in sediments from an extensive area of
the Mississippi Delta. Results from the present study confirm and expand the initial
observations and provide a more reliable time scale for examining the history of Delta
metal pollution.

2. Methods

Samples of suspended particulates, filtered water, and sediments were collected for this study from the Mississippi River, adjacent fresh and saltwater marshes and the Mississippi's marine delta region (Figure 2) over an 18 mo period in 1974–76. Collections were made at high, low, and intermediate river flow. Analysis of these phases for selected heavy metals was augmented by measurements of dissolved nutrients and other salts, suspended particulate load, sediment and particulate grain size distribution, sediment accumulation rate (using Pb-210 chronometry) and organic and inorganic carbon content.

Suspended particulates in gram quantities were separated from river and marine waters by 0.4 μm filtration using a closed, vacuum-driven system. Waters for dissolved metals analysis, on the other hand, were collected either by a closed pumping system held well away from the ship or by hand filling plastic bottles from a small rubber boat. Particulates were frozen for storage, whereas the water samples were passed through a 0.4 μm filter then acidified to pH 2. Sediment samples were collected with either a 7-cm diameter gravity corer or a 50 cm^2, NEL-type box corer. Dissolved metal concentrations in river water were determined by direct injection into a flameless (graphite furnace) atomic absorption spectrophotometer and confirmed by pre-analysis concentration and analysis of a few samples by the solvent extraction procedure of Brooks *et al.* (1967).
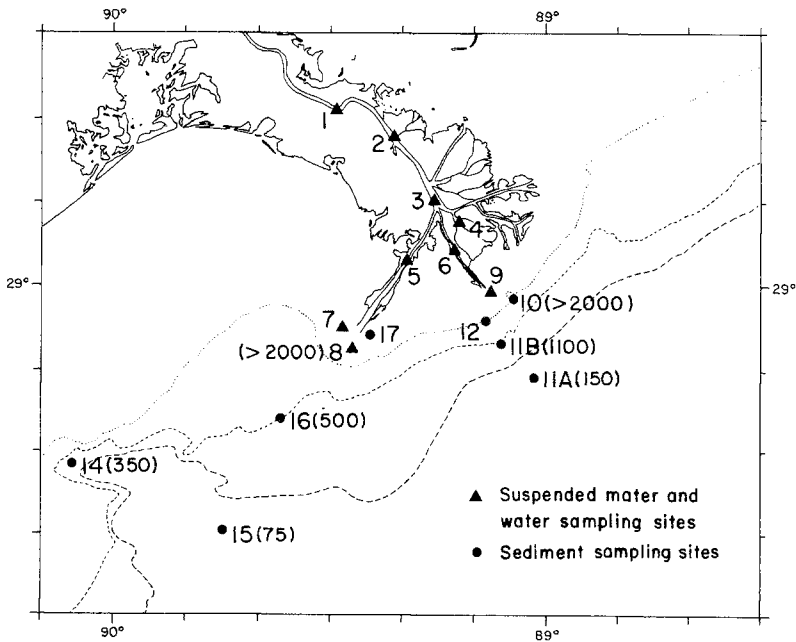

Fig. 2.   Sampling sites in the Mississippi River Delta area. Sediment accumulation rates as determined by the Pb-210 method are shown in parenthesis.

Direct injection proved to be a reliable method for determining Fe, Cr, Cu and Mn but was less reliable for Pb and Cd and not useable for Ni.

Total sediment and suspended particulate metal concentrations were determined by atomic absorption spectrophotometry after dissolution with Hf, $HClO_4$ and HNO_3, Background matrix interferences were compensated for by method-of-additions, instrumental background correction, matrix-matched standards and/or simultaneous monitoring of absorbance at nearby non-reasonance wavelengths. Total sediment V and Al were determined by instrumental neutron activation analysis (Trefry, 1977).

In addition to total dissolution, sediments and suspended particulates collected in this study were subjected to a sequential series of chemical leaches similar to those of Gibbs (1973). These included: (1) initial leaching of non-ashed solids with 1N NH_4Cl (at pH 7, with shaking for 18 h) to remove 'exchangeable' metal ions; followed by (2) removal of Fe and Mn hydrous oxides (and the metals associated with these oxides) using citrate buffered (pH 4.7) sodium dithionite solution and 2 h of shaking at 60°C (Coffin, 1963); (3) oxidative removal of organic matter-associated metals with sodium hypochlorite (pH 7) prior to another citrate dithionite treatment; and finally (4) the remaining solid residues were completely dissolved with the same $HF-HClO_4-HNO_3$ procedure used in total sediment dissolution.

Vertical distributions of sedimentary Pb-210 activity was determined to derive sediment accumulation rates. The 22 yr half-life of this naturally occurring U-238 series isotope enables its radioactive decay history to be followed over the past 125 to 175 yr, thereby encompassing the commencement and development of the U.S. industrial era. Assays for total Pb-210 activity were performed by low-level beta spectrometry of Bi-210 (a higher energy decay daughter) after leaching the sediments with hot, 6N HCl and separating interfering isotopes by anion exchange chromatography. Excess Pb-210 (that not in secular equilibrium with the rest of the U-238 decay series) was determined for all samples by measuring the Ra-226 activity by radon emanation (Chung, 1971) and subtraction from the total Pb-210 activity.

More detailed analytical methodologies are outlined in Trefry (1977) and Shokes (1976).

3. Present-Day Mississippi River Metal Flux

Dissolved metal concentrations at the locations shown in Figure 2 proved to be considerably below the EPA limits for safe drinking water. Values from the U.S.G.S. (1975) and our study are also generally lower than those reported by previous workers (Durum and Haffty, 1961; Kopp and Kroner, 1967; U.S.G.S., 1972, 1973, 1974) but are similar to Turekian's (1969) estimates for average river water (Table I). These low concentrations are most likely due to specific adsorption, as the abundant fine-grained suspended material in the river (100 to 500 mg l^{-1}) and high pH (7.5 to 8.1) favor this process.

TABLE I

Mississippi River dissolved and particulate heavy metal concentrations

	Dissolved metal concentrations in $\mu g\,l^{-1}$								
	(N)	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
Mississippi River (this study)	(20)	0.1	0.3	2	10	–	10	1	0.2	–
Mississippi River (U.S.G.S., 1975)	(94)	1	1	3	–	0.1	–	3	1	10
Average River Water (Turekian, 1969)	–	–	1	7	–	0.07	7	0.3	3	20
Water Quality Criteria (E.P.A., 1973, 1976)	–	10	50	60	300	2	50	100	50	–

	Particulate metal concentrations in $\mu g\,g^{-1}$								
	(N)	Cd	Cr	Cu	Fe	Co	Mn	Ni	Pb	Zn
Mississippi River (This study)	(73)	1.3	80	45	46,100	21	1300	55	46	193
Mississippi Delta (This study)	(34)	1.5	84	56	46,400	21	1290	56	49	244
Sediment Disposal Criteria (E.P.A., 1973)	–	2	–	50	–	–	–	–	50	75
Average Crustal Abundance (Taylor, 1964)	–	0.2	100	55	56,300	25	950	75	13	70

Temporal variations in Mississippi River dissolved metal concentrations ranged from a factor of 2 to greater than 20, depending on the metal. Chromium concentrations, for example, varied from only 0.5 to 1.0 $\mu g\,l^{-1}$ for the periods sampled whereas Mn ranged from ~1 to 30 $\mu g\,l^{-1}$ and Cu from 0.3 to 4 $\mu g\,l^{-1}$. Fluctuations in Cd, Fe, Ni and Pb values were intermediate of these extremes. In general, maximum dissolved concentrations for all metals were observed during the low river flow September and November periods.

Average metal concentrations in river particulates (Table I) were quite constant (<10% variability) for the June, February, July and November sampling periods when the river was near or above average flow. Differences in metal values among samples from several river locations (Figure 2) and depths were also consistently well below 10% for each period. During low river flow (September), however, the particulate organic matter content increased from <3% to 25%, bringing about a corresponding decrease in Fe and Al concentrations due to dilution of alumino-silicates by organic matter. No significant change in particulate Co, Ni or Pb concentrations was observed during low flow, however Cu, Mn and Zn concentrations were 30 to 40% higher and Cd values increased by 80%. Enrichment of particulate Cd, Cu, Mn and Zn at low flow suggests an association of these metals with the increased organic matter and/or surface coatings on the very fine-grained particles.

Relative to average crustal abundances (Table I), Mississippi River particulate Cd, Pb and Zn concentrations are quite high and suggestive of an anthropogenic source. Only Zn was found in significantly higher concentrations than those acceptable for dredged sediment disposal (Table I).

4. Partitioning of River-Borne Metals

Chemical leaching of the solid phase reveals, in a general way, the modes of particulate metal transport by a river and the relative availability of the metals. Figure 3 compares data from this study of the Mississippi with that of Gibbs (1977) for the Amazon. In leaching the Mississippi River suspended matter, the initial 1N NH_4Cl treatment (at pH 7) removed metal ions which were exchangeable (Exch.) with the ammonium ion at an ionic strength slightly greater than that of seawater. In all cases < 2 μg Fe per gram of suspended matter were leached with the NH_4Cl, indicating that iron hydrous oxides were not altered by this treatment. The second solution used, citrate-buffered sodium dithionite at pH 4.7, dissolved 'free' Fe and Mn oxides (Ox.). Sodium hypochlorite (pH 7), the third solution in sequence, oxidized organic matter and sulfides (Org.) and metals associated with these phases. Finally, after particle surfaces have been thrice attacked, residual silicate and other crystalline minerals and their lattice-held (Lat.) metals are dissolved in $HF-HNO_3-HClO_4$. The chemical leaching methodology used by Gibbs (1973) for Amazon samples is quite similar to that used for the Mississippi study.

Figure 3 shows that Mississippi and Amazon River particulate metals were predominantly in the oxide and lattice phases. Data for Fe from the rivers were similar showing relatively equal oxide-lattice partitioning. Cobalt and Ni distributions were also similar except that the absolute values were a factor of two higher for the Amazon particulates. Total Mn values are reasonably close for the Mississippi and Amazon, however the Mississippi suspended matter is present predominantly in oxide coatings
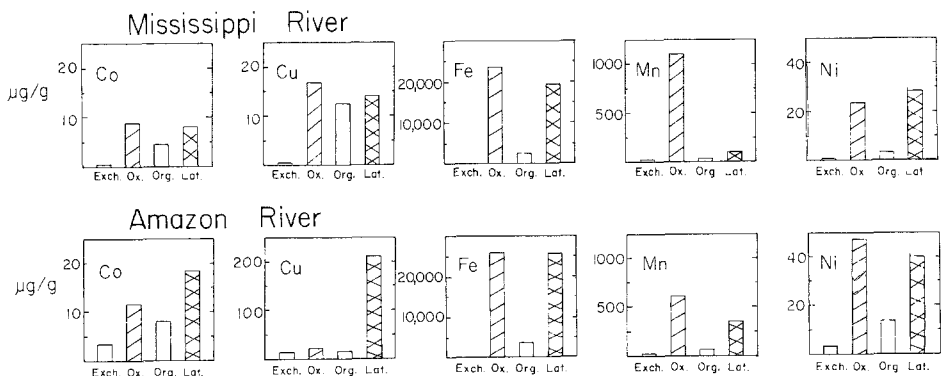

Fig. 3.   Distribution of trace metals in Mississippi and Amazon River suspended matter (Amazon data from Gibbs, 1977).

with a less significant lattice fraction than found for the Amazon material. Copper values show the greatest discrepancy, with Amazon totals six times greater than those for the Mississippi. This large excess Cu, which is mostly lattice held, may be indicative of significant Cu-bearing minerals in the Amazon basin. Partitioning of Mississippi River particulate Pb showed average of < 0.5 ppm exchangeable, 20.3 ppm oxide, 14.4 ppm organic/sulfide and 14.8 ppm in the lattice phase.

Calculation of the total annual flux of dissolved and particulate metals from the Mississippi River to the Gulf of Mexico (Table II) shows the overwhelming importance of the particulates. Table II does not include bed load transport, however Mississippi bed loads have been estimated to be less than 10 to 20% of suspended loads (Holle, 1952; Fisk *et al.*, 1954). Since Mississippi River bed sediments have 2 to 3 times lower metal content than the suspended particulates, they almost certainly contribute < 10% of the annual flux. As expected, only a small percentage of the metals are carried in solution and thus the primary modes of metal transport by the Mississippi are with the oxide and lattice phases of the river particulates.

Physico-chemical interactions involving heavy metals can occur in the freshwater/seawater mixing zone and thereby change both the ultimate area of metal deposition and the availability to nearshore marine organisms. Desorptive processes would make metals more available to organisms and delay their removal to the sediments whereas adsorptive processes would have an opposite effect. Comparing Mississippi River suspended matter composition with that from saline waters immediately outside the river mouth (Table I) shows that, with the exception of Cu and Zn, concentrations are essentially the same. These observations argue against extensive desorption of any of these metals and suggest that Cu and Zn levels actually increase upon entering the sea.

TABLE II

Annual flux of metals from the Mississippi River to the Gulf of Mexico

Element	Particulate ($\times 10^9$ g)	Dissolved ($\times 10^9$ g)	Particulate (% of total)	Dissolved (% of total)
Fe	12,900	5.7	> 99.9	0.02
Mn	364	5.7	98.5	1.5
Zn	54	5.7	90.4	9.6
Cr	22	0.3	98.7	1.3
Ni	16	0.6	96.4	3.6
Cu	13	1.1	92.2	7.8
Pb	13	0.3	97.7	2.3
As	4	0.6	87.0	13.0
Cd	0.4	0.06	87.0	13.0

Note: Calculations are based on average water and suspended matter metal data from Table I with the sediment discharge data of the U.S. Army Corps of Engineers (2.8×10^{14} g yr^{-1}; 1950–1975) and estimated water flow at the river mouths (5.7×10^{14} l yr^{-1}; Iseri and Langbein, 1974).

5. Heavy Metal Record in Mississippi Delta Sediments

The Pb-210 method was used to derive sedimentation rates for delta stations utilized in this study. Using them, it is possible to assign approximate ages to the vertical sediment strata. This then makes it possible to evaluate the vertical distribution of heavy metals in these cores as historical records of elemental input.

Figure 4 shows the excess Pb-210 activity profiles measured at two locations (Stations 11A and 15) where sediments are accumulating at rates ideal for determination with this particular isotope (0.05 to 0.75 g cm^{-2} yr^{-1}). These rates are found at the seaward extremities of the main depositional platform of the delta. Rates increase in going toward the river mouth and the activity profiles of Pb-210 become harder to interpret. The near-ideal exponential decreases in activity seen in the two profiles in Figure 4 indicate undisturbed, constant-rate sedimentation in one case (Station 15) and constant-rate sedimentation overlain by a surface zone of sediment mixing in the other (Station 11A).

In the mid-delta area, the 50–60 cm cores collected in this study provide a record back to about the turn of the century. Figure 5 for a typical mid-delta station indicates that Fe, Al, Cu, Zn, Ni and Co concentrations have been uniform over the past 75 yr. The same trend holds for Cr and V. Sedimentary Pb concentrations, however, have increased by 65% during this time interval. The major onset of pollutant Pb has occurred since the mid-1940s, a period of increased usage of leaded gasoline. Also, the
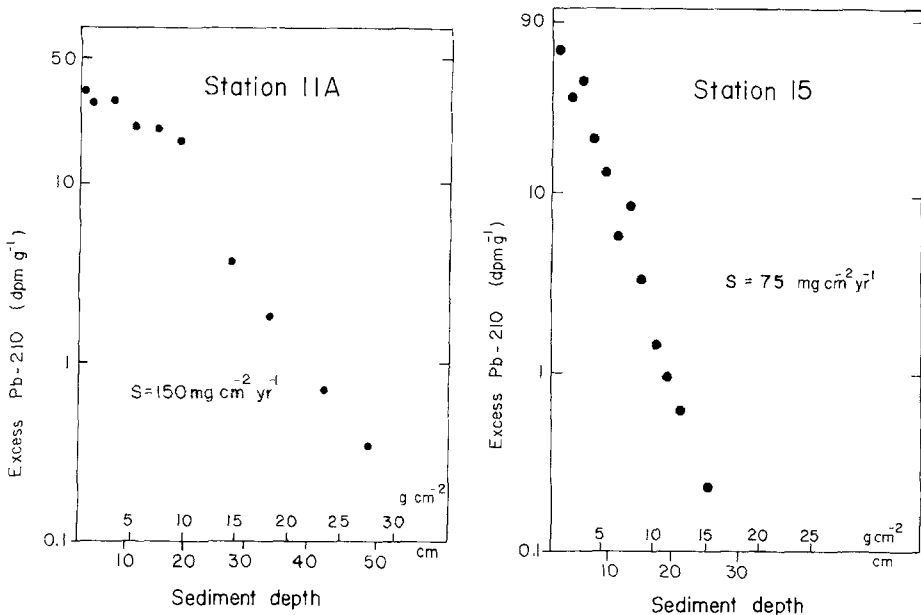

Fig. 4.   Excess Pb-210 activity versus depth in sediments from the Mississippi River Delta.
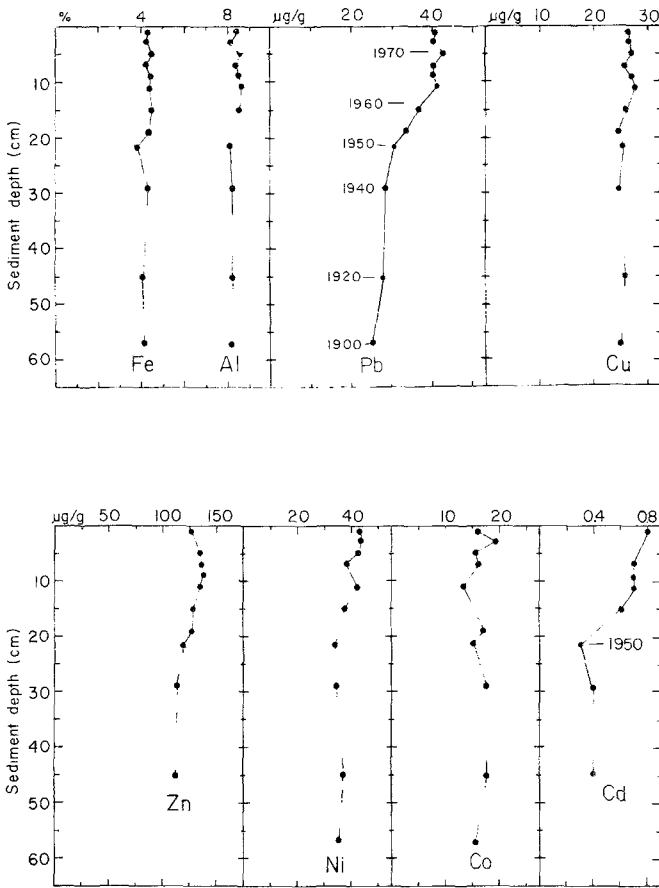
Fig. 5. Vertical metal profiles in Mississippi River Delta Station 16 sediment.
Water depth is 110 m.

surface sediment Pb concentrations at this location are comparable with those of present-day river particulates (46 ppm). Surface sediment Cd concentrations at this mid-delta station are also high, about double their pre-1950 values. Moreover, the 0.4 ppm Cd baseline concentration is still in excess of values found in deeper (older) sediments on the delta.

Rapidly accumulating sediments (> 2 g cm^{-2} yr^{-1}) from near the river mouth have relatively straight vertical metal profiles (Figure 6). Lead and Cd concentrations, however, are 70 and 200%, respectively, above "base" values found in mid-delta sediments and are in good agreement with present day river particulate concentrations. These constant sediment Pb and Cd concentrations for 50 to 60 cm profiles in this area indicate a relatively constant input during the past 10 to 15 yr.

Outer delta sediments, which are accumulating at rates on the order of 0.1–0.5 g cm^{-2} yr^{-1}, also have relatively constant Fe, Al, Cu, Zn, Ni, V, Cr and Co concentrations
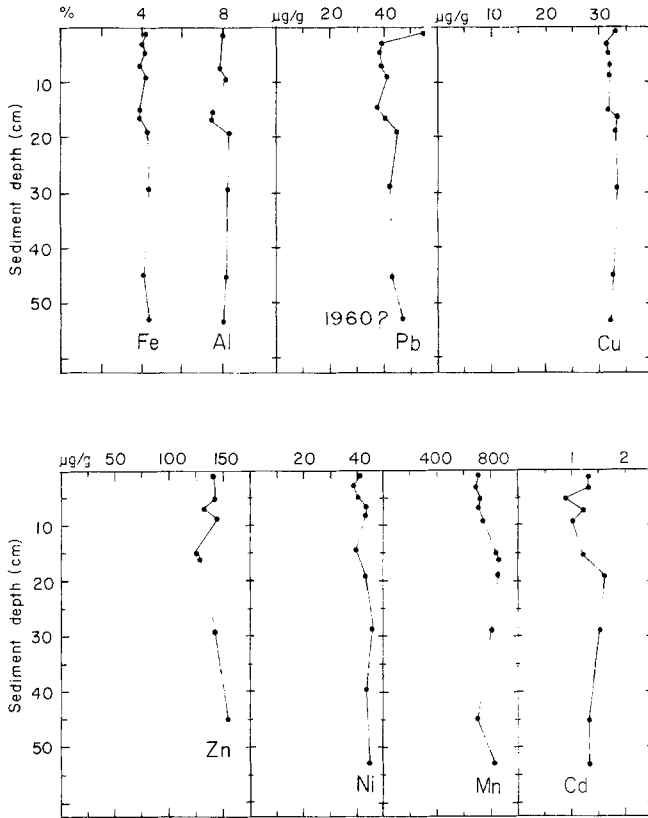
Fig. 6.   Vertical metal profiles in Mississippi River Delta Station 10 sediment.
Water depth is 50 m.

(or at least uniform metal/Al ratios; Figure 7). However, sedimentary Pb concentrations (Figure 7) exhibit a decrease from 43 ppm at the surface to 20 to 25 ppm in the lower core section. The 50 to 60 cm outer delta core extends the historical record of sedimentation back to pre-1800, indicating that substantial amounts of pollutant Pb began being added to Mississippi Delta sediments around the mid-1800s, with an accelerated increase after 1940. This record corresponds remarkably with the advent of mining lead and other ores, extensive agricultural development, fossil fuel burning and other industrial-age activities in the last half of the 19th century, followed by the accelerations in urbanization and gasoline engine use in the post-1940 era.

Similar historical records have been established for Pb in Lake Michigan sediments (Edgington and Robbins, 1976) and in Southern California (Bruland *et al.,* 1974). In the Lake Michigan study, where historic anthropogenic emissions are well documented, increased Pb fluxes have been attributed solely to a combination of coal and gasoline combustion. In Southern California coastal sediments, which quite efficiently collect in a series of near-shore basins, several metals including Pb, Cr, Cu, Ag, and Zn have been
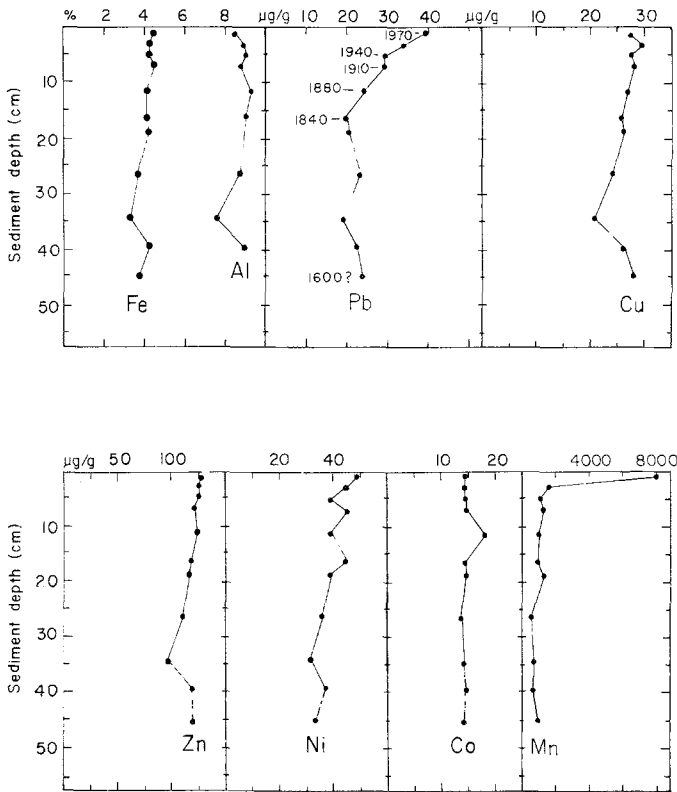
Fig. 7.   Vertical metal profiles in Mississippi River Delta Station 7 sediment.
Water depth is 550 m.

found in excess of natural concentration levels since the 1930–1940 period. This has been related to industrial/municipal discharges and run-off entrainments as well as to major contributions by atmospheric transport, especially in the case of Pb. In contrast to Southern California, only Pb and Cd are found to be enthropogenically enriched in Mississippi Delta sediments. Evidently, the enormous annual detrital load of the Mississippi River grossly dilutes any man-induced amounts of the other metals.

6. Partitioning of Metals in Deltaic Sediments

Metals in Mississippi Delta sediments were chemically partitioned using the previously described leaching scheme. Sediment total Fe concentrations were about 10% lower than those of the river particulates with the difference in absolute amounts accounted for by lower oxide-phase Fe in sediments. Similarly, sediment Mn concentrations were 45% less than those of the river suspended matter with the change attributable to a greatly lower level of Mn oxide. Trefry and Presley (1980), have shown that the decrease

in oxide-phase Fe and Mn results from remobilization of reduced species of these metals with subsequent diffusion to the overlying seawater and advection away from the Delta area. Cobalt, Cu and Ni follow Fe and Mn, showing concentrations 20 to 30% lower in the delta sediments. Decreased Ni values result entirely from lower oxide-phase content whereas Co and Cu depletion is explained by reductions in both oxide and organic/sulfide levels. The mechanism for this depletion is probably diagenetic, but we have no supporting interstitial water data or other confirmation.

Sediment Pb partitioning shows, as with all metals studied, very similar lattice concentrations between river suspended matter and sediments. Lower total Pb concentrations were observed in deeper core sections (Figures 5 and 7) where less pollutant Pb was found. Lead decreases were attributable to significant Pb depletion in the oxide and organic/sulfide phases. Partitioning, then shows the importance of an organic phase to Co, Cu and Pb transport to the oceans and a lack thereof for Fe, Mn and Ni. Lattice phases remain surprisingly constant across the Mississippi River/Gulf of Mexico transition with the oxide phase universally susceptible to physico-chemical alteration.

Pollutant metal inputs will most likely associate with oxide and/or organic phases, as outlined above. Where oxide phases are involved, strong reducing conditions in delta sediments can bring into solution significant amounts of some metals. For example, dissolved interstitial Mn concentrations were as high as 10 mg l^{-1} in the top centimeters of sediment, more than 1000 times higher than the overlying bottom water. Organic decomposition in the sediments may thus release potential toxic metals directly, or indirectly through reduction.

7. Summary and Conclusions

Mississippi River Delta sediments provide an ongoing historical record of pollutant discharge from the central United States. This record shows no evidence of Co, Cr, Cu, Fe, Mn or Ni pollution, but strong indications of anthropogenic Cd and Pb additions. Sediment Pb concentrations have increased by 70% and Cd values by 200% over the past several decades. These man-derived inputs may be traced to the advent of mining, agricultural and industrial activities during the latter half of the 1800s, which have accelerated since the 1940s.

Pollutant Pb fluxes from the Mississippi River to the Gulf of Mexico are on the order of 6000 tonne yr^{-1}, or about 30 times higher than these estimated for the Southern California coastal zone (Bruland *et al.,* 1974). Similarly, anthropogenic Cd inputs from the Mississippi ($\sim$ 300 tonne yr^{-1}) are about 35 times greater than those reported for Southern California. The massive sediment load of the Mississippi ($\sim$ 300 Mtonne yr^{-1}), however, dilutes these fluxes to concentration levels comparable to those observed off Southern California, and may even obscure pollution inputs of some of the other metals. In this manner then, the Mississippi provides a viable outlet for carrying

enormous loads of industrial and municipal metal wastes without significantly increasing natural (background) metal levels.

Since delta sediments give only a time-averaged picture of metal inputs, river dissolved and particulate fluxes have more value as real-time evaluators and prognosticators of metal pollution. Our data show that dissolved trace metal concentrations are low and most likely non-problematic, a function of the high suspended load and pH of the river. River particulate Al, Cd, Cr, Fe, Pb and V values are essentially the same as those for delta surface sediments; however river suspended matter Co, Cu, Mn, Ni and Zn concentrations are 20 to 40% higher than those in the delta sediments. The 40% lower Mn in the sediments can be accounted for by diagenetic loss of Mn^{2+} from the delta sediments (Trefry, 1977). Variations in the other four metals may also be diagenetic; however, recent pollutant input and physical fractionation of river-borne particles may also prove important.

Using a geochemical leaching scheme, we found oxide and lattice phases of the particulates to be of primary importance for most metals, with Co, Cu and Pb having significant organic/sulfide fractions. Most of the river particulates (which carry $\sim 90\%$ of the river metal load) settle out very quickly upon entering the ocean, thus only a small percentage ($< 1\%$) of the Gulf of Mexico shows measureable Pb and Cd pollution.

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