Heavy Metals in Stream Sediments: Effects of Human Activities

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ABSTRACT / The content of 11 heavy metals in the sediments of a stream system was determined by atomic absorption analysis. Geochemical phases were investigated using a sequential extraction scheme, and bulk contents were assessed with a single HNO_3 extraction. Certain heavy metals were associated with different geochemical phases. Co, Mn, and Ba concentrated primarily in the carbonate and Mn phases, while all the remaining metals concentrated in the Fe and remnant phases. Features located along the stream system influenced the content of heavy metals. Results from the geochemical phases indicated Cu, Pb, Zn, Cd and Ag were emitted by one landfill, while Cd, Ba, and Ag were emitted by a second landfill. A wastewater treatment facility appeared to emit Ni and Cu. A stream draining a reservoir and joining the study stream resulted in dilution of the heavy metals in the sediments. A populated area along the study stream appeared to emit Mn. The single HNO_3 extraction procedure is quicker to perform than the sequential extraction but does not indicate the phase associations.

Introduction

Various studies have reported heavy metals adsorbed on or residing in stream sediments. Castaing and others (1986), Ramamoorthy and Rust (1978), and Rule (1986) studied the enrichment of heavy metals in river sediments influenced by industrial wastes. These include Cu, Pb, Zn, Ni, Cd, Hg, Co, Cr, Fe, and Mn. Reece and others (1978) and Yim (1981) reported the quantities of Cu, Pb, Zn, Cd, Sn, As, W, Fe, and Mn in the sediments of rivers affected by mining activities. Mantei and Coonrod (1989) studied the Cu, Pb, Zn, Cd, and Ag content in the stream sediments adjacent to a sanitary landfill. Other studies indicate the relative affinity of heavy metals within the geochemical phases formed under laboratory conditions. Murray (1975) reports a relative affinity of heavy metals with hydrous manganese dioxide ($Cu^{2+} > Co^{2+} > Mn^{2+} > Zn^{2+} > Ni^{2+} > Ba^{2+}$). Kinniburgh and others (1976) indicate some heavy metals are adsorbed by iron oxide in the order ($Pb^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Cd^{2+} > Co^{2+}$) and are adsorbed by aluminum oxide in the order ($Cu^{2+} > Pb^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+} > Cd^{2+}$). Forbes and others (1976) list some heavy metals that have an affinity for goethite ($Cu^{2+} > Pb^{2+} > Zn^{2+} > Co^{2+} > Cd^{2+}$). However, there are no known data in the literature relating heavy metal distributions, concentrations, or affinities for specific geochemical phases in natural stream sediments.

This study deals with the variation of the quantities of Cu, Pb, Zn, Cd, Co, Ni, Mn, Fe, Cr, Ba, and Ag in the geochemical phases and in a single HNO_3 extraction of the stream sediments located along a stream system in a populated region in southwest Missouri, U.S.A. Features located in the vicinity of the stream have the potential to affect the heavy metal concentration in the sediments. These features include two landfills, one wastewater treatment facility, a stream that drains a reservoir and joins with the study stream, and a more densely populated area.

Location and Setting

The study area is located on the Springfield Plateau in southwestern Missouri and lies just north of the city limits of Springfield, Missouri (Fig. 1). The city has a population of about 160,000 and can be classified as a regional market center or service-oriented city with a particular emphasis in medicine and education. The detailed map of the study area shows the sediment sampling sites along the westward-flowing South Dry Sac and Little Sac rivers and the features that constitute the points of interest in this study (Fig. 2).

The two municipal sanitary landfills along the stream were active for six to seven years before closing in 1968. Records indicate quantities of photographic, battery, electronic, and medical wastes were added to the landfills. Leachates from both landfills were observed flowing into the study stream.

The wastewater treatment facility is located at the edge of landfill 2. This facility in part treats solutions from solid-state circuitry companies. The treated solutions are then added to the study stream. Records indi-

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Figure 1. The location of the study area.

cate these solutions contain quantities of heavy metals including Cu, Ni, Ag, and Zn.

The Lake McDaniel reservoir is an important source of municipal water for the Springfield area. The stream draining the reservoir joins with the study stream between sampling locations 33 and 34 (Fig. 2).

A more densely populated area lies along part of the study stream and includes primarily residential and farming facilities. A municipal golf course also is located in this area.

The entire study area is underlain by the Burlington-Keokuk limestone formation. This slightly westward-dipping formation consists of a light buff, very coarsely crystalline, fossiliferous, crinoidal limestone and is quarried for agricultural limestone, road metal, and lime manufacture in this region.

Methods

Choice of Sediment Size and Sample Collection

Higher quantities of metals generally accumulate on smaller sediment grain fractions because of the higher surface area-to-grain size ratio (Gibbs 1973; Griffen and others 1976; Harding and Brown 1978; Ramamoorthy and Rust 1978; Rule 1986; Sinex and Helz 1981; Mantei and Coonrod 1989; Yanful and others 1988). We believed that very fine sand would be a grain size fine enough to accumulate higher quantities of heavy metals in the sediments yet would be large enough to resist transport and to have longer residence at a stream location.

Forty-six stream sediment samples were collected at approximately 0.4-km intervals along the study stream system (Fig. 2). Each sample was taken as near to the center of the stream as possible. The samples were wet sieved at each collection site and the <0.88- to >0.074-mm (very fine sand) size saved for chemical analysis. The pH of the streamwaters was measured at each collection site. In addition, ten equally spaced pH measurements were taken along the stream draining the Lake McDaniel reservoir.

Chemical Extraction Methods

Two different chemical extraction procedures were used on each of the 46 sediment samples to study the heavy metal content and trends along the study stream. A 1-g portion of each sample was subjected to a sequential extraction of the geochemical phases. These phases include the exchangeable cations, carbonate, Mn oxides/hydrous oxides, Fe oxides/hydrous oxides, organics, and remnants (Table 1). This is a modified version of the procedure described by Yanful and others (1988). A second 1-g portion was treated with a single wash of 6 N HNO_3 at 85°C for 18 h to yield total heavy metal content. A shaker bath was used in all washings for both procedures. Although the sequential extraction procedure is tedious and time-consuming to perform, the results reveal important heavy metal concentrations, trends, and other information obtained from the geochemical phases not available from the results of the single HNO_3 extraction.

Chemical and Data Analysis

The Cu, Pb, Zn, Cd, Co, Ni, Mn, Fe, Cr, Ba, and Ag contents in each sample for both the geochemical phases and single HNO_3 extraction procedures were determined using a Varian 1475 atomic absorption spectrophotometer. Duplicate analyses for each heavy metal on the same ten sample locations for each extraction procedure were performed only to obtain an estimate of the precision for the analyses. The data generated by the duplicate analyses were not used in the calculation of other statistical values.

The mean, median, standard deviation, correlation coefficients, and threshold values of the data were computed with the aid of a software computer program called Minitab. The trend charts for the heavy metals were generated by Quattro Pro.

Results

Heavy Metal Affinity for Geochemical Phases

The results of the concentrations of the heavy metals in the geochemical phases of the stream sediments are

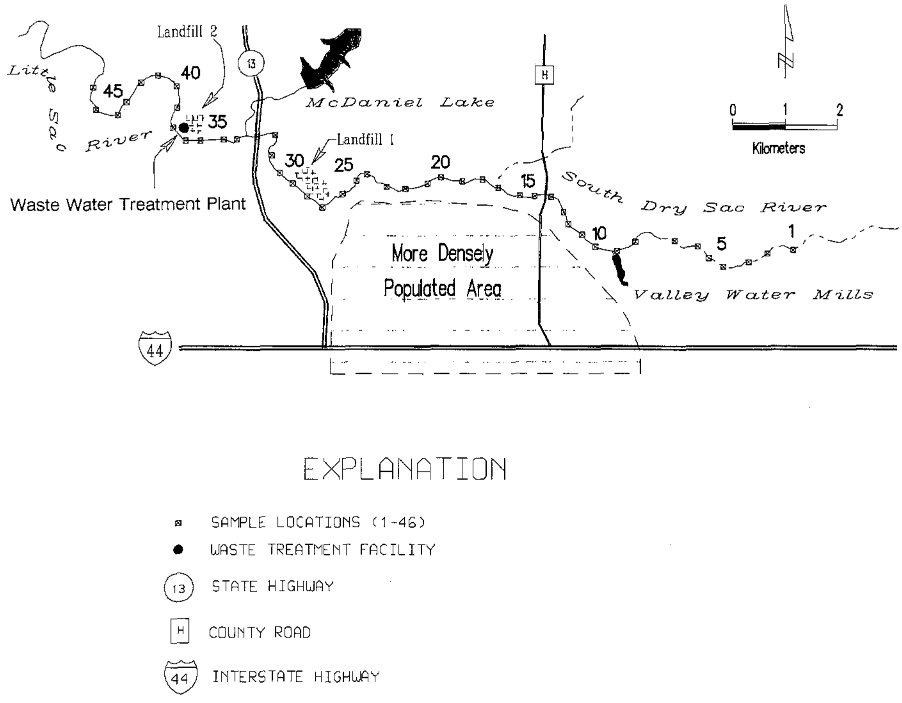

Figure 2. Sample location sites and detailed map of the study area.

Table 1. Sequential extractions of the geochemical phases in the stream sediments

Extraction method	Geochemical phase released
1. Single wash with a solution of 1 M $MgCl_2$ at pH 7.0 and 20°C for 1½ h	Exchangeable cations
2. Two washes with a solution of 1 M sodium acetate–acetic acid buffer at pH 5.5 and at 85°C for 10 h each washing	Carbonates
3. Single wash with a solution of 0.1 M hydroxylamine hydrochloride at pH 2 with HNO_3 and at 22°C for 1 h	Manganese oxides/hydrous oxides (Mn phase)
4. Single wash with a solution of 1 M hydroxylamine hydrochloride in 35% acetic acid at 65°C for 6 h	Iron oxides/hydrous oxides (Fe phase)
5. Two washes with a solution of 20% H_2O_2 at 85°C and acidified to a pH 2.0 with HNO_3 for 10 h each washing	Organics
6. Single wash with a solution of 6 N HNO_3 at 85°C for 18 h	Remnant phase(s) such as sulfides, and/or aluminum oxides/hydrous oxides

summarized in Table 2. The mean content, relative error value (referring to the precision of the analytical method), and standard deviation of the sample are included. An NDA designation is given where metals were not detectable for a geochemical phase by the chemical method of analysis.

The Fe oxides/hydrous oxides phase (Fe phase) and the Mn oxides/hydrous oxides phase (Mn phase) are not commonly separated and are usually reported as a single phase (Tessier and others 1979; Yanful and others 1988). It was believed that the Mn phase could reveal important information about the heavy metal content or trends in the sediments that would not appear in the combined Fe and Mn phases. A method isolating the Mn phase (Chao 1972) was used in this study. The results in Table 2 show the mean content of Fe in the Mn phase to be low and the Mn mean content in the Fe phase to be quite high. This appears to indicate the Mn phase was cleanly separated from the Fe phase, but the separation was incomplete. Hence, the Zn, Co, and Ba

Table 2. Metal content (μg/g) in geochemical phases of sediments

Geochemical phase	Cu	Pb	Zn	Cd	Co	Ni	Mn	Fe	Cr	Ba	Ag
1. Exchangeable cations	0.10[a] ± 0.01[b] (0.31)[c]	NDA[d]	NDA	NDA	NDA	NDA	43.99 ± 6.6 (46.9)	NDA	NDA	18.6 ± 5.9 (12.0)	NDA
2. Carbonates	0.55 ± 0.06 (1.0)	2.05 ± 0.28 (0.65)	12.8 ± 1.35 (4.7)	NDA	4.65 ± 0.7 (2.0)	4.7 ± 0.5 (0.9)	878.00 ± 131.00 (138.1)	NDA	NDA	86.7 ± 10.4 (24.9)	NDA
3. Manganese oxides/ hydrous oxides	NDA	NDA	2.31 ±0.7 (1.1)	NDA	6.5 ±0.8 (4.2)	NDA	584.00 ±36.20 (355.1)	52.4 ±9.4 (18.7)	NDA	47.0 ±10.3 (25.5)	NDA
4. Iron oxides/ hydrous oxides	8.7 ± 0.8 (3.1)	36.2 ± 1.8 (10.3)	19.8 ± 1.8 (9.6)	0.17 ± 0.03 (0.08)	9.8 ± 0.9 (2.8)	7.5 ± 0.8 (1.9)	427.00 ± 68.3 (151.0)	8,430.0 ± 1,290.00 (1838.0)	10.8 ± 1.1 (2.5)	38.7 ± 8.6 (13.4)	0.14 ± 0.02 (0.06)
5. Organics	1.5 ± 0.15 (0.7)	0.15 ± 0.04 (0.89)	5.9 ± 0.7 (2.0)	NDA	NDA	NDA	4.5 ± 2.2 (14.5)	101.8 ± 20 (36.8)	3.8 ± 0.6 (0.86)	NDA	NDA
6. Remnant	5.1 ± 0.2 (1.68)	5.99 ± 0.3 (2.24)	18.2 ± 1.2 (4.8)	0.24 ± 0.06 (0.09)	3.7 ± 0.3 (1.1)	7.3 ± 0.5 (2.6)	25.3 ± 3.9 (7.4)	182.0 ± 30 (4.9)	13.6 ± 0.7 (3.8)	13.5 ± 0.5 (4.0)	0.31 ± 0.05 (0.09)

[a] Mean content.

[b] Relative error value referring to the precision of the analytical method.

[c] The standard deviation of the sample.

[d] Nondetectable amounts.

quantities appearing in the Mn phase should be wholly associated with that phase, while a portion of the quantity of each of these metals appearing in the Fe phase is thought to be associated with the incompletely separated Mn phase. A proportion relating the content of the Mn in the Mn and Fe phases was used to determine the portions of Zn, Co, and Ba associated with the Mn phase included in the Fe phase. The quantities of each of these metals then was adjusted to give the equated metal amounts in both of these phases. Hence, the adjusted mean content in micrograms per gram of Zn, Co, and Ba in the Mn phase would be: Zn (4.01), Co (11.3), and Ba (81.3). The adjusted mean content of these metals in the Fe phase would be: Zn (18.1), Co (4.7), and Ba (4.4). It can be seen the Zn content in the Fe phase is predominantly associated with that phase. However, in this phase, a large portion of each of the Co and Ba quantities is associated with the Mn phase. The association of Co and Ba with the Mn in both the Mn and Fe phases is indicated by the correlation coefficient. In the Mn phase the correlation coefficients between Mn and Ba and Mn and Co are 0.93 and 0.97 respectively, while in the Fe phase, Mn–Ba and Mn–Co are 0.90 and 0.92 respectively. No such high correlation exists between Fe and Ba or Fe and Co in the Fe phase.

The high quantity of manganese in the carbonate phase is not thought to represent an incomplete separation between this phase and the Mn phase but represents the Mn^{2+} as a carbonate mineral. Moreover, it is apparent that the Fe and remnant phases contain detectable amounts of all the heavy metals in this study while the fewest number of detectable heavy metals (Cu, Mn, Ba) occur in the exchangeable cation phase.

Based on the mean content of the heavy metals in Table 2 and the adjusted Zn, Co, and Ba quantities in the Mn and Fe phases, the following metals appear to concentrate in the geochemical phases of the sediments in the following order: Cu (Fe > remnant > organics > carbonates > exchangeable cations); Pb (Fe > remnant > carbonates > organics); Zn (Fe = remnant > carbonates > organics > Mn); Cd (remnant > Fe); Co (Mn > carbonates = Fe > remnant); Ni (Fe = remnant > carbonates); Fe (Fe > remnant > organics > Mn); Cr (remnant > Fe > organics); Ba (carbonates > Mn > exchangeable > remnant > Fe); Ag (remnant > Fe).

Heavy Metal Trends in Geochemical Phases of Sediments

Specific trends occur in the heavy metal content in the geochemical phases of the sediments along the study stream (Fig. 3A and B). High quantities of certain metals are present in the sediments adjacent to landfill

Figure 3. **(A)** The trends of the Cu, Pb, Zn, Cd, and Co content in the geochemical phases of the sediments along the stream. NDA signifies nondetectable amounts. **(B)** The trends of the Ni, Mn, Fe, Cr, Ba, and Ag content in the geochemical phases along the stream. NDA signifies nondetectable amounts.

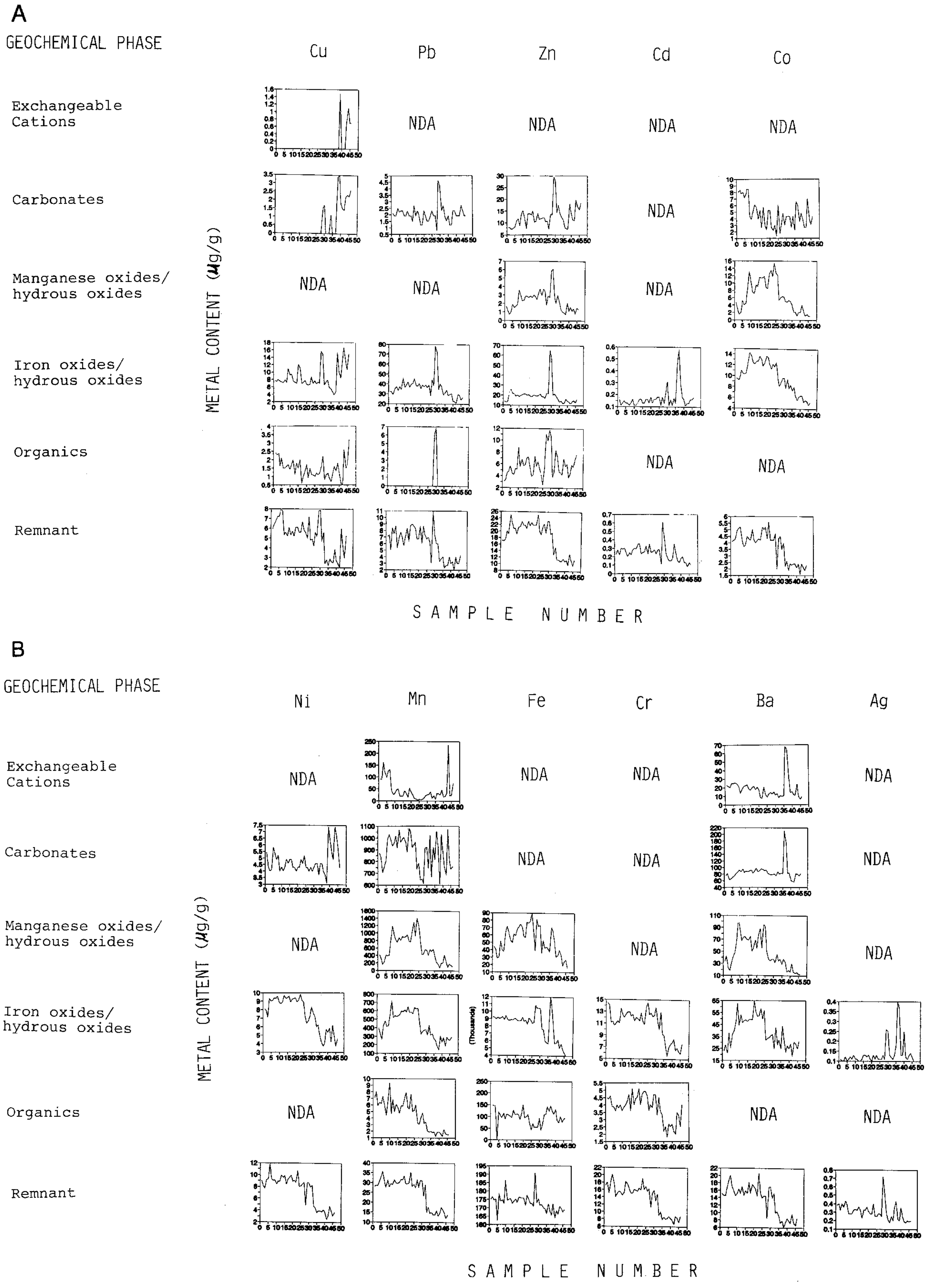
A
GEOCHEMICAL PHASE
Cu
Pb
Zn
Cd
Co
Exchangeable Cations
Carbonates
Manganese oxides/ hydrous oxides
Iron oxides/ hydrous oxides
Organics
Remnant
NDA
METAL CONTENT (µg/g)
SAMPLE NUMBER
B
GEOCHEMICAL PHASE
Ni
Mn
Fe
Cr
Ba
Ag
Exchangeable Cations
Carbonates
Manganese oxides/ hydrous oxides
Iron oxides/ hydrous oxides
Organics
Remnant
NDA
(Thousands)
METAL CONTENT (µg/g)
SAMPLE NUMBER

Table 3. Sample numbers with anomalously high metal values in the geochemical phases

Geochemical phase	Cu	Pb	Zn	Cd	Co	Ni	Mn	Ba	Ag
1. Exchangeable cations	39[a] 43, 44[a] 45, 46	—	—	—	—	—	3, 43[a]	36[a], 37[a]	—
2. Carbonates	38[a], 39[a] 46	29[a], 30[a]	29[a], 30[a]	—	—	39[a], 40 43[a], 44	—	36[a], 37[a]	—
3. Manganese oxides/ hydrous oxides	—	—	29[a], 30[a]	—	24	—	24	—	—
4. Iron oxides/ hydrous oxides	29, 30 39, 43 46	29[a], 30[a]	29[a], 30[a]	36[a], 37[a]	—	—	—	—	29, 30 36[a], 37[a]
5. Organics	46	29[a], 30[a]	27, 28 29, 30	—	—	—	—	—	—
6. Remnant	—	29	—	29[a], 30[a]	—	—	—	—	29[a], 30

[a] Sample numbers with metal values in excess of the mean plus 3 standard deviations.

1 (samples 29 and 30), landfill 2 (samples 36 and 37), and in some samples downstream from the wastewater treatment facility. A statistical method was desired that would indicate the sample numbers along the stream having anomalous or significantly high heavy metal values. The anomalously high heavy metal values in the samples in the vicinity of the landfills should indicate which metals are emitted by the landfills. Rose and others (1979) describe a common method to establish the threshold value (mean content plus 2 standard deviations) and the anomalous values for a single symmetrically distributed population. The threshold value for each metal population in each geochemical phase was calculated using the mean content and standard deviation values given in Table 2.

Table 3 lists the sample numbers of the heavy metals that have anomalously high values in the geochemical phases. Sample numbers 29, 30, 36, and 37 frequently repeat for many of the heavy metals. It appears that landfill 1 emitted Cu, Pb, Zn, Cd, and Ag into the stream and that landfill 2 added Cd, Ba, and Ag. However, the wastewater treatment facility located at the edge of and downstream from landfill 2 could be the cause of the anomalous Ni and Cu quantities observed in some of the downstream samples. As mentioned before, this facility adds treated solutions with quantities of Ni and Cu to the study stream. Furthermore, no high or significant Ni or Cu quantities are found in the sediment samples affected by landfill 2.

Another interesting area of heavy metal variation in the sediments first appears at the confluence of the study stream and the stream draining the Lake McDaniel reservoir located between sample sites 33 and 34. A lower quantity of many of the heavy metals in the sediments occurs at this confluence and continues downstream except at sites influenced by landfill 2 and/or the wastewater treatment facility. A sharp drop in the heavy metal content in the sediments at the confluence is most evident for specific metals in the following phases: Ni, Fe, and Cr in the Fe phase; Cr in the organic phase; and Cu, Pb, Zn, Co, Ni, Mn, Cr, and Ba in the remnant phase. The heavy metals that do not show a sharp drop but indicate a lower quantity trend in specific geochemical phases downstream from the confluence are: Pb and Zn in the Fe phase; Mn in the organic phase; and Cd, Fe, and Ag in the remnant phase.

Heavy metal solubility is influenced by the pH of natural waters, and this relationship may be a factor in this stream system. The pH measurements taken along the study stream and the stream draining the reservoir showed that the mean pH of the main stream was 7.74, with a range of 7.6–7.9, while that of the side stream was 8.45 (range 8.35–8.6). The higher pH of the reservoir stream may indicate lower quantities of metals in its waters, thereby diluting the heavy metal concentration in the waters of the study stream at and downstream from the confluence. The dilution would explain the lower quantities of metals adsorbed or precipitated in these sediments. The higher pH of the reservoir stream may be a function of the higher algae concentration and activity observed in this stream as compared to the study stream, as explained by Wetzel (1983). It is interesting to note that some of the detectable heavy metals in the geochemical phases do not display lower quantities at and downstream from the confluence of the two streams. This includes Pb and Mn in the carbonate phase and Zn and Fe in the organic phase.

A trend towards higher Mn, Co, and Ba quantities in the sediment samples appears in the vicinity of the more densely populated area along the stream. This trend occurs between sample locations 6 and 26 and is shown in the Mn and Fe phases (Fig. 4). As mentioned

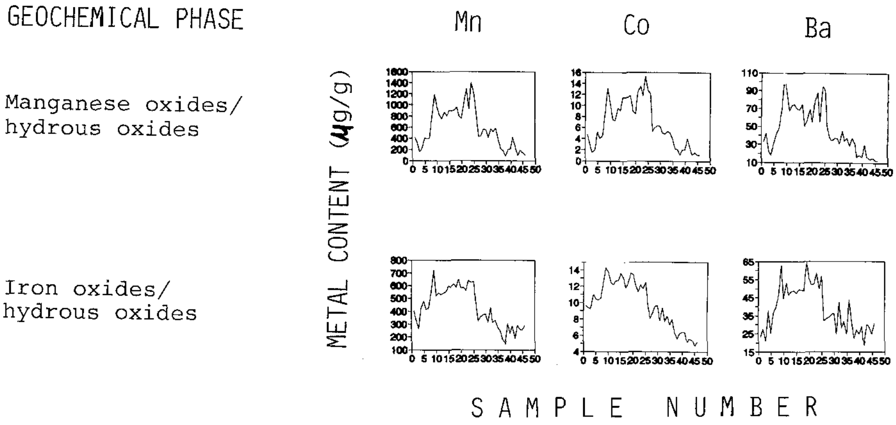

Figure 4. Higher Mn, Co, and Ba content trends in the oxides/ hydrous oxides geochemical phases of Mn and Fe in the sediments along the stream in the more densely populated area between sample sites 6 and 26. (Taken from Figs. 3A and B.)

Table 4. Metal content (µg/g) of combined extractions versus single HNO_3 extraction

Phase	Cu	Pb	Zn	Cd	Co	Ni	Mn	Fe	Cr	Ba	Ag
Combined extractions	16.05[a] (4.8)[b]	44.6 (13.3)	59.0 (13.0)	0.41 (0.13)	24.7 (7.4)	19.6 (4.3)	1,965 (549)	8,560 (1,854)	28.2 (6.7)	204.2 (55.4)	0.45 (0.13)
Single HNO_3 extraction	15.99 ± 0.8[c] (4.7)	43.8 ± 2.5 (11.9)	54.8 ± 3.7 (11.7)	0.4 ± 0.1 (0.17)	20.9 ± 1.9 (6.0)	17.3 ± 1.4 (3.6)	1,985 ± 313 (539)	12,028 ± 2,105 (1,811)	26.4 ± 1.5 (5.7)	198.9 ± 8.4 (53.7)	0.47 ± 0.07 (0.12)

[a] Mean content.

[b] Standard deviation of the sample.

[c] Relative error value referring to the precision of the analytical method.

earlier, the Mn has a very high correlation coefficient with Co and Ba in both the Mn and Fe phases. Hence, the higher quantities of Co and Ba in this area are thought to be a function of the adsorptive property of the Mn content and are considered natural in origin.

Two major factors were considered to explain a natural occurrence of the high Mn (Mn^{4+} oxide/hydrous oxide) content in the sediments of this region. A higher pH of the streamwaters and/or a higher oxidation environment might precipitate enhanced quantities of Mn. However, there was no difference in the pH of the streamwaters in this region as compared to the rest of the stream. A higher oxidation environment also was ruled out since Fe, which has a similar chemistry to Mn, does not show the same high trend in either the Mn or Fe phases in this area.

Two possible natural sources for the higher Mn can be cited. First, the Valley Water Mill's drainage into the study stream could be a source. However, its confluence with the study stream is located a considerable distance downstream from the initiation of the higher Mn trend. Second, natural springs that occur along the study stream could be a source of the higher Mn. However, there are no data that can be used to test this possibility.

It is believed that some activity associated with the more densely populated area along the stream is the source of the higher Mn trend in this region. However, a specific source of Mn is not known.

Comparison of Geochemical Extraction Phases with Single HNO_3 Extraction

A total extraction quantity for each heavy metal was determined by summing the quantity of the heavy metal within each geochemical phase for each sample location. This is identified as the combined extraction and is compared with the single HNO_3 extraction method. The heavy metal content and trends of the two methods should be similar. Table 4 shows the mean content of the heavy metals for both extraction procedures. The mean content for all heavy metal quantities in the two extraction methods compares favorably except for iron. Possibly a "matrix effect" could have caused this deviation in the atomic absorption procedure. Figures 5A and B show the trends of the heavy metal content in the sediments along the stream for both the combined and the single HNO_3 extractions. It is evident that the trends of the total heavy metal content from both extraction methods are quite similar.

In the single HNO_3 extraction, high quantities of certain metals appear in the sediment samples located adjacent to landfill 1 (samples 29 and 30), landfill 2 (samples 36 and 37), and downstream from the waste-

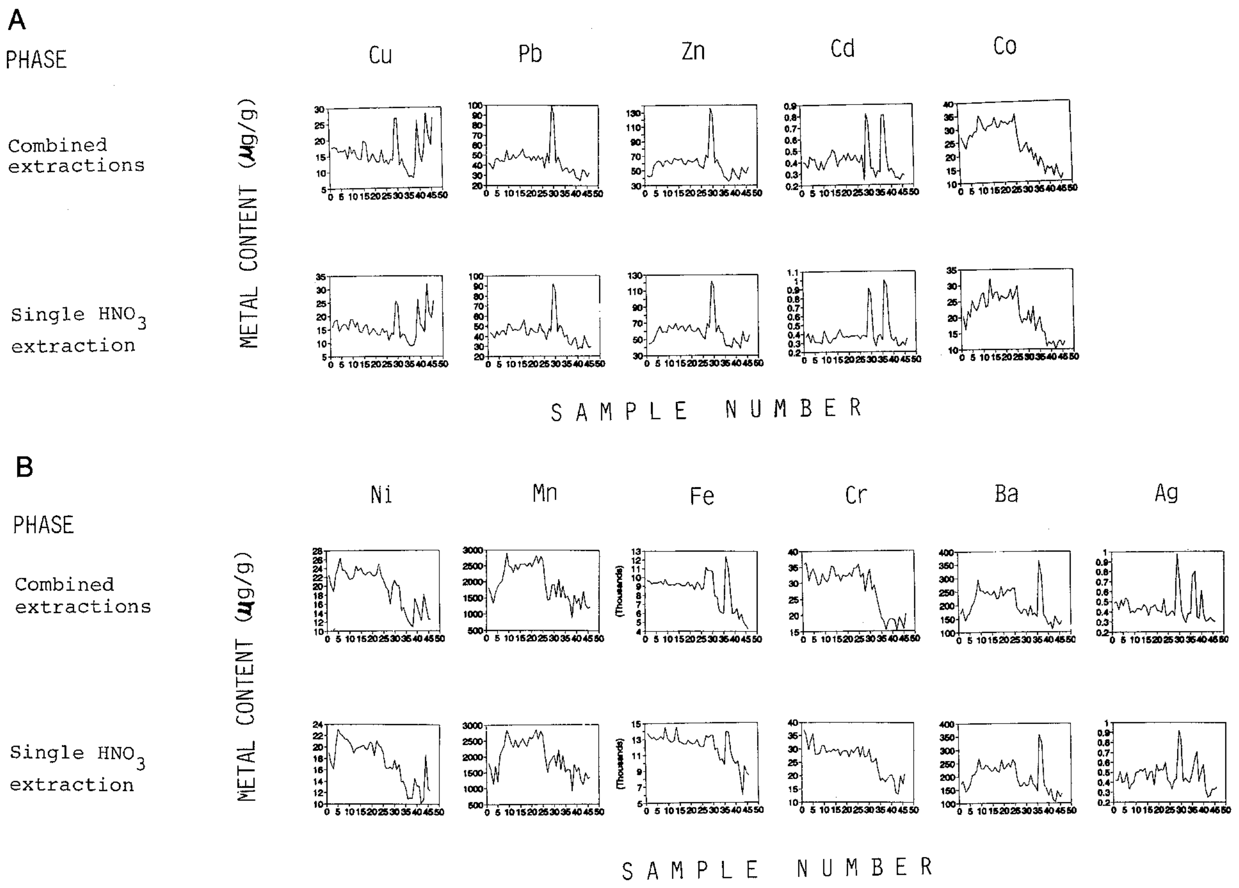

Figure 5. (A) The trends of the Cu, Pb, Zn, Cd, and Co content in the combined extraction phases versus the single HNO_3 extraction in the sediments along the stream. (B) The trends of the Ni, Mn, Fe, Cr, Ba, and Ag content in the combined extraction phases versus the single HNO_3 extraction in the sediments along the stream.

water treatment facility. This is the same as observed in the combined extractions. The sample numbers having anomalous heavy metal values were determined for both the single HNO_3 and combined extractions. Table 5 summarizes the samples that have anomalously high heavy metal values in both extractions. The comparison shows a strong similarity. For both extraction methods, the results indicate landfill 1 emitted Cu, Pb, Zn, Cd, and Ag into the stream, and landfill 2 added Cd, Ba, and Ag to the stream. Anomalous Cu values appear in the sediments downstream from the wastewater treatment facility. Except for the lack of anomalous Ni values downstream from the wastewater treatment facility, these results are the same as those obtained from the individual geochemical phases. The Ni anomaly in the carbonate phase is suppressed by the very low quantities of Ni in the Fe and remnant phases in this area along the stream (Fig. 3B). The suppression would explain why a Ni anomaly failed to show in both the combined and single HNO_3 extractions. The failure of the Ni anomalous samples to appear using the single HNO_3 extraction may indicate a disadvantage in using this method.

A trend that did not appear to be as definitive in the single HNO_3 extraction was the lower quantities of heavy metals in the sediments at and downstream from the confluence of the study stream and the stream draining the reservoir. As can be seen in Figures 5A and B, this trend may have gone unnoticed if only the single HNO_3 extraction procedure were used in this study.

The higher Mn, Co, and Ba content trends in the vicinity of the more densely populated region along the study stream is indicated in both the single HNO_3 and the combined extractions (Fig. 6). This same result was obtained from the Fe and Mn phases shown in Figure 4.

Conclusion

Co, Mn, and Ba concentrate primarily in the carbon-

Table 5. Sample numbers with anomalous values (combined phase vs. single HNO_3 extraction)

Phase	Cu	Pb	Zn	Cd	Ba	Ag
Combined extractions	29 30, 39 43, 46	29[a], 30[a]	29[a], 30[a]	29[a], 30 36[a], 37[a]	36, 37	29[a], 30 36, 37
Single HNO_3 extraction	29 30, 39 43[a], 46	29[a], 30[a]	29[a], 30[a]	29[a], 30 36[a], 37[a]	36, 37	29[a], 30 37

[a] Samples with values above the mean plus three standard deviations.

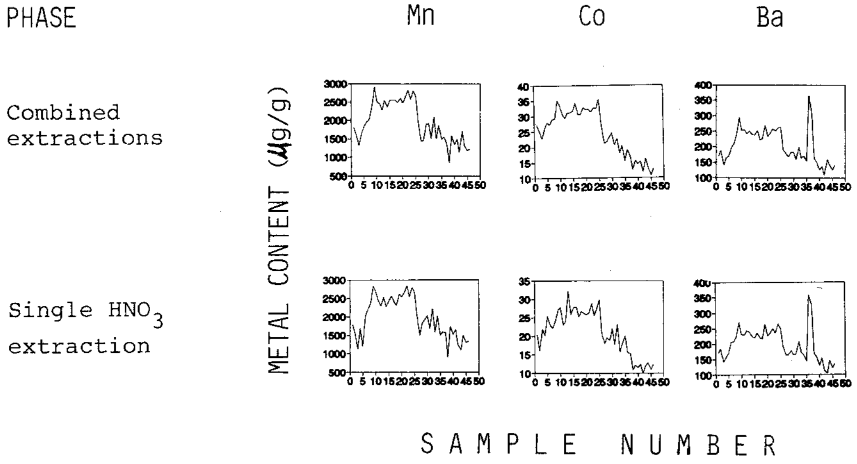

Figure 6. The higher Mn, Co, and Ba content trends in the combined extraction phases versus the single HNO_3 extraction in the sediments along the stream in the more densely populated area between sample sites 6 and 26. (Taken from Figs. 5A and B).

ate and Mn phases in stream sediments. All the remaining heavy metals in this study have the highest affinities for the Fe and remnant phases.

Although the sequential extraction procedure is tedious and time consuming to perform, there appear to be advantages employing it in a study such as this. The use of the individual geochemical phases can help to verify and/or clarify trends and significant values of heavy metals in the samples of stream sediments. The single HNO_3 extraction is a relatively quick procedure; however, when compared to the sequential extraction method, it does not show the same results as clearly in some cases. It is believed stream sediments can be used effectively to determine heavy metal emissions from point and nonpoint sources.

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