

Use of normalized metal concentrations in the Mn oxides/hydrous oxides extraction phase of stream sediments to enhance the difference between a landfill emission plume and background

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Abstract—Normalized concentrations of Fe, Zn, Ba and Co bound to the Mn phase were determined using a ratio of metal concentration to Mn concentration. Metal concentrations were taken from a previous study which found elevated concentrations of heavy metals in the stream sediments in the vicinity of 2 landfills using a HNO_3 extraction of the whole sediment sample and geochemical phases. Results from the normalized metal concentrations for Zn, Fe and Ba showed a clearer distinction between background and emission plume regions along the stream compared to the same for the HNO_3 and Mn phase extractions. Lack of elevated concentrations and normalized concentrations for Co indicated the concentrations represented the background. The small distance used in the study could explain the lack of a decreasing trend of metal concentrations and normalized metal concentrations downstream in the emission plume of the sediments. Although Mn^{+2} concentrations are known to be incorporated into the natural state of the Mn phase, these concentrations were thought to be small enough not to influence the results from the normalized concentrations. Non-selectivity of extractants and metal redistribution among chemical phases during extraction procedures are thought to be small and did not invalidate the results. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Numerous studies have reported enrichment of metal concentrations in sediments affected by anthropogenic activities. In most of these studies, metal concentrations have been determined using HF (total) or HNO_3 (partial) extraction procedures. Ramamoorthy and Rust (1978), Castaing *et al.* (1986) and Rule (1986) reported enrichment of heavy metals in river sediments influenced by industrial wastes. These include Cu, Pb, Zn, Ni, Cd, Hg, Co, Cr, Fe and Mn. Other authors have reported Cu, Pb, Zn, Cd, Sn, As, Cr, Fe and Mn in river sediments affected by mining activities (Reece *et al.*, 1978; Wolfenden and Lewin, 1978; Yim, 1981; Chapman *et al.*, 1983; Mann and Lintern, 1983; Moore, 1985; Leenaers *et al.*, 1988; Axtmann and Luoma, 1991). Studies of the enrichment of Cu, Pb, Zn, Cd, Ag and Ba concentrations in drainage sediments affected by landfill leachate and a waste water treatment facility have been reported (Mantei and Coonrod, 1989;

Mantei and Foster, 1991; Mantei and Sappington, 1994). However, only a few studies have reported affects of human activities on sediments using sequentially extracted geochemical phases. Yanful *et al.* (1988) studied migrations of Cu, Zn, Pb and Fe in a clay layer underlying a sanitary landfill using the carbonate, organic, Mn and Fe oxides/hydrous oxides, and residual phases. Mantei and Foster (1991) found elevated concentrations of Cu, Pb, Zn, Cd, Ag and Ba in the exchangeable cation, carbonate, Mn oxides/hydrous oxides, Fe oxides/hydrous oxides, organic and remnant phases of drainage sediments affected by landfill leachate from 2 sanitary landfills.

It is well known that metals selectively incorporate in geochemical phases in sediments and soils (Gadde and Laitinen, 1974; Murray, 1975; Forbes *et al.*, 1976; Zachara *et al.*, 1988; Mantei and Foster, 1991; Kooner, 1993). There are numerous studies which report factors that influence enrichment of metals in sediments. Burton (1991) summarizes these factors. The concentration of a metal associated with a geochemical phase may be influenced by the quantity of the geochemical phase. Assuming this to be true, the concentration of a geochemical phase in a soil and sediment sample may influence the concentration of a metal in the total sample. Kooner (1993)

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reports the amounts of Cu, Pb and Zn incorporated into goethite is a function of the amount of goethite. In 2 aforementioned studies (Yanful *et al.*, 1988; Mantei and Foster, 1991) concentrations of the geochemical phases were not considered in the evaluation of data.

We believe that within a geochemical phase extracted from a sediment or soil sample, a ratio of the concentration of a metal to the concentration of a substance representing the phase can be used to normalize the metal concentration. Manganese and Fe concentrations could represent concentrations of the extracted Mn oxides/hydrous oxides (Mn phase) and Fe oxides/hydrous oxides (Fe phase) phases, respectively. The Ca concentrations could represent concentrations of the carbonate phase. Significant concentrations of undesired solubilized geochemical phases and associated metals in an extraction phase may invalidate the results of the normalization method. Manganese carbonate and associated metals may be present in the carbonate phase extraction (Mantei and Foster, 1991). Concentrations of solubilized phases and associated metals present in the Fe and Mn extraction phases are discussed later. Normalized metal concentrations in a geochemical phase in sediments affected by anthropogenic activities may differ from the same for control sediments. There are no known data in the literature which make this comparison.

In this paper we report normalized concentrations of metals bound to the Mn phase in stream sediments affected by 2 landfills and compare these concentrations with the same in control sediments. The normalized metal concentrations are derived from metal concentrations reported from a previous study (Mantei and Foster, 1991).

Possible problems associated with chemical separations of geochemical phases from sediments

Some investigators question the status of sequential extraction procedures as a useful analytical tool. One problem is the non-selectivity of extractants. Chemical extractants used to solubilize one geochemical phase and associated metals have dissolved other phases and bound metals. Miller *et al.* (1986) reported this to occur during Mn, Fe and organic phase extractions in soils. Another problem encountered is trace metal redistribution among phases during sequential extractions; that is, trace metals released by one extractant may reassociate with other undissolved phases. Some have reported significant redistribution (Tipping *et al.*, 1985; Kheboian and Bauer, 1987; Gruebel *et al.*, 1988; Tu *et al.*, 1994). Others argue that the occurrence of redistribution may not be sufficiently large to invalidate the extractions (Belzile *et al.*, 1989; Kim and Fergusson, 1991).

Choice of the Mn phase

The Mn phase was chosen for this study primarily because the extraction of this phase from the undissolved Fe phase appeared to be very effective. This conclusion was based on the low mean concentration of 52 µg/g of Fe present in the Mn phase extraction. The mean concentration of Fe in the Fe phase was 8430 µg/g. There may be a redistribution of metals from the previous exchangeable cation and carbonate phase extractions. Mantei and Foster (1991) report Zn and Ba concentrations present in the exchangeable cation and carbonate phases while Zn concentrations are present in the carbonate phase. Iron was not detectable in either phase. Solubilized Zn and Ba concentrations could redistribute in the undissolved Mn phase. The scavenged metals would then be dissolved in a hydroxylamine hydrochloride solution used to solubilize the Mn phase and associated metals. An extraction procedure using this chemical reagent was used to extract the Mn phase (Chao, 1972). However, redistributed concentrations of Zn and Ba may not affect the results in this paper. As mentioned before some believe the occurrence of redistribution is small enough not to invalidate the extractions.

Some may question the use of Mn concentrations to normalize metal concentrations associated with the Mn phase. If high concentrations of Mn^{+2} are naturally bound to the Mn phase, a false representation of normalized concentrations could result. Murray (1975) reports a relatively high affinity of Mn^{+2} for hydrous MnO_2 .

Metal concentrations bound to the carbonate and Fe phases in the sediments were not normalized in this study. Unfortunately, Ca concentrations in the carbonate phase were not determined by Mantei and Foster (1991). Iron concentrations in the Fe phase were available. Large concentrations of Al were present in the solubilized extraction of this phase. Mason and Moore (1982) showed a high solubility for $Al(OH)_3$ at a pH value which is commonly used for the Fe phase extraction. Kinniburgh *et al.* (1976) reported very similar adsorption preferences for metals present in both amorphous Al and Fe oxide phases. The presence of high concentrations of Al in the Fe phase extraction could indicate the occurrence of an Al oxide/hydrous phase with associated metals. Concentrations of a common metal associated with the Fe and Al phases present in the Fe phase extractant would result in a false representation of normalized metal values.

Background of study area

Mantei and Foster (1991) reported elevated concentrations of heavy metals bound to 6 geochemical phases in sediments collected along a stream affected by leachate from 2 landfills. They also compared these

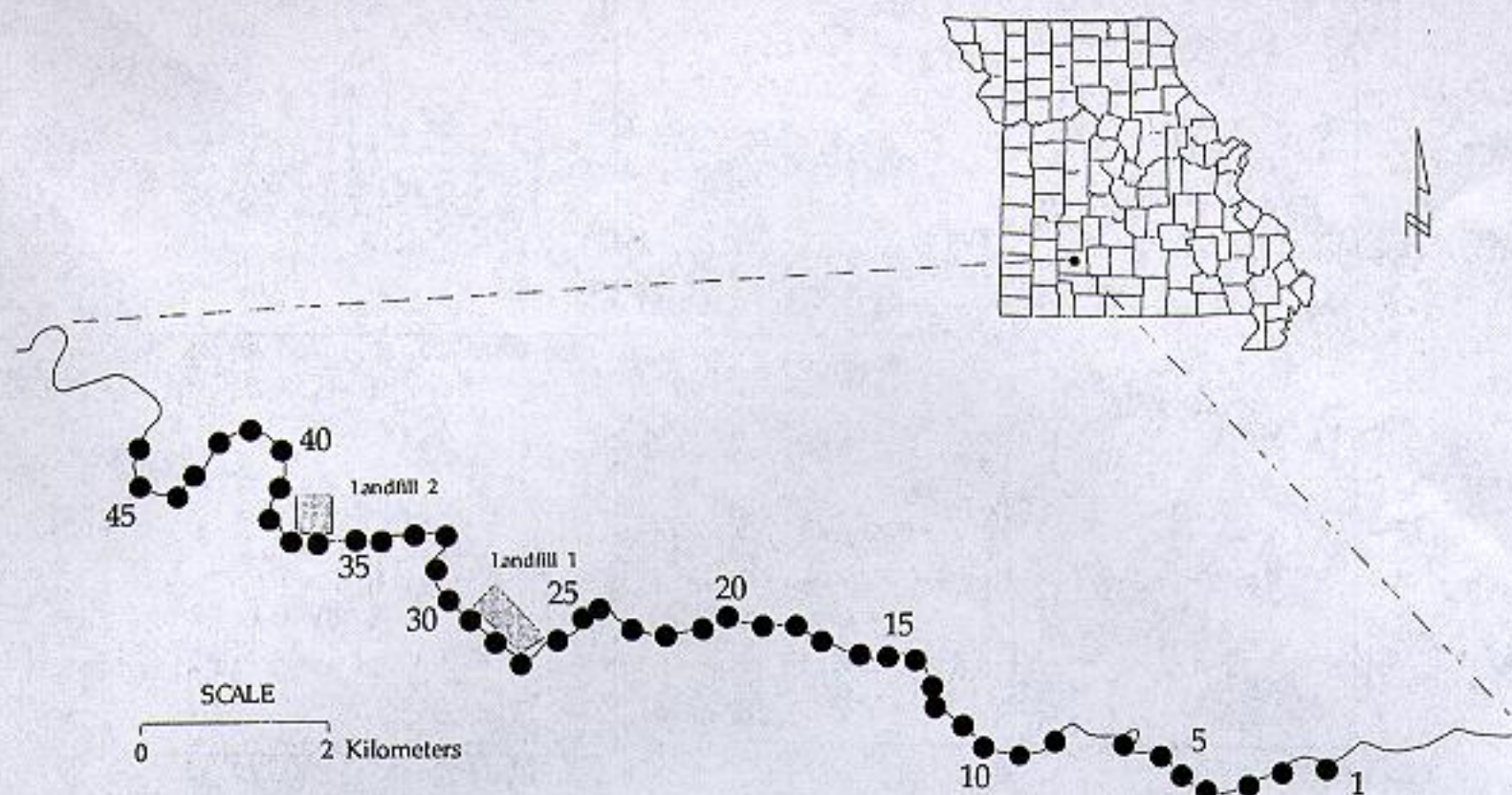


Fig. 1. Location of study area and detailed map of collection sites (modified from Mantei and Foster, 1991). Stream waters flow to the W.

elevated concentrations with that in a hot single HNO_3 extraction portion of the whole sediment (NAEWS). The study area is located in SW Missouri, just N of the city of Springfield. Figure 1 shows the location of the area and sample collection sites along the stream. Samples 1–26 are sediments collected upstream from the landfills. These represent the control or background samples. Samples 27–46 are located downstream from the landfills. These samples are located in the emission plume of the landfills and are affected by leachate.

METHODOLOGY

Only Zn, Fe, Ba, Co and Mn were found in detectable concentrations in the Mn phase of sediment samples along the study stream (Mantei and Foster, 1991). From these data we calculated normalized concentrations for Zn, Fe, Ba and Co in all samples. A trend chart representing the variations of each normalized metal concentration along the stream was generated. These variations were compared with the same for metal concentrations in the Mn phase and with that in the NAEWS. A mean was established for each metal concentration and normalized metal concentration in the Mn phase. Each mean value in the respective background was compared with that in the emission plume. The coefficient of variation (CV) was used to show the difference in variability of normalized metal concentrations in sediments in the landfill emission plume with that in background sediments. This was also done for metal concentrations in the Mn phase. Axtmann and Luoma (1991) and Mantei and Sappington (1994) used CV values to show differences between sediments affected by anthropogenic activities and the control. A correlation coefficient was used to show the dependence of the concentrations of Zn, Fe, Ba and Co on the concentrations of the Mn phase.

RESULTS AND DISCUSSION

Comparison of metal concentration trends with that of normalized metal concentrations.

Figure 2A, B (Mantei and Foster, 1991) show the variation of metal concentrations along the stream for the NAEWS and the Mn extraction phase, respectively. In Fig. 2B, the variations in concentrations of Ba, Co and Mn appear to have a similar overall pattern especially for that of Co and Mn. These similarities are most evident in the area between samples 1 to 26. There is a trend of increasing concentration of all metals with an increase in sample number in the background and a decreasing concentration with increasing sample number in the landfill emission plume. This decreasing trend begins slightly up stream from landfill 1. Mantei and Foster (1991) attribute variations in metal concentration in the background area to a higher population density along the stream between samples 6 to 26. They did not account for the decreasing concentration of metals in the landfill emission plume area. The reason for a sudden decrease in metal concentrations is treated later in this paper. The similarities in the metal trends may indicate a dependence of the concentrations of Fe, Zn, and Ba and Co on that of Mn which is assumed to represent the concentration of the Mn phase.

Enriched concentrations of Zn and Fe are present in the NAEWS in the vicinity of landfill 1 along the stream. The same is true for Fe and Ba concentrations in the vicinity of landfill 2. An enrichment of Zn concentrations in the vicinity of landfill 1 is also

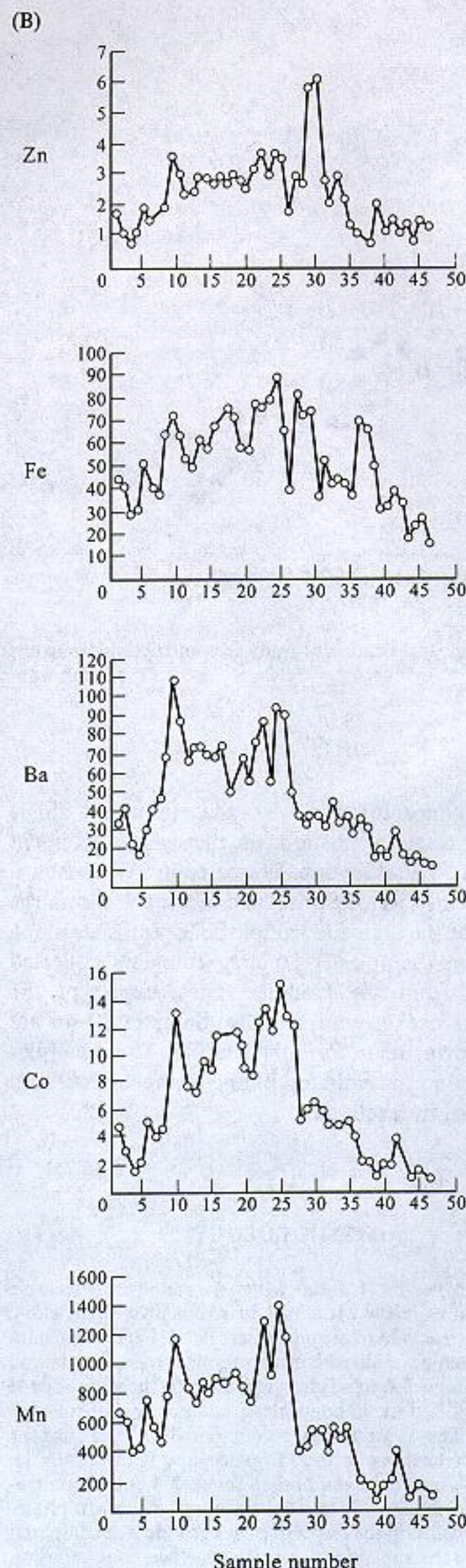
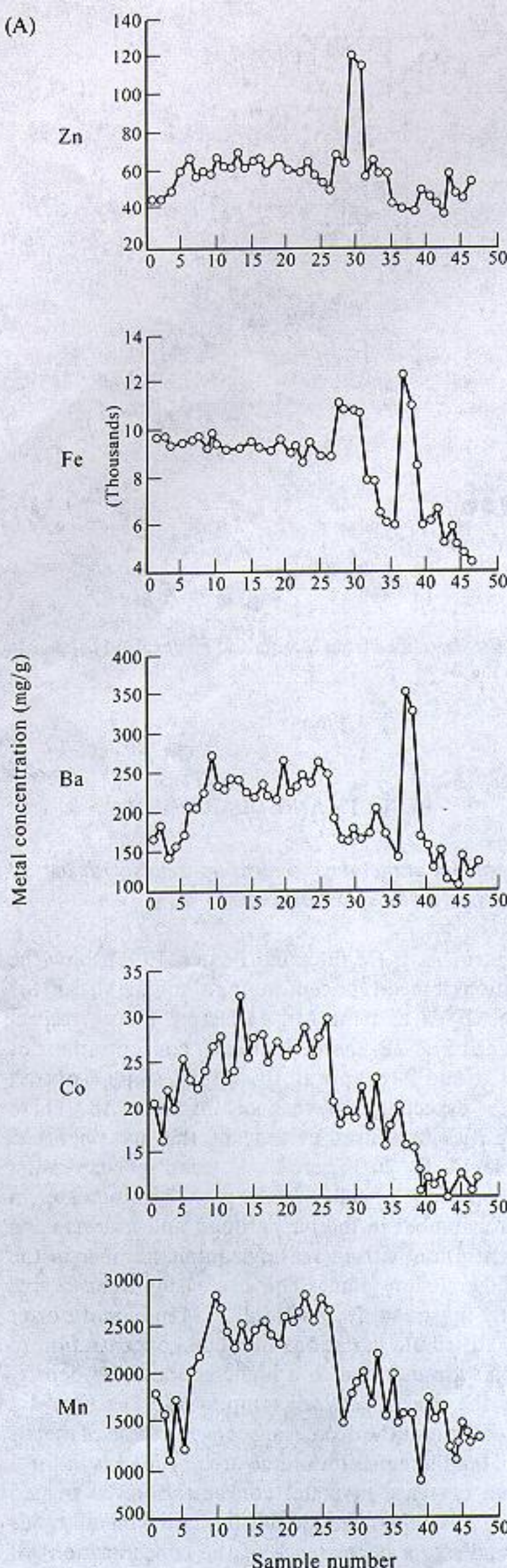


Fig. 2. (A) Trends of metal concentrations in the hot single HNO_3 extraction portion of the whole sediment (NAEWS) taken from Mantei and Foster (1991). The landfill emission plume begins at landfill 1 (sample 27). Landfill 2 is located at sample 36. (B) Trends of metal concentrations in the Mn oxides/hydrous oxides (Mn phase) extraction of the sediments taken from Mantei and Foster (1991). The landfill emission plume begins at landfill 1 (sample 27). Landfill 2 is located at sample 36. (C) Trends of normalized metal concentrations in the Mn oxides/hydrous oxides (Mn phase) extraction phase of the sediments. The landfill emission plume begins at landfill 1 (sample 27). Landfill 2 is located at sample 36. Selective enlargement of normalized values ($\times 100$ or 1000) made for visual comparison between background and emission plume regions.

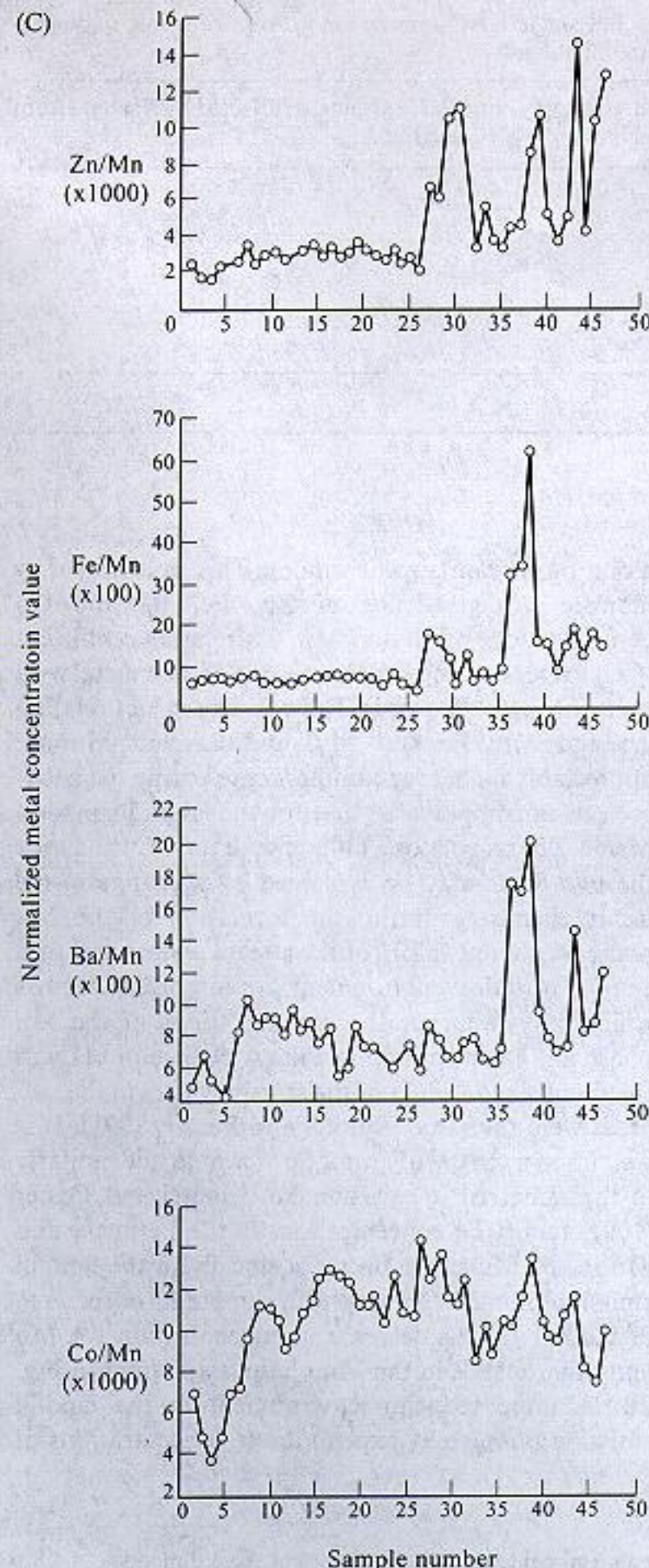


Fig. 2. (continued)

apparent in the Mn phase of the sediments. Metals associated with the Mn phase whose concentrations are enriched in the NAEWS and geochemical phases of the sediments are summarized in Table 1 (Mantei and Foster, 1991). Variations in concentrations for each metal along the stream in the NAEWS and Mn phase are noticeably different than that for the normalized metal concentrations in Fig. 2C. Normalized metal concentrations for Zn appear to clearly define the background and emission plume areas along the stream. Concentrations of Fe and Ba show

a lack of enrichment in the Mn phase of the sediments in the vicinity of either landfill. Although areas of higher Fe concentrations are present in the vicinity of both landfills there is a lack of distinction between the background and emission plume for this metal. A lack of distinction between these areas is also apparent for Ba concentrations. An area of enriched normalized Fe concentrations is present in the vicinity of both landfills and a background and emission plume region are clearly defined. Also, an area of enriched normalized Ba concentrations occurs in the vicinity of landfill 2 and a clearly defined background and emission plume region are also present. In the normalized Ba concentrations there are two small areas in the enriched region between landfills which have values below the highest value in the background. Otherwise all normalized concentrations for Zn, Fe and Ba in the landfill emission plume are higher than all normalized background concentrations. The use of normalized metal concentrations for Zn, Fe and Ba appears to define the background and landfill emission plume areas along the stream more clearly than that for the NAEWS or metal concentrations in the Mn phase.

Various studies report decreasing metal concentrations in whole sediments in a downstream direction from a contamination source. Axtmann and Luoma (1991) report this trend for Cu, Zn, Pb, Cd and Ag concentrations in sediments affected by mining activities over a distance of 380 km. There are other studies that show this trend for metals over smaller distances (Wolfenden and Lewin, 1978; Chapman *et al.*, 1983; Mann and Lintern, 1983; Rybicka and Kyzol, 1987; Leenaers *et al.*, 1988). There appears to be a lack of decreasing normalized concentrations for Zn, Fe and Ba downstream in the enriched sediments. Such a trend may be undetectable over the small distance used in this study. Mantei and Coonrod (1989) and Mantei and Sappington (1994) observed a lack of decreasing trend for elevated concentrations of Cu, Zn and Ag in the NAEWS in a stream affected by landfill leachate. Their study included samples collected over a distance of 1.5 km. Lack of enrichment of Co in the sediments along the stream indicates the concentrations represent natural background fluctuations. This is indicated in Fig. 2A to C.

Content of metals and normalized metals in the Mn phase

Table 2 compares the content of metals with that of normalized metals in the Mn phase. The mean concentration of each metal in the landfill emission plume is lower than that in the background. As mentioned before, Ba concentrations are not enriched in the sediments from landfill 1 leachate. Therefore, samples 27 to 35 between landfills are treated as background for Ba concentrations. The mean normalized concentration for Zn, Fe and Ba is significantly higher in the landfill emission plume than in the

Table 1. Metals enriched in the geochemical phases and in the hot single HNO_3 extraction portion of whole sediments (NAEWS) in the landfill plume^a

Sequentially separated geochemical phase	Metals in this study enriched in sediments affected by leachate from	
	landfill 1	landfill 2
exchangeable cations	—	Ba
carbonate	Zn	Ba
Mn oxides/hydrous oxides (Mn phase)	Zn	—
Fe oxides/hydrous oxides (Fe phase)	Zn, Fe	Fe
organics	Zn	—
remnant	Fe	—
NAEWS	Zn, Fe	Fe

^aData-summarized from Mantei and Foster (1991)

background while that for Co is similar. This result for Co would be expected since the sediments are not enriched in Co concentrations. If metal concentrations are proportionately dependent on that of the Mn phase the normalization method should result in a similar normalized metal value from sample to sample. This similarity may be indicated in the background especially for normalized Fe and Zn concentrations. Higher values for normalized Zn, Fe and Ba concentrations in the landfill emission plume as compared with that in the background would appear to indicate a higher loading of metal concentrations with respect to Mn concentrations. The coefficient of variation (CV) for Zn and Fe concentrations are higher in the emission plume than in the background while that for Ba and Co are similar to background values. The CV values for Zn, Fe and Ba normalized concentrations are significantly higher in the samples in the landfill emission plume than in the background while that for Co is similar. Mantei and Sappington (1994) found significantly higher CV values for metal concentrations in sediments affected by landfill leachate compared to that for control sediments.

As mentioned earlier, variations of the concentrations of each metal in the Mn phase of the sediments

along the stream appear similar. This similarity may indicate a dependence of Zn, Fe, Ba and Co concentrations on that of Mn. Correlation coefficient (CC) values relating concentrations of each metal with that of Mn are shown in Table 2. The values relating Zn and Mn, Fe and Mn, and Ba and Mn are appreciably higher for samples representing the background as compared to that for the landfill emission plume. The reason for a difference in the CC values for the two areas may be explained by a change in the water chemistry during the formation of the Mn phase. A change in pH of the stream waters and/or a change in redox environment are important factors which may influence the concentrations of the Mn phase and incorporated metals. A change in pH was ruled out since the pH of the stream waters in the two areas were the same (Mantei and Foster, 1991). It is well known that Mn^{+4} and Fe^{+3} would act similarly in the same redox environment. Mantei and Foster (1991) report Fe concentrations in the Fe phase and Mn in the Mn phase decrease sharply in the landfill emission plume beginning with sample 27 in the area of landfill 1. This decrease in concentration for Mn and other metals in the Mn phase is apparent in Fig. 2B. A more reducing environment in the landfill emission plume may explain lower concentrations of

Table 2. Comparison of metal content with normalized metal content in the Mn phase of the sediments

metal	background samples			samples within landfill emission plume		
	$\bar{x}$ ($\mu\text{g/g}$)	σ ($\mu\text{g/g}$)	CV ^a	$\bar{x}$ ($\mu\text{g/g}$)	σ ($\mu\text{g/g}$)	CV ^a
Zn	2.46	0.84	0.34	2.12	1.51	0.71
Fe	58.50	16.50	0.28	44.50	19.10	0.43
Ba	55.50	23.00	0.41	20.10	8.76	0.44
Co.	8.40	4.10	0.49	3.54	1.95	0.55
Mn	843.00	253.00	0.30	323.00	177.00	0.55
Normalized Metal						
	$\bar{x}$	σ	CV ^a	$\bar{x}$	σ	CV ^a
(Zn/Mn) $\times$ 1000	2.89	0.55	0.19	7.2	3.5	0.49
(Fe/Mn) $\times$ 100	7.0	0.98	0.14	17.8	12.9	0.73
(Ba/Mn) $\times$ 100	7.4	1.6	0.22	11.9	4.7	0.40
(Co/Mn) $\times$ 1000	11.2	1.3	0.12	10.7	1.7	0.16
			CC ^b			CC ^b
			+0.91			+0.68
			+0.88			+0.40
			+0.87			+0.56
			+0.94			+0.95

^aCoefficient of variation (CV): ($\sigma/\bar{x}$).

^bCorrelation coefficient for metal and Mn concentrations.

Mn and Fe in their respective phases and lower concentrations of the metals associated with the Mn phase. Unfortunately, no Eh measurements were taken along the stream to determine if there was a difference in redox conditions between the two areas.

Another mechanism which may explain the lower concentration of metals in the landfill plume area is a dilution of the stream waters. A large spring contributes water to the study stream in the vicinity of landfill 1. However, a mechanism to account for a difference in the CC values of the two areas cannot be given. Correlation coefficient values for concentrations of metals and Fe from the Fe phase extraction were calculated from raw data used by Mantei and Foster (1991). Values for metals enriched in the landfill emission plume and Fe were compared with the same for the background. Results indicated a lack of consistently higher CC values in the background samples as compared to that in the emission plume. As mentioned before, an Al phase with associated metals may be included in the Fe phase extraction. This could explain the inconsistent CC values in this phase as compared to that in the Mn phase.

The CC value between Co and Mn concentrations in the background samples is similar to that in the landfill emission plume. This similarity suggests that concentrations of Co available for incorporation into the Mn phase would be similar in the background and landfill emission plume areas.

Concentrations of Zn and Fe in the Mn phase are very small compared to the total concentration of each metal in the whole sediment sample while that for Ba and Co are much higher. The percentages of Zn, Fe, Ba, and Co in the Mn phase are 4.5, 0.6, 23, and 26 respectively. Some may argue that the validity of the results obtained for Zn and Fe may be questioned because the concentrations of both metals may not reflect the principal behavior of these metals in the total sediments. For example, in the sequential extraction of phases from the sediments, Fe and Zn concentrations reported in the Mn phase extraction may originate in part or totally from the undissolved Fe phase. However, Chao (1972) reports small concentrations of Fe in the Mn phase extraction which originate from the Fe phase. The Fe phase is also known to contain relatively high Zn concentrations (Mantei and Foster, 1991). We believe the results obtained by the normalized metal concentration method are valid because they are consistent with the findings of Mantei and Foster (1991) concerning metal enrichment in the landfill emission plume.

SUMMARY AND CONCLUSIONS

The similarity in the variations of Zn, Fe, Ba and Co concentrations with that of Mn and the relatively high correlation coefficient values for these metals and Mn indicates a dependency of the concentrations of these metals on that of the Mn phase. Based on this

similarity it is believed a ratio of the concentrations of each metal and that of Mn justify a normalized metal concentration in the Mn phase. The analysis of data indicates the use of normalized metal concentrations in the Mn phase of the sediments clearly differentiates the landfill emission plume from the background along the study stream.

Mantei and Foster (1991) found Fe and Ba concentrations enriched in the Fe and remnant phases of the sediments while Ba concentrations were enriched in the exchangeable cations and carbonate phases (Table 1). These metal concentrations are not enriched in the Mn phase, yet normalized concentrations for these metals show an enrichment in the sediments. The normalization method appears to indicate those metals whose concentrations are enriched in other geochemical phases but not in the Mn phase.

Normalization of metal concentrations in the carbonate and Fe phases of sediments might also prove useful, but use of the Fe phase and bound metals as commonly extracted may not be practical in this case. It is believed metal concentrations reported in the Mn phase extract were representative for the phase. We believe the non-selectivity of phase extractions and metal redistribution during the chemical separation of the Mn phase and prior geochemical phases did not appear sufficiently large to invalidate the results of this research. Use of normalized metal concentrations in some geochemical phases of sediments affected by anthropogenic activities may aid in data evaluation.

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