

Project No.: 03

**Heavy Metal Concentrations
in Drainage Sediments Possibly
Affected by Landfill Leachate**

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Abstract

Leachate was observed outside the confines of the Stone County Landfill, Missouri. Ants Creek and South Ants Creek located in the vicinity of the landfill may have received leachate. Both streams drain into Table Rock Lake. Previous studies of other landfills in southwestern Missouri revealed the presence of enriched concentrations of some heavy metals in drainage sediments of streams affected by leachate. Sediments were collected from the same location sites along the two aforementioned streams in 1992 and 1995. The purpose of this research was to determine if the two streams were affected by leachate and if there was a change in metal content between 1992 and 1995. Samples were also collected in 1995 from a stream which acted as the control for the study. Two different sediment size fractions were used in the study. The concentrations of Cu, Pb, Zn, Cd, Co, Ni, Cr, Fe, Mn, Ba, Ca, and Ag were determined in some geochemical phases of the finer grain size fraction while the same metals were determined from a nitric acid extraction in the larger grain size fraction. Atomic absorption techniques were used in the study. More than 4,200 metal concentration determinations were made in this study. The results indicated no enrichment of metal concentrations in the sediments of Ants Creek and South Ants Creek. Also there was no significant difference in the content of each metal in the sediments of Ants Creek compared to the same in South Ants Creek. This result was the same in samples representing both years. It was concluded that leachate from the landfill had no noticeable effects on sediments in both streams. Therefore it appeared that waters and sediments in Table Rock Lake were not enriched in these metals from landfill activity.

Introduction

Various studies have reported elevated concentrations of metals in stream sediments caused by contamination sources. There have been studies dealing with enrichment of heavy metals in river sediments influenced by industrial wastes (Ramamoorthy and Rust 1978; Castaing and others 1986; Rule 1986). These include Cu, Pb, Zn, Ni, Cd, Hg, Co, Cr, Fe and Mn. Some authors have reported Cu, Pb, Zn, Cd, Sn, As, Cr, Fe, and Mn concentrations in sediments of rivers affected by mining activities (Reece and others 1978; Wolfenden and Lewin 1978; Yim 1981; Chapman and others 1983; Mann and Lintern 1983; Moore 1985; Leenaers and others 1988; Axtmann and Luoma 1991). Studies of the enrichment of Cu, Pb, Zn, Cd, Ag, Ba, and Cr concentrations in stream sediments affected by landfills and a water treatment facility have been reported (Mantei and Coonrod 1989; Mantei and Foster 1991; Mantei and Sappington, 1994).

Traditionally, fine-grained sediment fractions have been used to study metal contamination in sediments. Eliminating coarse grained portions reduces biases resulting from differences among samples (Solomons and Forstner 1984; Bradley and Cox 1987). Higher concentrations of metals generally accumulate in smaller sediment grain fractions because of the higher surface area-to-grain size ratio (Whitney 1975; Ramamoorthy and Rust 1978; Harding and Brown 1978; Sinex and Helz 1981; Solomons and Forstner 1984; Horowitz and Elrick 1987; Moore and others 1989). Some authors have used restricted fine-grain size sediments in studies of heavy metal emissions from landfills to reduce the grain size bias in metal concentrations. Mantei and Coonrod (1989) used the <0.25-mm

to >0.149-mm (fine sand) size. The <0.088-mm to >0.074-mm (very fine sand) size fraction was used by Mantei and Foster (1991). Some studies have used less restricted grain size fractions. Compest (1991) found that trace metal trends in sediments downstream from an emission source may not be recognized in the <2-mm sediment size fraction. Rule (1986) concludes the <0.0625-mm size sediment fraction contains the greatest concentration of heavy metals. Axtmann and Luoma (1991) and Luoma and others (1989) used the <0.060 mm size sediment fraction to study metal trends in sediments affected by mining activities. Mantei and Sappington (1994) studied the metal content in two grain size fractions in stream sediments affected by landfill leachate. They concluded the <0.060 mm size fraction showed a greater enrichment of metal concentrations than the very fine sand size fraction.

There are only a few investigations which have used geochemical phases to study enrichment of metal concentrations in sediments affected by landfill leachate. Yanful and others (1988) studied the attenuation of metal concentrations in seven geochemical phases in a clay layer located below a sanitary landfill. Mantei and Foster (1991) studied the metal concentrations in six geochemical phases in stream sediments and concluded the use of these phases helped verify and/or clarify metal concentration trends and significant concentrations of heavy metals. Mantei and others (in press) reported that the ratio between a metal concentration and that for Mn in the Mn phase can enhance the difference between a landfill emission plume and the background. It is known that landfill leachate can affect the environment years after the landfill has become inactive.

There is no known comprehensive study which compares the difference in metal concentrations in sediments of a stream affected by landfill leachate from different years.

In this study we report the affects of landfill leachate on the sediments of two streams located in the vicinity of the landfill. Landfill leachate was observed to enter these streams via tributary streams. The two streams drain into Table Rock Lake. If leachate has affected these streams and drainage sediments, the landfill may have an impact on the lake. We determine if the very fine sand grain size and coarse silt size fractions of the sediments contain elevated metal concentrations, and if so, whether there is a greater extent of enrichment in one size. We compare metal concentrations in the geochemical phases of the sediments to the same for a single nitric acid extraction. We compare the metal concentrations in the sediments collected from the two streams from two different years to show if there is a change in metal concentrations.

Location and Setting

The Stone County (Renfro) Sanitary Landfill and study area are located immediately to the west of the city of Branson West, Missouri (Fig. 1). Leachate seeps were found in small streams whose channels originated near the base of the landfill and joined South Ants Creek located approximately 1 km to the south. The geology and topography of the area indicated Ants Creek located approximately 0.8 km north of the landfill may also receive leachate. Fractures present in the rocks below the landfill may contain leachate which could migrate across the drainage divide into the stream. The

sediments in Peach Orchard Creek located approximately 8 km north-northwest of the landfill was chosen as the control for the study. This stream is not affected by landfill leachate. Each of the three streams flow westward into Table Rock Lake. The channels of Ants Creek, South Ants Creek, and the control stream are located in the same geologic rock formation. The tributaries of each stream drain the same rock formations. The physical nature of the three streams are similar. They are similar in size, associated with similar vegetation cover and have similar peak and average water flow. Other than landfill activity there are no known land use practices or natural mineral deposits which could affect the aforementioned streams.

The landfill received permission to operate in 1976. In 1988 the landfill filled to capacity, closed and an extension of the landfill site was given permission to operate. The extension is located adjacent and to the west of the old landfill site. Violations against emission standards resulted in the closing of the landfill complex on April 1, 1993.

Methods

Sample Collection

Two sediment collection periods were in this study. In 1995, 15, 14, and 30 sediment samples were collected from Ants Creek, South Ants Creek, and the control stream, respectively. Sediment samples were also collected from the same location sites in Ants Creek and South Ants Creek in 1992. Each sample in Ants Creek and South

Ants Creek were collected at approximately 440-m intervals (Fig. 1). Each sample from the control stream was collected at approximately 220-m intervals. All samples were taken as near to the center of the stream as possible and from the top 6-15 cm of the sediment deposit. All samples collected from both years were wet sieved in the field and the very fine sand size sediment fraction retained for analyses. In addition, the coarse silt size fraction was retained from the location sites along Ants Creek, South Ants Creek, and the control stream during the 1995 collection. A similar collection procedure was used by Mantei and Foster (1991) and Mantei and others (1993). The aforementioned wet sieving procedure resulted in no significant contamination to the samples (Mantei and Sappington 1994). The pH of the stream waters was measured at every sample location site along Ants Creek, South Ants Creek, and the control stream during sample collection for both years to determine if and to what extent it may have influenced the variation of metal concentrations in the sediments.

Sample preparation; chemical and data methods

Each sample was suspended in deionized water to eliminate clay size fragments that may have remained on the sediments (Mantei and others 1993). After drying, each sample was disaggregated and slightly mixed with a glass stirring rod.

Two chemical extraction procedures were used to determine metal concentrations in the sediment samples. A 1.5 gram portion of each sample representing the very fine sand size fraction was subjected to a sequential chemical extraction of the geochemical

phases. These phases included the exchangeable cations, carbonates, Mn oxides/hydrous oxides (Mn phase), Fe oxides/hydrous oxides (Fe phase), and remnants. These phases were used in similar studies (Yanful and others 1988; Mantei and Foster 1991). A 1.5 gram portion of each sample representing the coarse silt size fraction was treated with a single wash of 6 N HNO₃. The HNO₃ extraction procedure is the more popular and widely used procedure (Mantei and Coonrod 1989; Mantei and Foster 1991; Mantei and Sappington 1994).

The Cu, Pb, Zn, Cd, Co, Ni, Cr, Fe, Mn, Ba, Ca, and Ag concentrations in each geochemical phase was determined using the Shimadzu 680U model atomic absorption spectrophotometer. A selective incorporation of metals in the geochemical phases resulted in non-detectable concentrations of some metals in some phases. This speciation of metals in geochemical phases was reported by Mantei and Foster (1991). Interferences in the aqueous chemistry did not allow the determination of Ba concentrations in the single HNO₃ extraction procedure. Concentrations of all the other metals were determined in this extraction. A total of 4246 metal concentration determinations were made in this study.

The mean, standard deviation, and coefficient of variation for each detectable metal in the sediments of each stream, in each geochemical phase for each year and in the single HNO₃ extraction were determined. A trend chart representing the variation of metal concentration in the sediments along each stream were also prepared.

Results and Discussion

Figures 2 to 6B inclusive show the metal concentration trends in geochemical phases of the very fine sand size fraction of the sediments along Ants Creek, South Ants Creek and the control stream. Figures 7A and 7B show the results of the combined metal concentrations for the geochemical phases. The aforementioned figures contain the metal concentration trends in the sediments from the 1992 and 1995 collections. Figures 8A and 8B show the trends of metal concentrations in the coarse silt size fraction of the sediments. Tables 1 to 5 inclusive show the metal content in the geochemical phases of the very fine sand size sediments. Table 6 shows the metal content in the combined phases of the very fine sand size sediments. The aforementioned tables contain the metal content in the sediments from the 1992 and 1995 collections. Table 7 shows the metal content in the coarse silt size sediments.

The mean pH and range values for waters in each stream for the 1992 collection are 7.37 and 7.10-7.55 for Ants Creek; 7.40 and 7.15 - 7.60 for South Ants Creek. The same for the samples collected in 1995 are 7.33 and 7.15 - 7.55 for Ants Creek; 7.41 and 7.30 - 7.55 for South Ants Creek; 7.36 and 7.12 for the control stream. Since the pH mean and range values for the streams are similar, a significant difference of metal concentrations and variations which may appear in the stream sediments cannot be attributed directly to pH differences.

Metal concentration trends along the stream.

Various studies report decreasing metal concentrations in sediments in a downstream direction from a contamination source. Axtmann and Luoma (1991) report this trend for Cu, Zn, Pb, Cd, and Ag concentration in the <0.060-mm size sediments affected by mining activity over a distance of 380 km. There are other studies that show this trend for metals over smaller distances (Wolfenden and Lewin 1978; Chapman and others 1983; Mann and Lintren 1983; Rybicka and Kyzoil 1987; Leenars and others 1988). Mantei and Coonrod (1989) and Mantei and Sappington (1994) observed a lack of decreasing metal concentrations in a downstream direction from an emission source in sediments affected by landfill leachate. They concluded that such a trend may be undetectable over small distances.

There appears to be decreasing concentration for some metals in the sediments in a downstream direction in Ants Creek in some extraction phases. The concentrations of Ni and Mn in the carbonate extraction phase (Fig. 3) indicate such a trend. This trend is present in the sediments collected from 1992 and 1995. A similar trend for Zn and Ba concentrations is apparent in the Fe phase (Figs. 5A and 5B) and combined phases (Figs. 7A and 7B) for both years. Zinc and Cr concentrations show a similar trend in the HNO₃ extraction phase (Figs. 8A and 8B). However, all of the aforementioned trends are thought to be non representative patterns for the metal concentrations along Ants Creek and may result from the small collection distance and/or small number of samples collected.

Comparison of metal content in the sediments of the study streams

Significantly higher mean concentrations of some heavy metals in the sediments of streams affected by landfill leachate have been reported from various studies (Mantei and Coonrod 1989; Mantei and Foster 1991; Mantei and Sappington 1994). In the latter study the coefficient of variation for metals enriched in the sediments were significantly higher than the same for the control. The mean concentrations and coefficient of variation for each metal in the sediments of Ants Creek and South Ants Creek are similar to the same for that in the control sediments. The same is true for the metal content in coarse silt size sediments collected in 1995 representing the HNO₃ extraction.

Comparison of metal content in samples collected in 1992 with those from 1995.

The content of each metal in the geochemical phases of the sediments in Ants Creek collected in 1992 is similar to the respective metal content in the sediments collected from that stream in 1995. The same is true comparing respective metal contents for sediments in South Ants Creek. There are slight differences in the mean concentration of the metals in the above comparisons. The mean concentrations of most metals in the exchangeable cation phase (Table 1) and carbonate phase (Table 2) in the sediments of Ants Creek and South Ants Creek collected in 1992 are slightly higher than the same from the respective stream collected in 1995. The opposite is true for most metal concentrations in the Mn phase of the sediments for both streams (Table 3). The slightly higher mean concentration of metals in the carbonate and Mn phases of the

sediments in a stream may be the result of higher concentrations of the respective phase in the sediment samples. A higher Mn concentration in the Mn phase would represent a higher concentration of the Mn phase in a sample. Correspondingly, a higher concentration of Ca in the carbonate phase would signify a higher concentration of Ca. Mantei and others (in press) report a dependency of the concentration of all metals detectable in the Mn phase on the concentration of the Mn phase. There is a high degree of inconsistency of higher concentrations for most metals in the Fe phase extraction of the sediments in 1992 as compared to the same for the sediments collected in 1995 (Table 4). A high mean concentration for Ca and Mn in the Fe phase may indicate an incomplete separation of the Ca and Mn phases in the sequential extraction procedure. This would result in high concentrations of Ca and Mn phase with associated metals present in the Fe phase extraction. The contribution of metals from the carbonate and Mn phases common to those in the Fe phase could cause the aforementioned inconsistency. There are slightly higher mean concentrations for most metals in the residual phase (Table 5) and in the combined phases (Table 6) of the sediments in Ants Creek and South Ants Creek compared to the same collected in 1995.

Comparison of metal concentrations in the sediments of Ants Creek with that of South Ants Creek in samples collected in the same year.

The mean concentration of most metals in the sediments of Ants Creek collected in 1992 are slightly higher than the same for South Ants Creek. This is true for all

geochemical phases and combined phases. The same is true for the sediments collected in 1995. In addition, the mean concentration of most metal in the sediments of Ants Creek are slightly higher than the same in South Ants Creek in the HNO₃ extraction.

Conclusions

The content of Cu, Pb, Zn, Cd, Co, Ni, Cr, Fe, Mn, Ba, Ca, and Ag in sediments of Ants Creek and South Ants Creek are similar to that in the control stream. This is apparent from the data obtained from the geochemical phases in the very fine sand size sediments and from the single nitric acid extraction of the coarse silt size sediments. The content of each of the aforementioned metals in the sediments of Ants Creek compared to that in South Ants Creek are also similar. This is true for the metal content in the sediments collected in 1992 and in 1995. Since the metal concentrations in the sediments of Ants Creek and South Ants Creek are not enriched by landfill leachate, it would appear the sediments in Table Rock Lake should not be enriched in these metals from landfill activities related to the Stone County Landfill.

Renfro Landfill Area

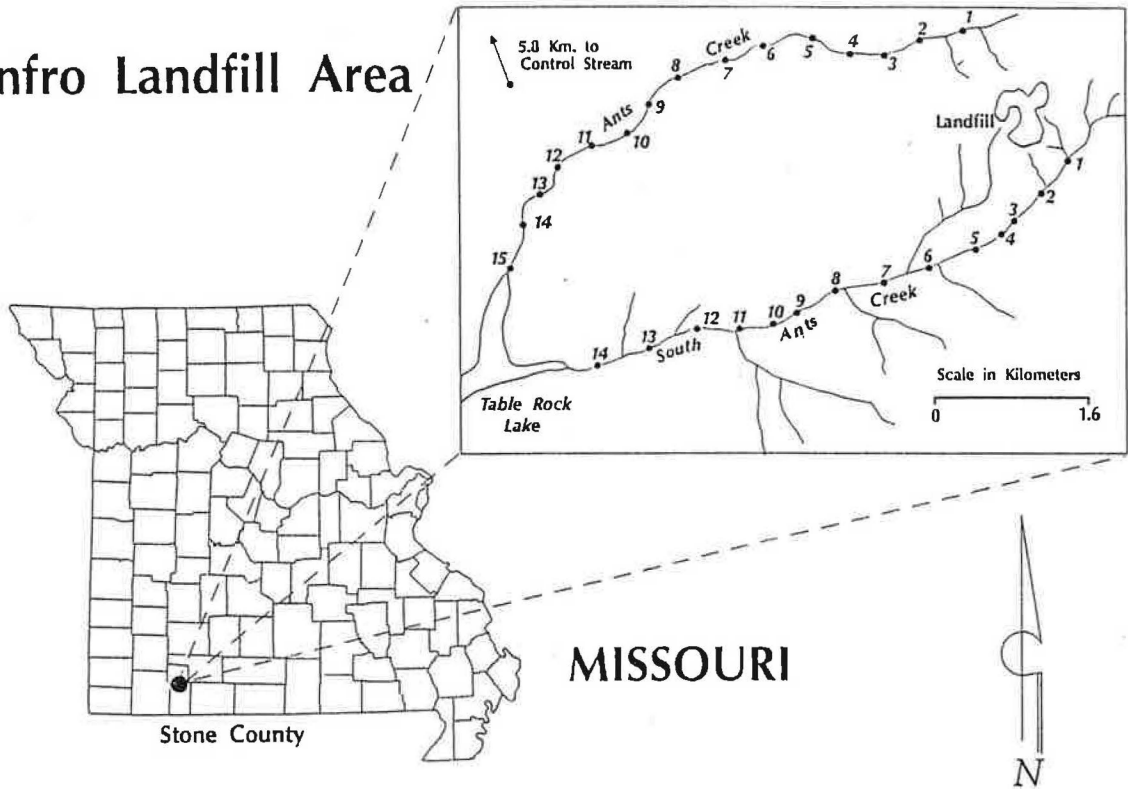


Figure 1. Location of study area and sample collection sites.

METAL CONCENTRATION ($\mu\text{g/g}$)

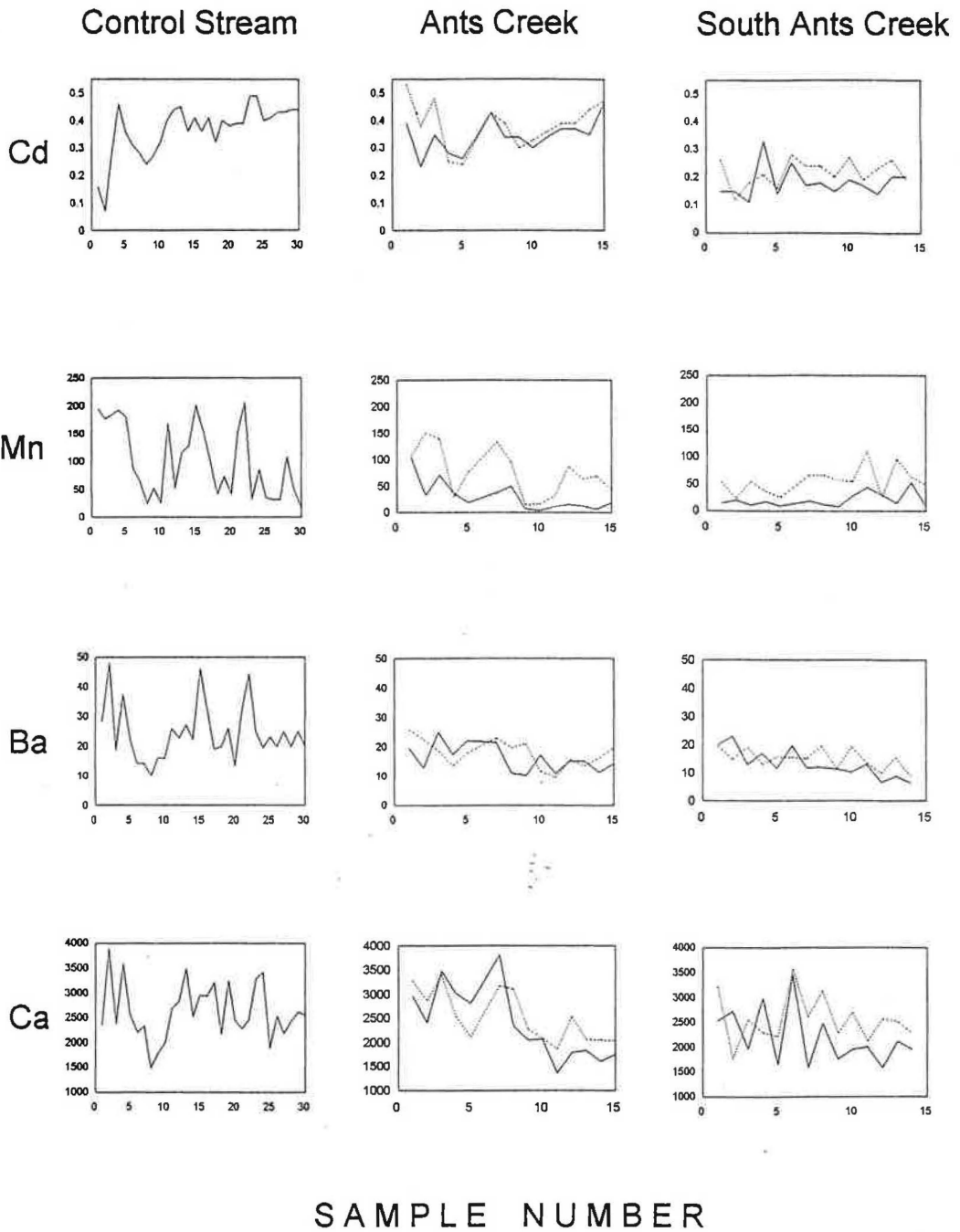


Figure 2. Trend charts of detectable metal concentrations in the exchangeable cation phase of the very fine sand size fraction of the sediments along the study streams. Dashed and solid concentration lines represent results from samples collected in 1992 and 1995 respectively

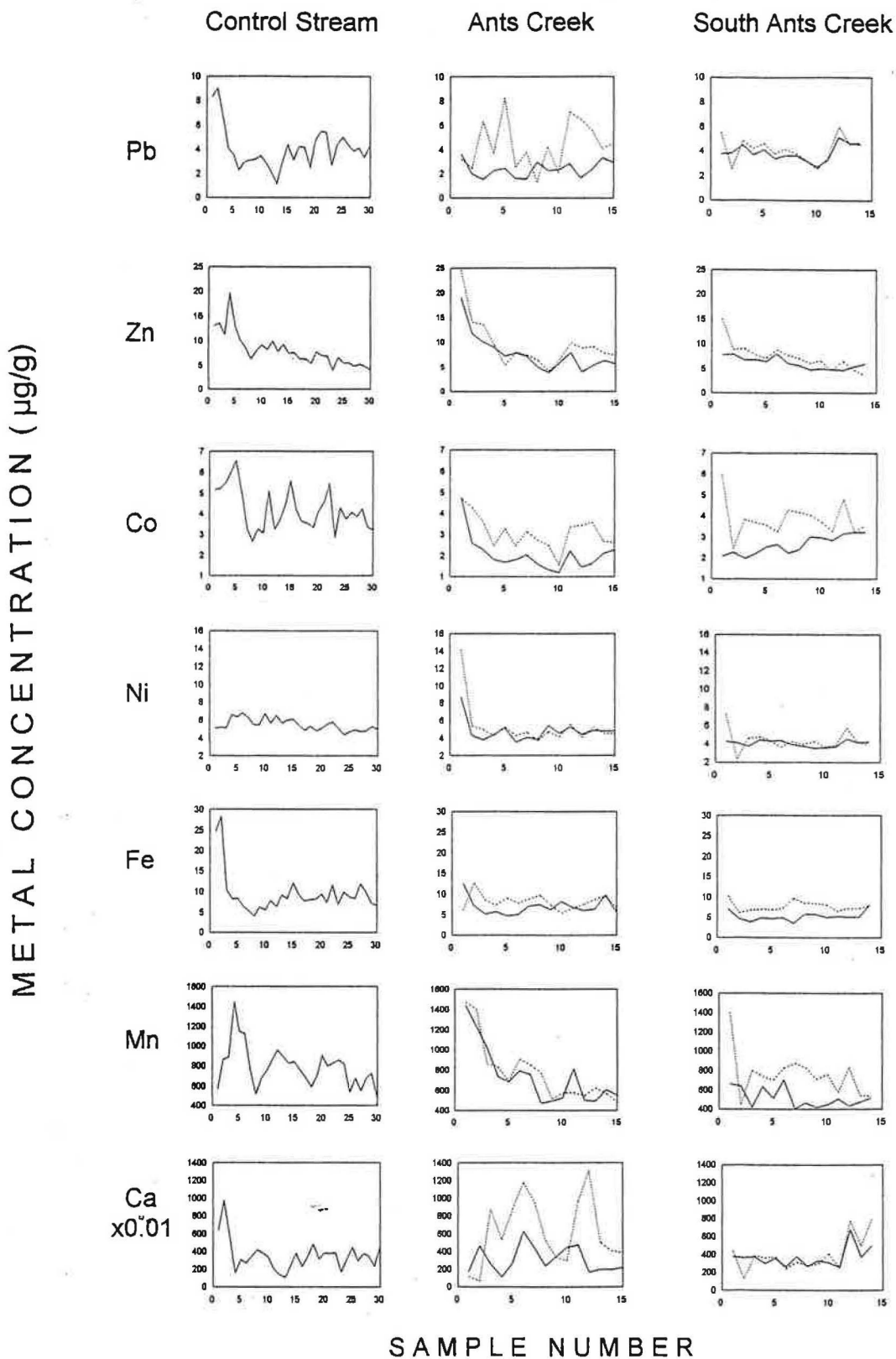


Figure 3. Trend charts of detectable metal concentrations in the carbonate phase of the very fine sand size fraction of the sediments along the study streams. Dashed and solid metal concentration lines represent results from samples collected in 1992 and 1995 respectively.

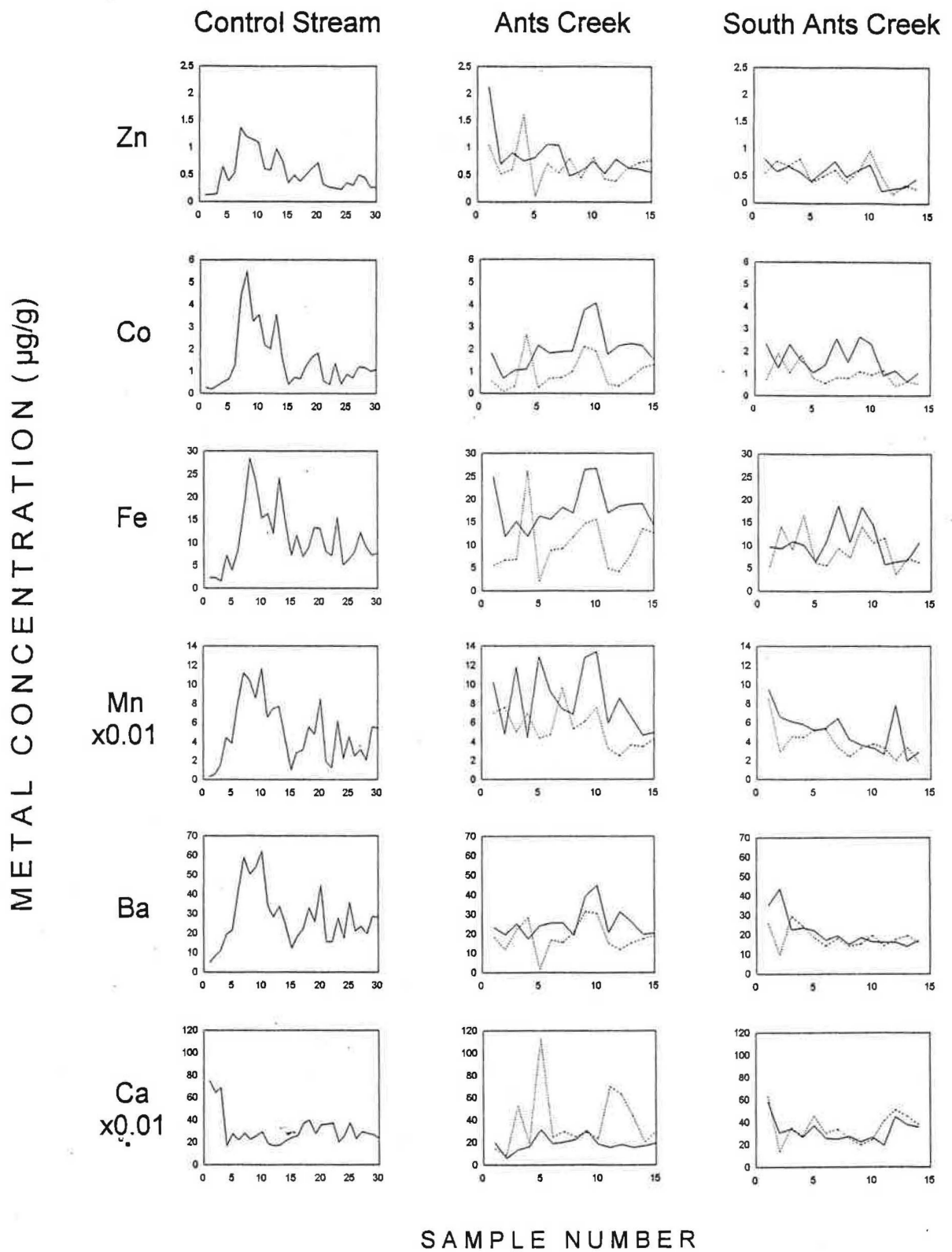


Figure 4. Trend charts of detectable metal concentrations in the manganese phase of the very fine sand size fraction of the sediments along the study streams. Dashed and solid metal concentration lines represent results from samples collected in 1992 and 1995 respectively

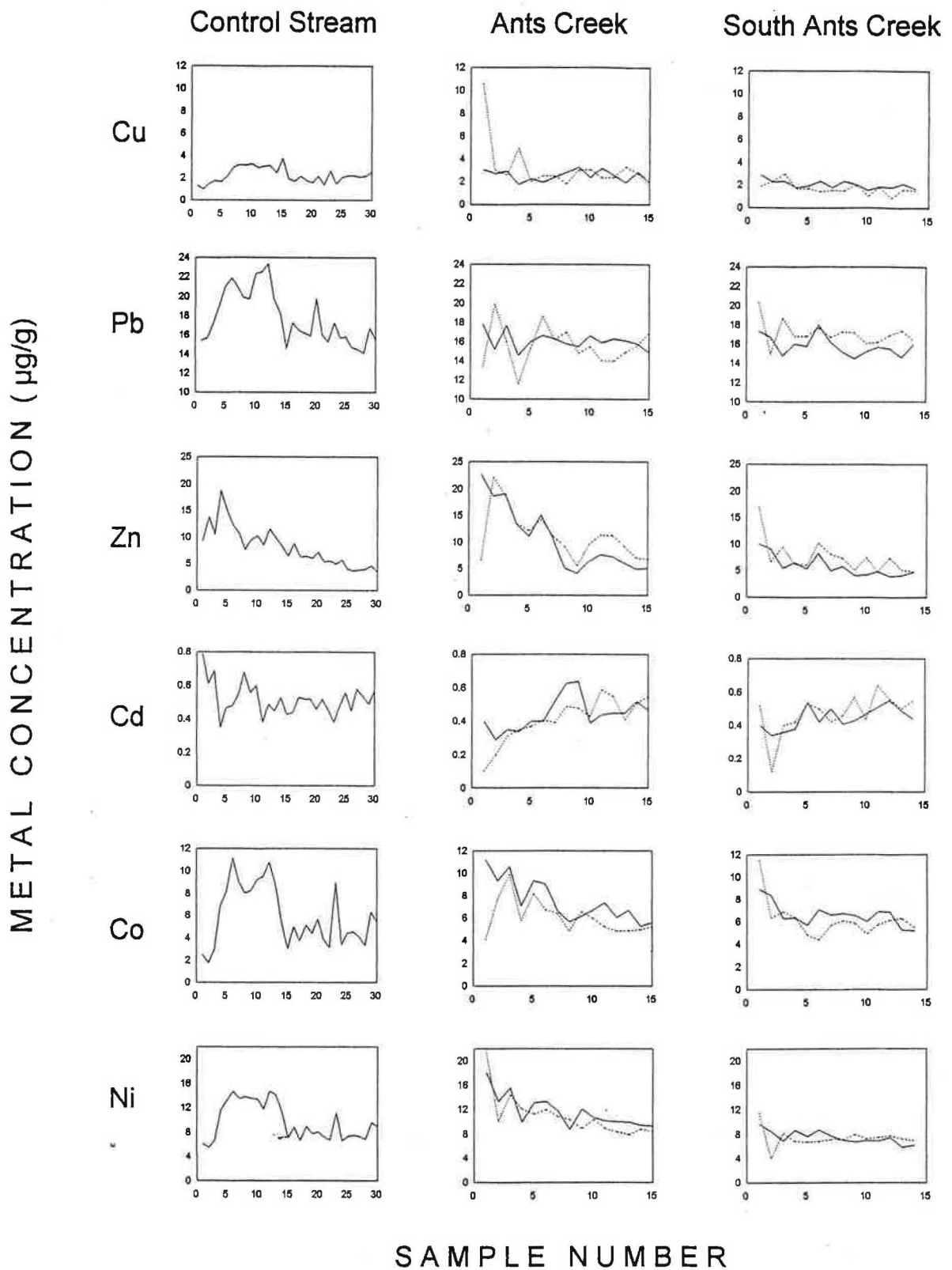


Figure 5A. Trend charts of detectable metal concentrations in the iron phase of the very fine sand size fraction of the sediments along the study streams. Dashed and solid concentration lines represent results from samples collected in 1992 and 1995 respectively.

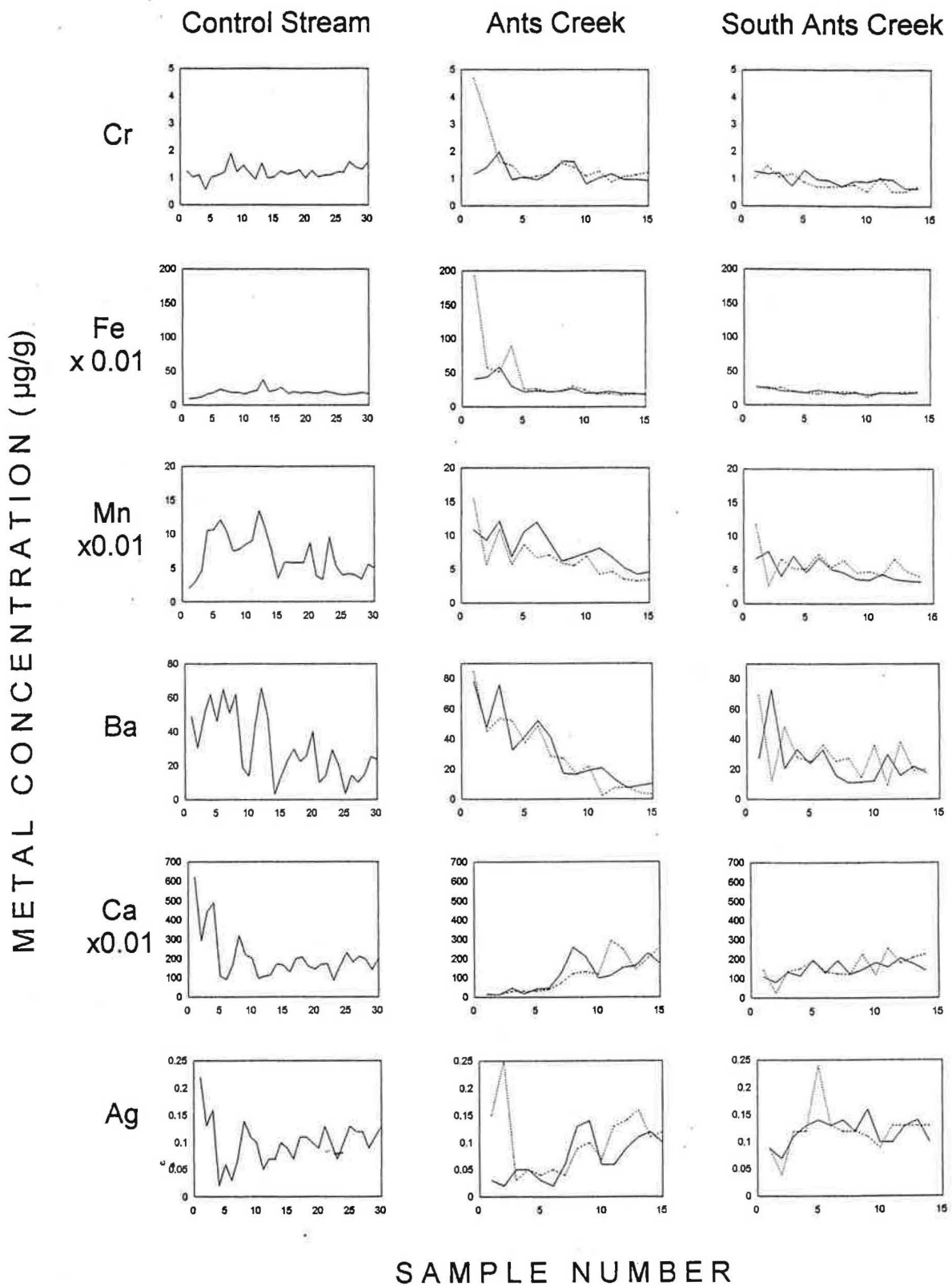


Figure 5B. Trend charts of detectable metal concentrations in the iron phase of the very fine sand size fraction of the sediments along the study streams. Dashed and solid metal concentration lines represent results from samples collected in 1992 and 1995 respectively.

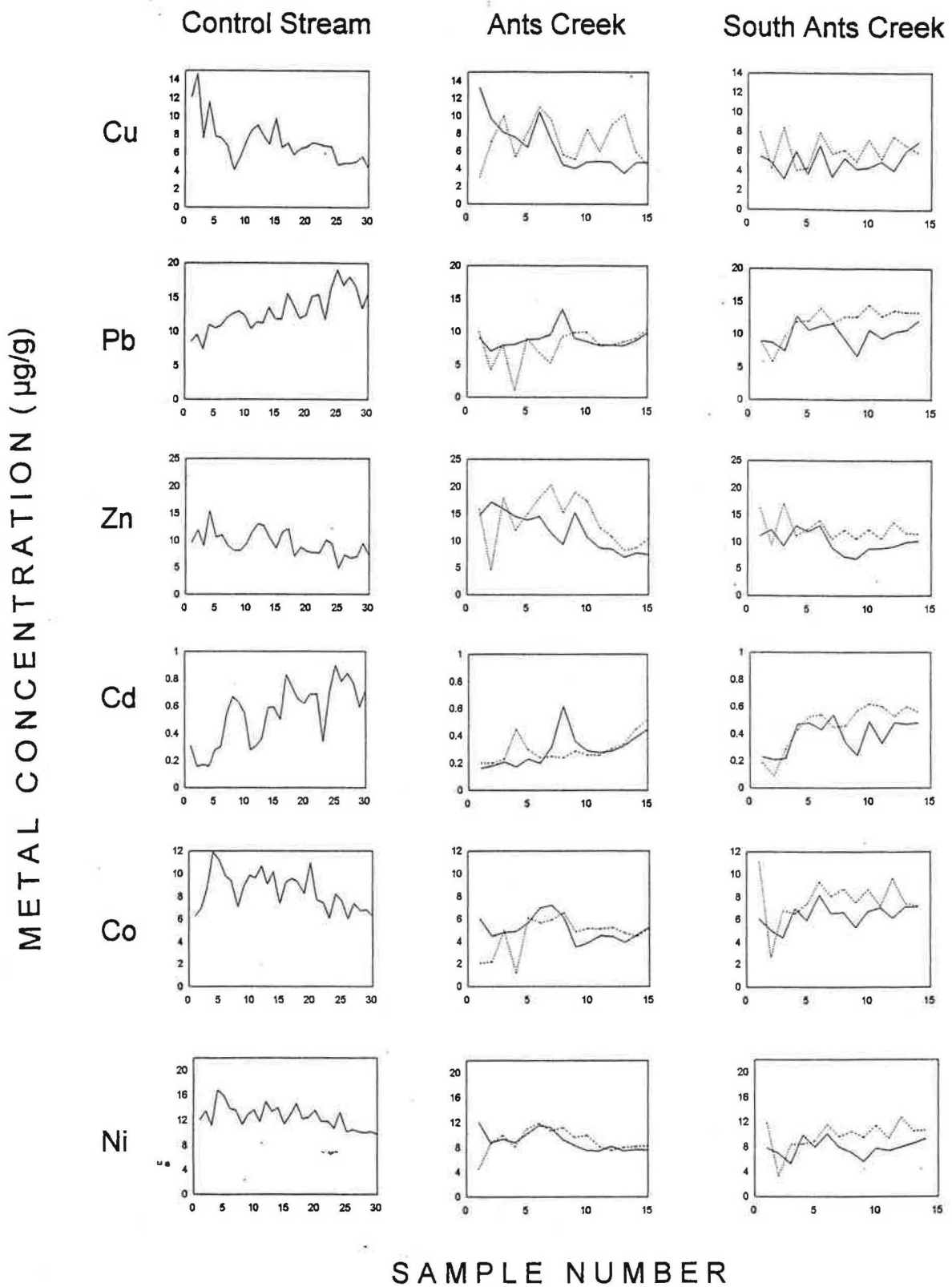


Figure 6A. Trend charts of detectable metal concentrations in the residual phase of the very fine sand size fraction of the sediments along the study streams. Dashed and solid metal concentration lines represent results from samples collected in 1992 and 1995 respectively.

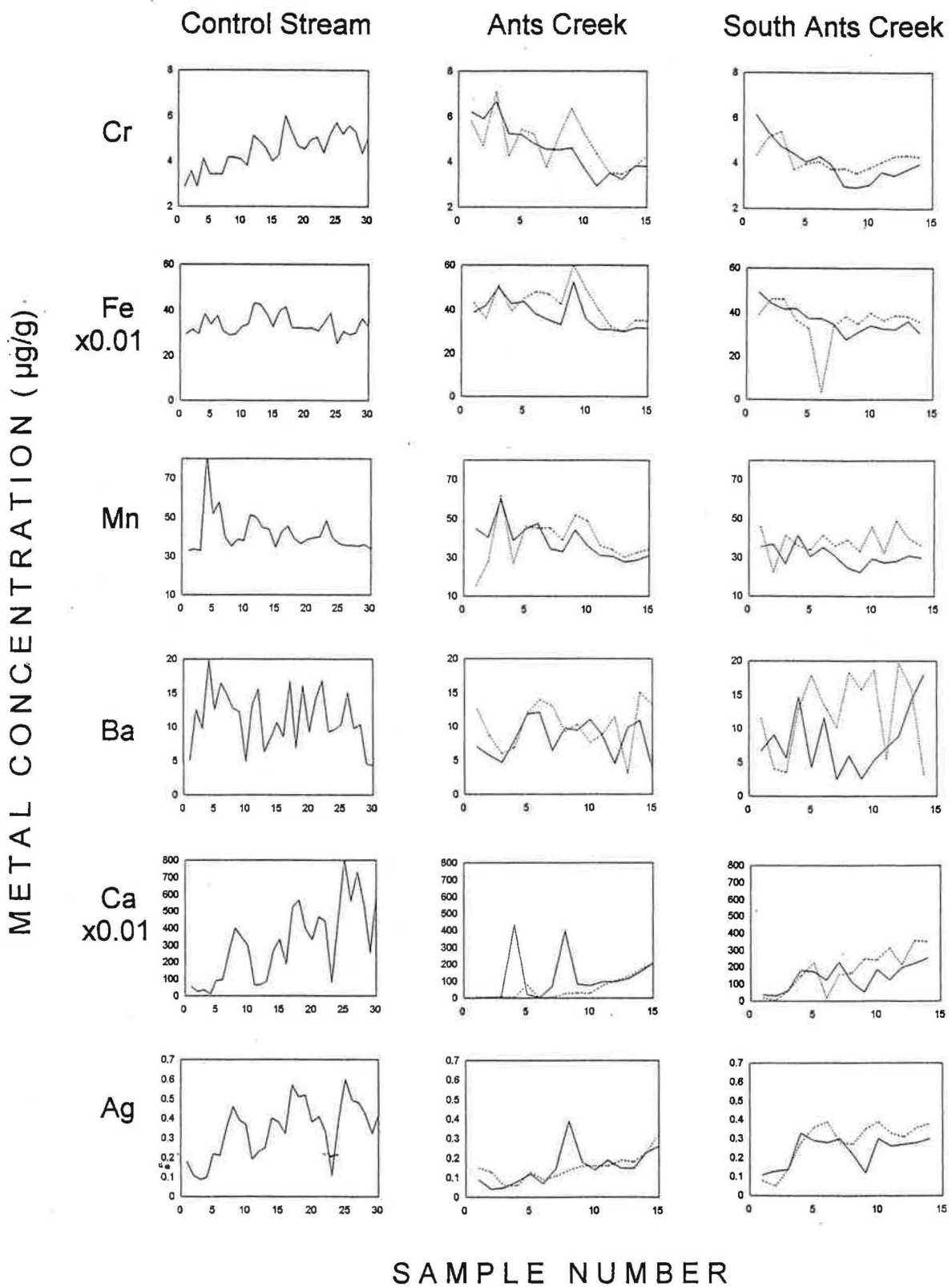


Figure 6B. Trend charts of detectable metal concentrations in the residual phase of the very fine sand size fraction of the sediments along the study streams. Dashed and solid metal concentration lines represent results from samples collected in 1992 and 1995 respectively,

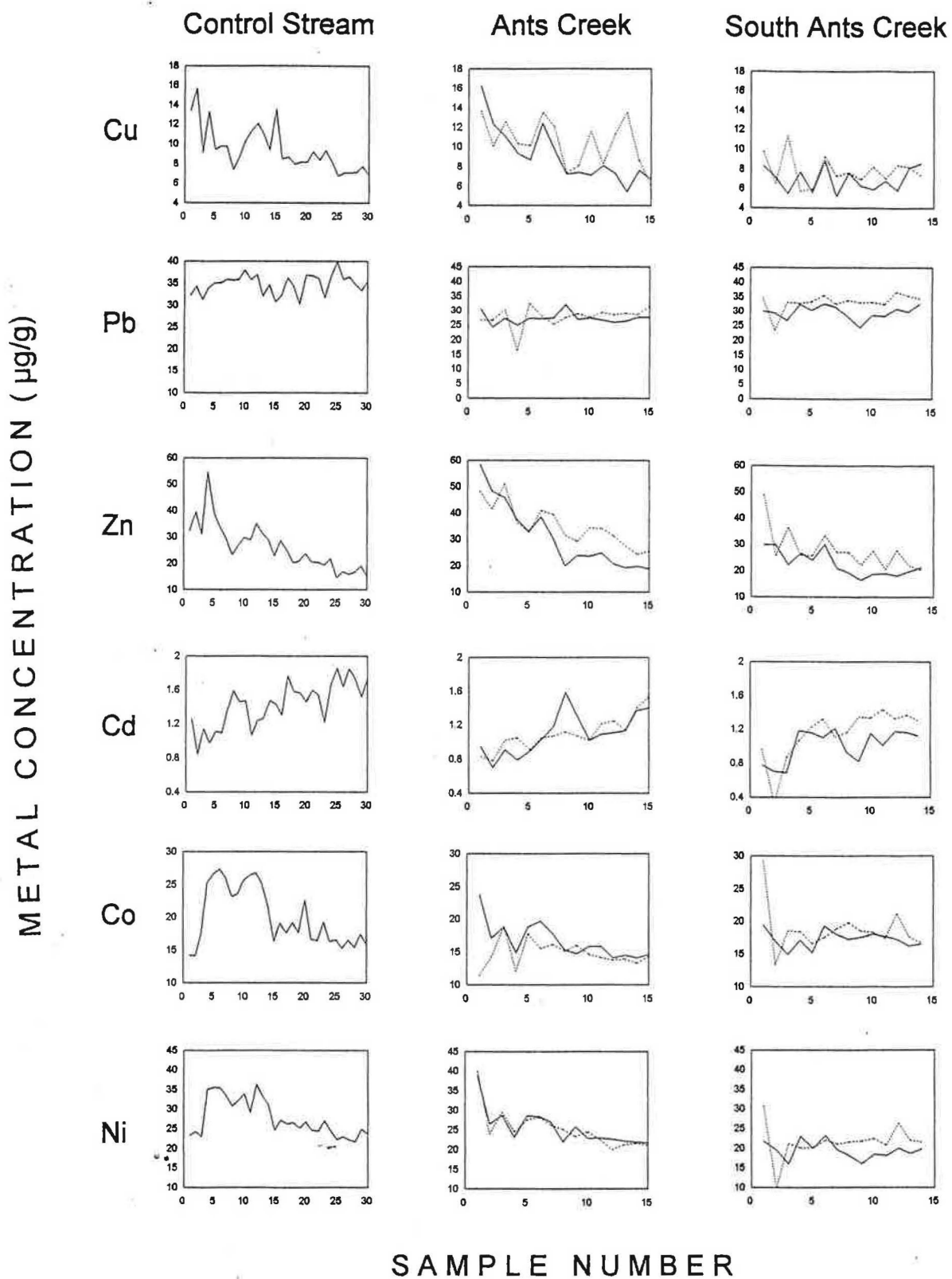


Figure 7A. Trend charts of metal concentrations in the combined phases of the very fine sand size fraction of the sediments along the study streams. Dashed and solid metal concentration lines represent results from samples collected in 1992 and 1995 respectively.

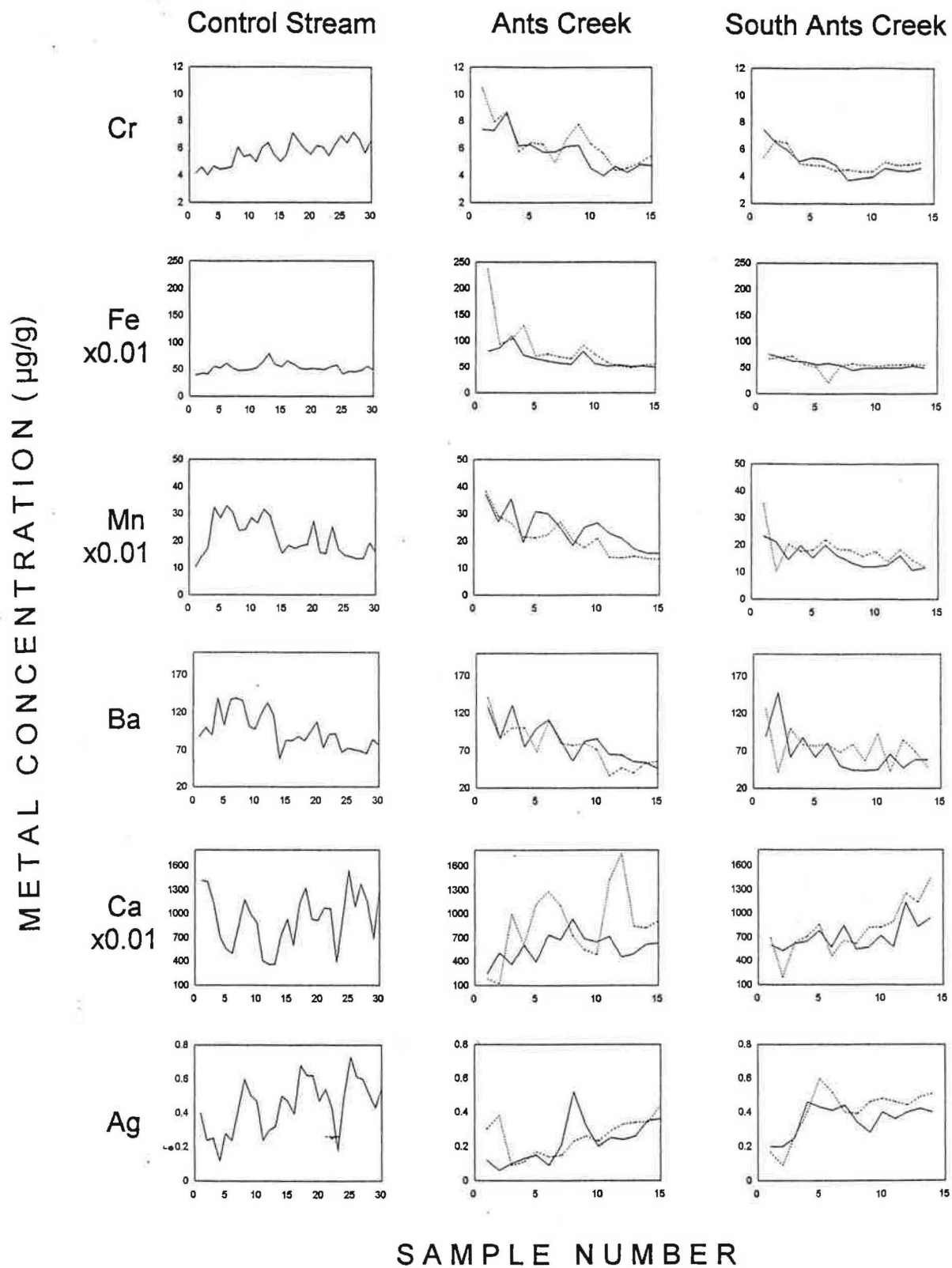


Figure 7B. Trend charts of metal concentrations in the combined phases of the very fine sand size fraction of the sediments along the study streams. Dashed and solid metal concentration lines represent results from samples collected in 1992 and 1995 respectively.

METAL CONCENTRATION ($\mu\text{g/g}$)

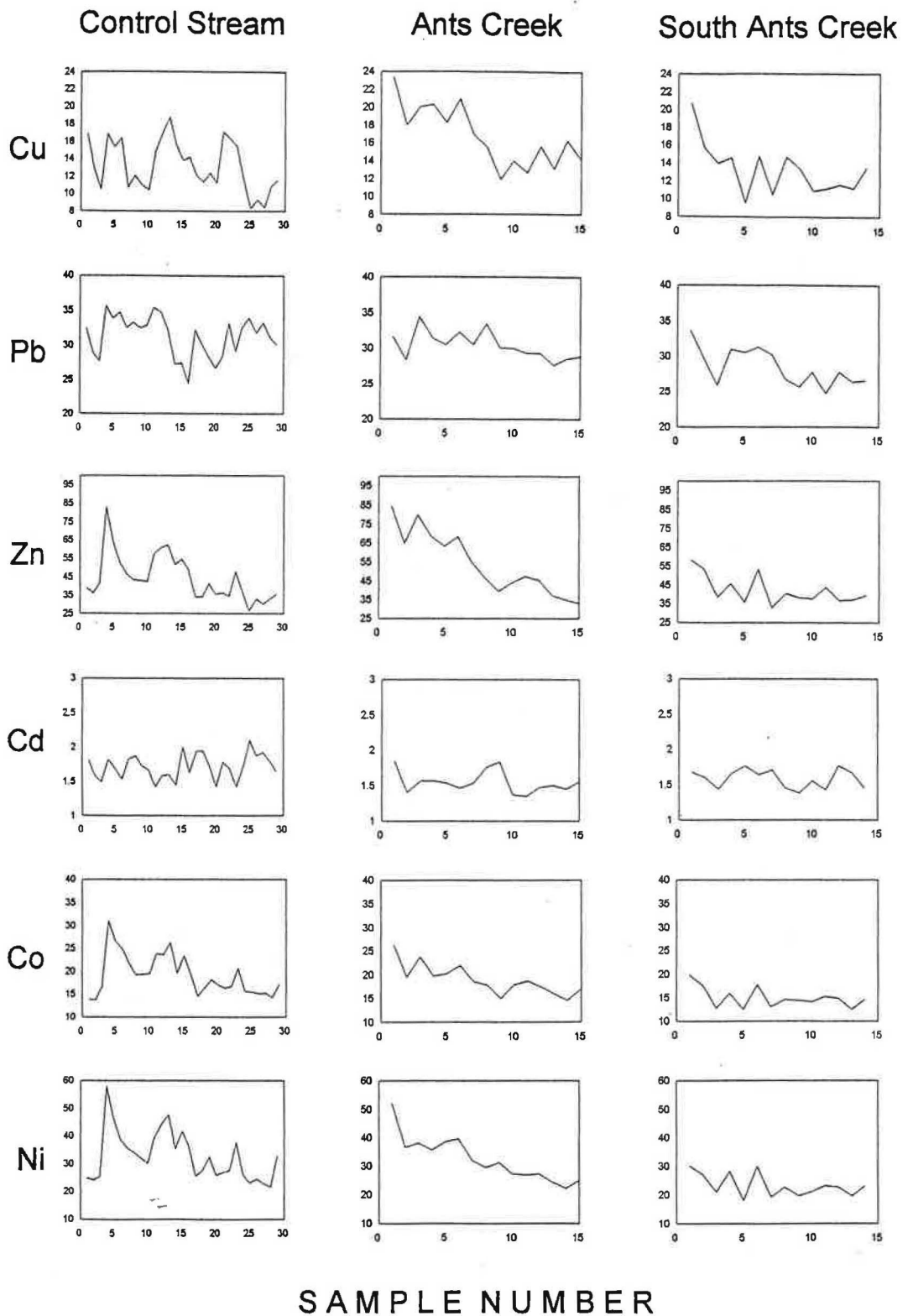


Figure 8A. Trend charts of metal concentrations in the nitric acid extraction of the coarse silt size fraction of the sediments along the study streams. Metal concentration lines represent results from samples collected in 1995.

METAL CONCENTRATION ($\mu\text{g/g}$)

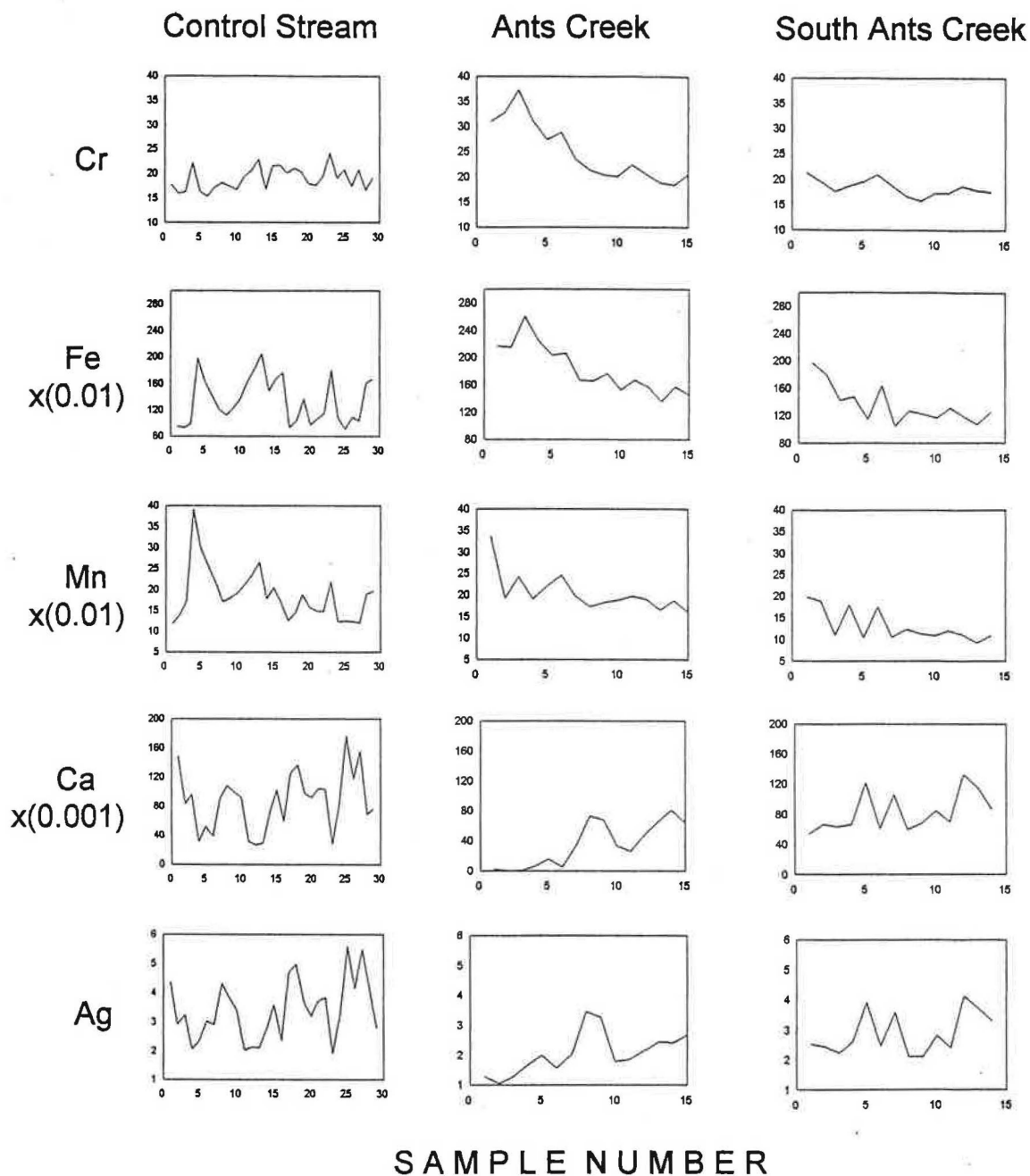


Figure 8B. Trend charts of metal concentrations in the nitric acid extraction of the coarse silt size fraction of the sediments along the study streams. Metal concentration lines represent results from samples collected in 1995.

Table 1. Metal content in the exchangeable cation phase of the very fine sand size fraction of the sediments in the study streams.

	<u>Control Stream '95</u>			<u>Ants Creek '92</u>			<u>Ants Creek '95</u>		
	\bar{x}	σ	σ/\bar{x}	\bar{x}	σ	σ/\bar{x}	\bar{x}	σ	σ/\bar{x}
Cd	0.35	0.11	0.31	0.38	0.08	0.21	0.35	0.07	0.20
Mn	97.4	66.8	0.69	75.4	45.6	0.60	29.1	27.9	0.96
Ba	23.7	10.3	0.44	17.3	4.67	0.27	15.7	4.65	0.30
Ca	2541	732	0.29	2526	537	0.21	2311	753	0.33

	<u>South Ants Creek '92</u>			<u>South Ants Creek '95</u>		
	\bar{x}	σ	σ/\bar{x}	\bar{x}	σ	σ/\bar{x}
Cd	0.22	0.05	0.23	0.18	0.05	0.28
Mn	56.1	25.0	0.45	20.5	13.5	0.66
Ba	15.0	3.48	0.23	13.1	5.03	0.38
Ca	2559	480	0.19	2195	567	0.26

\bar{x} mean ($\mu\text{g/g}$)
 σ standard deviation ($\mu\text{g/g}$)
 σ/\bar{x} coefficient of variation

Table 2. Metal content in the carbonate phase of the very fine sand size fraction of the sediments in the study streams.

	<u>Control Stream '95</u>			<u>Ants Creek '92</u>			<u>Ants Creek '95</u>		
	\bar{x}	σ	σ/\bar{x}	\bar{x}	σ	σ/\bar{x}	\bar{x}	σ	σ/\bar{x}
Pb	3.91	1.82	0.47	4.38	2.01	0.46	2.39	0.64	0.27
Zn	7.81	3.65	0.47	9.52	4.96	0.52	7.74	3.80	0.49
Co	4.06	1.25	0.31	3.10	0.79	0.25	2.05	0.85	0.41
Ni	5.32	1.18	0.22	5.32	2.52	0.47	4.81	1.21	0.25
Fe	9.13	5.25	0.58	8.12	1.78	0.22	6.95	2.02	0.29
Mn	767	246	0.32	777	301	0.39	739	290	0.39
Ca	342	178	0.52	623	381	0.61	308	148	0.48

	<u>South Ants Creek '92</u>			<u>South Ants Creek '95</u>		
	\bar{x}	σ	σ/\bar{x}	\bar{x}	σ	σ/\bar{x}
Pb	4.15	1.00	0.24	3.86	0.65	0.17
Zn	7.41	2.76	0.37	6.13	1.17	0.19
Co	3.85	0.83	0.22	2.64	0.44	0.17
Ni	4.37	1.11	0.25	4.08	0.35	0.09
Fe	7.75	1.19	0.15	5.29	1.22	0.23
Mn	757	227	0.30	518	102	0.20
Ca ($\times 0.01$)	399	189	0.47	369	108	0.29

\bar{x} mean ($\mu\text{g/g}$)

σ standard deviation ($\mu\text{g/g}$)

σ/\bar{x} coefficient of variation

Table 3. Metal content in the manganese phase in the very fine sand size fraction of the sediments in the study streams.

	<u>Control Stream '95</u>			<u>Ants Creek '92</u>			<u>Ants Creek '95</u>		
	\bar{x}	σ	σ/\bar{x}	\bar{x}	σ	σ/\bar{x}	\bar{x}	σ	σ/\bar{x}
Zn	0.53	0.33	0.62	0.67	0.34	0.51	0.82	0.40	0.49
Co	1.48	1.32	0.89	0.95	0.75	0.78	2.00	0.90	0.45
Fe	10.9	6.54	0.60	10.0	6.05	0.61	18.1	4.69	0.26
Mn(x0.01)	4.92	3.20	0.65	5.52	2.00	0.36	8.31	3.25	0.39
Ba	28.1	14.6	0.52	18.4	7.79	0.42	25.5	7.69	0.30
Ca(x0.01)	31.2	14.6	0.47	37.8	27.3	0.72	19.1	6.24	0.33

	<u>South Ants Creek '92</u>			<u>South Ants Creek '95</u>		
	\bar{x}	σ	σ/\bar{x}	\bar{x}	σ	σ/\bar{x}
Zn	0.54	0.23	0.43	0.53	0.19	0.36
Co	0.95	0.44	0.46	1.63	0.68	0.42
Fe	9.09	3.87	0.42	10.7	4.10	0.38
Mn(x0.01)	3.88	1.71	0.44	5.10	2.15	0.42
Ba	18.4	5.36	0.29	21.3	8.38	0.39
Ca(x0.01)	35.4	13.2	0.37	32.2	10.3	0.31

\bar{x} mean ($\mu\text{g/g}$)

σ standard deviation ($\mu\text{g/g}$)

σ/\bar{x} coefficient of variation

Table 4. Metal content in the iron phase in the very fine sand size fraction of the sediments in the study streams.

	<u>Control Stream '95</u>			<u>Ants Creek '92</u>			<u>Ants Creek '95</u>		
	\bar{x}	σ	σ/\bar{x}	\bar{x}	σ	σ/\bar{x}	\bar{x}	σ	σ/\bar{x}
Cu	2.24	0.71	0.32	3.20	2.19	0.68	2.52	0.50	0.20
Pb	17.8	2.73	0.15	15.6	2.05	0.13	16.1	0.89	0.06
Zn	8.10	3.71	0.46	11.3	4.58	0.40	10.5	6.00	0.57
Cd	0.51	0.09	0.18	0.41	0.13	0.32	0.45	0.10	0.22
Co	5.90	2.67	0.45	6.09	1.56	0.26	7.52	1.90	0.25
Ni	9.70	3.06	0.32	10.9	3.41	0.31	11.7	2.63	0.22
Cr	1.21	0.25	0.21	1.61	1.02	0.63	1.20	0.33	0.28
Fe(x0.01)	18.7	4.92	0.26	42.8	46.3	1.08	27.6	11.6	0.42
Mn(x0.01)	6.75	3.10	0.46	6.56	3.22	0.49	8.05	2.55	0.32
Ba	31.1	19.1	0.61	29.5	24.1	0.82	32.3	23.4	0.72
Ca(x0.01)	207	121	0.58	118	95.8	0.81	114	82.4	0.72
Ag	0.10	0.04	0.40	0.10	0.06	0.61	0.07	0.04	0.57
	<u>South Ants Creek '92</u>			<u>South Ants Creek '95</u>					
	\bar{x}	σ	σ/\bar{x}	\bar{x}	σ	σ/\bar{x}			
Cu	1.67	0.52	0.31	2.02	0.36	0.18			
Pb	17.1	1.28	0.08	15.8	1.01	0.06			
Zn	7.62	3.23	0.42	5.85	2.00	0.34			
Cd	0.47	0.12	0.25	0.45	0.07	0.16			
Co	6.19	1.67	0.27	6.63	1.04	0.16			
Ni	7.36	1.54	0.21	7.50	1.05	0.14			
Cr	0.86	0.07	0.08	0.97	0.23	0.24			
Fe(x0.01)	19.9	4.00	0.20	19.5	11.5	0.59			
Mn(x0.01)	5.74	2.19	0.38	4.94	1.59	0.32			
Ba	29.3	16.0	0.55	24.9	1.59	0.64			
Ca(x0.01)	163	61.0	0.37	150	38.6	0.26			
Ag	0.12	0.04	0.33	0.12	0.02	0.17			

\bar{x} mean ($\mu\text{g/g}$)
 σ standard deviation ($\mu\text{g/g}$)
 σ/\bar{x} coefficient of variation

Table 5. Metal content in the residual phase in the very fine sand size fraction of the sediments in the study streams.

	<u>Control Stream '95</u>			<u>Ants Creek '92</u>			<u>Ants Creek '95</u>		
	\bar{x}	σ	σ/\bar{x}	\bar{x}	σ	σ/\bar{x}	\bar{x}	σ	σ/\bar{x}
Cu	7.12	2.36	0.33	7.25	2.42	0.33	6.58	2.78	0.42
Pb	13.0	2.79	0.21	7.86	2.57	0.32	8.87	1.47	0.16
Zn	9.47	2.28	0.24	13.8	4.56	0.33	11.8	3.47	0.29
Cd	0.54	0.22	0.40	0.30	0.10	0.33	0.30	0.12	0.40
Co	8.48	1.66	0.19	4.62	1.57	0.33	5.09	1.10	0.21
Ni	12.5	1.84	0.14	9.06	1.86	0.34	9.04	1.57	0.17
Cr	4.47	0.81	0.18	4.82	1.06	0.22	4.58	1.10	0.24
Fe(x0.01)	33.6	4.55	0.13	42.8	8.18	0.19	37.6	7.23	0.19
Mn	41.6	9.95	0.23	38.4	11.7	0.30	38.2	8.80	0.23
Ba	11.2	4.16	0.37	10.1	3.37	0.33	8.23	2.76	0.33
Ca(x0.01)	312	224	0.71	58.5	67.5	1.15	118	135	1.14
Ag	0.34	0.14	0.41	0.15	0.07	0.46	0.15	0.09	0.60

	<u>South Ants Creek '92</u>			<u>South Ants Creek '95</u>		
	\bar{x}	σ	σ/\bar{x}	\bar{x}	σ	σ/\bar{x}
Cu	6.14	1.49	0.24	4.91	1.18	0.24
Pb	12.0	2.40	0.20	10.1	1.74	0.17
Zn	12.5	2.22	0.17	10.1	1.95	0.19
Cd	0.46	0.16	0.34	0.39	0.12	0.30
Co	7.75	1.94	0.25	6.40	0.99	0.15
Ni	9.83	2.28	0.23	7.89	1.37	0.17
Cr	4.18	0.52	0.12	4.05	0.91	0.22
Fe(x0.01)	35.6	10.1	0.28	36.3	6.08	0.16
Mn	38.2	6.83	0.17	30.9	5.10	0.16
Ba	12.2	6.03	0.49	8.35	4.75	0.56
Ca(x0.01)	181	122	0.67	142	75.5	0.53
Ag	0.28	0.11	0.39	0.24	0.08	0.33

\bar{x} mean ($\mu\text{g/g}$)
 σ standard deviation ($\mu\text{g/g}$)
 σ/\bar{x} coefficient of variation

Table 6. Metal content in the combined phases in the very fine sand size fraction of the sediments in the study streams.

	<u>Control Stream '95</u>			<u>Ants Creek '92</u>			<u>Ants Creek '95</u>		
	\bar{x}	σ	σ/\bar{x}	\bar{x}	σ	σ/\bar{x}	\bar{x}	σ	σ/\bar{x}
Cu	9.44	2.88	0.24	10.5	2.43	0.23	9.10	2.84	0.31
Pb	34.8	2.24	0.06	27.8	3.74	0.13	27.3	1.96	0.07
Zn	26.2	8.81	0.33	35.2	7.80	0.22	30.9	12.5	0.40
Cd	1.43	0.27	0.18	1.10	0.20	0.18	1.10	0.24	0.21
Co	20.1	4.43	0.22	14.8	1.97	0.13	16.7	2.69	0.16
Ni	27.7	4.74	0.17	25.3	4.93	0.19	25.5	4.55	0.17
Cr	5.68	0.88	0.15	6.44	1.69	0.26	5.78	1.32	0.22
Fe(x0.01)	52.5	8.43	0.16	85.2	47.6	0.55	65.5	17.2	0.26
Mn(x0.01)	21.0	6.70	0.31	20.9	7.15	0.34	24.4	6.88	0.28
Ba	95.0	23.9	0.25	76.5	29.0	0.37	81.7	26.6	0.32
Ca(x0.01)	930	343	0.36	863	445	0.51	583	175	0.30
Ag	0.44	0.16	0.36	0.25	0.11	0.44	0.22	0.13	0.59
	<u>South Ants Creek '92</u>			<u>South Ants Creek '95</u>					
	\bar{x}	σ	σ/\bar{x}	\bar{x}	σ	σ/\bar{x}			
Cu	7.81	1.56	0.19	6.93	1.26	0.18			
Pb	32.2	3.08	0.09	29.8	2.38	0.07			
Zn	28.0	7.61	0.27	22.6	4.76	0.21			
Cd	1.15	0.29	0.25	1.01	0.19	0.18			
Co	18.7	3.52	0.18	17.3	1.28	0.07			
Ni	21.6	4.14	0.19	19.5	2.19	0.11			
Cr	5.04	0.70	0.13	5.02	1.06	0.21			
Fe(x0.01)	55.6	12.1	0.21	56.0	9.13	0.16			
Mn(x0.01)	18.1	5.88	0.32	15.7	4.00	0.25			
Ba	75.0	23.6	0.31	67.7	28.2	0.41			
Ca(x0.01)	804	319	0.39	714	178	0.24			
Ag	0.41	0.14	0.34	0.36	0.09	0.25			

\bar{x} mean ($\mu\text{g/g}$)
 σ standard deviation ($\mu\text{g/g}$)
 σ/\bar{x} coefficient of variation

Table 7. Metal content in the single nitric acid extraction phase in the coarse silt size fraction of the sediments in the study streams.

	<u>Control Stream '95</u>			<u>Ants Creek '95</u>			<u>South Ants Creek '95</u>		
	\bar{x}	σ	σ/\bar{x}	\bar{x}	σ	σ/\bar{x}	\bar{x}	σ	σ/\bar{x}
Cu	13.2	2.91	0.22	16.8	3.39	0.20	13.3	2.86	0.22
Pb	31.3	2.93	0.09	30.4	1.93	0.06	28.4	2.63	0.09
Zn	44.4	12.5	0.28	54.2	16.4	0.31	42.3	7.79	0.18
Cd	1.71	0.18	0.11	1.55	0.15	0.10	1.59	0.13	0.08
Co	19.1	4.42	0.23	19.0	3.20	0.17	15.0	2.18	0.15
Ni	32.7	8.91	0.27	32.5	7.82	0.24	23.3	4.03	0.17
Cr	19.0	2.29	0.12	25.0	5.96	0.24	18.5	1.54	0.08
Fe(x0.01)	134	35.0	0.26	184	35.6	0.19	136	27.7	0.20
Mn(x0.01)	18.7	6.11	0.33	20.5	4.37	0.21	13.2	3.68	0.28
Ca(x0.01)	87.0	40.0	0.46	35.0	29.6	0.85	82.8	25.9	0.31
Ag	3.40	1.03	0.30	2.06	0.70	0.33	2.89	0.70	0.24

\bar{x} mean ($\mu\text{g/g}$)

σ standard deviation ($\mu\text{g/g}$)

σ/\bar{x} coefficient of variation

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