

Comparison of metal homogeneity in grab, quartered, and crushed – sieved portions of stream sediments and metal content change resulting from crushing – sieving activity

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Abstract Restricted grain size sediment samples were collected along two streams. Metal content in some samples may have been influenced by landfill emissions. Each sample was divided into a grab portion, a quartered portion, and a portion crushed and sieved to a smaller size and then quartered. A duplicate sample from each of these portions was extracted. The Cu, Pb, Zn, Co, Ba, Fe, Mn, and Ca quantities were determined for each duplicate sample. Relative standard deviation was used to reflect homogeneity of metal content. Metal occurrence represented speciated metals or major components of chemical phases. Results indicated that variation of metal content among portions was uniform and did not vary as a function of absolute metal quantity. Homogeneity was similar in the same size grab and quartered samples. A more homogeneous metal state was displayed by the crushed and sieved sediments. However, this activity enriched softer chemical phases and associated speciated metals. It was concluded that sediments need not be quartered to obtain a better homogeneity of metal distribution and that field samples should not be crushed and sieved prior to chemical analyses. Assessment of sediments affected by metal emission sources must include a knowledge of metal homogeneity in individual samples.

Key words Metal distribution — Sediments — Crushing — Sieving activity

Introduction

Metals in streams may speciate in chemical phases in stream sediments. Some of these phases include the oxide/hydrous oxide phases of Fe and Mn and the carbonate phase. Metals may also occur in sediments as individual fragmental mineral particles, in which case the quantity of a metal may often vary radically in portions of an individual sediment sample. Statistical methods may be used to analyze the variation of metal quantities in sediment samples along a stream affected by a point or nonpoint emission source. The purpose of this analysis would be to establish if elevated metal quantities in individual samples within the sample population can be attributed to the emission source.

Various studies have reported elevated quantities of metals in stream sediments caused by emission 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 content in sediments of rivers affected by mining activities (Reece and others 1978; Yim 1981; Moore 1985) and, more recently, the enrichment of Cu, Pb, Zn, Cd, Ag, and Ba quantities in stream sediments affected by landfills (Mantei and Coonrod 1989; Mantei and Foster 1991). In such studies, it may be important to know the variation of a metal quantity in portions of an individual sample because this knowledge may establish confidence in individual metal values, especially for elevated values in a sample population.

In this paper we report on the homogeneity of metal content in stream sediments and effects of laboratory treatment prior to chemical analyses. We determine if metal quantities indicate a more uniform distribution in unsplit or grab portions compared to quartered portions of sediment samples. In the aforementioned studies, and related studies, grab or unsplit sample portions are commonly used prior to chemical treatment. We also report the change

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in homogeneity of metal quantities in sediment portions crushed and sieved to a finer grain size for chemical analyses. The Cu, Pb, Zn, Co, Ba, Fe, Mn, and Ca quantities are determined in duplicate for each sediment portion for each sample. The relative standard deviation based upon the range is then used to establish homogeneity for each metal. It is assumed the metals in this study occur speciated in chemical phases or are major components of the phases. Some samples are not associated with any known point or nonpoint emission source, while others are thought to be affected by landfill effluent.

There appears to be sparse data in the literature dealing with replicate analyses for metals in individual sediment samples to establish the degree of homogeneity of metal quantities. Two papers using relative standard deviation in this endeavor are reported (Mantei and Coonrod 1989; Mantei and Foster 1991).

Experimental procedure

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; Ramamoorthy and Rust 1978; Harding and Brown 1978; Sinex and Helz 1981). We believed that "very fine sand" would be a grain size fine enough to accumulate higher quantities of metals in the sediments yet would be large enough to have longer residence at a stream location. This size and occurrence would allow samples to be more representative for that location site. Furthermore, this size sediment is similar to that used in past studies to establish elevated metal quantities in sediments from emission sources (Mantei and Coonrod 1989; Mantei and Foster 1991).

Fifteen sediment samples were collected from two small streams in southwestern Missouri located 15 km apart. Both streams were located within the same carbonate bedrock unit. Nine samples were collected from one stream not associated with any known point or nonpoint emission source. The remaining samples were taken from the second stream with four samples located upstream from a landfill site, one sample adjacent to the landfill, and one downstream from that site. All samples were collected at approximately 0.4-km intervals. Each sample was taken as near to the center of the stream as possible and from the top 6 cm of the sediment deposit. The samples were wet sieved at each collection site with stainless steel USA Standard Testing Sieves with E-11 specification. The <0.105-mm to >0.074-mm (very fine sand) size was saved for physical preparation and chemical analyses. The pH of the streamwaters was taken at each collection site to determine if and to what extent it may have influenced variation of metal quantities in the sediments.

Sample preparation and chemical analyses

Each sample was suspended in deionized water to eliminate clay or silt size fragments that may have remained on the sediments. After drying, each sample was disaggregated and slightly mixed with a glass stirring rod. From each sample the following were extracted: (1) duplicate 0.5000-g unsplit or grab portions; (2) duplicate 0.5000-g portions taken after quartering; and (3) duplicate 0.5000-g <0.053-mm to >0.044-mm (coarse silt) portions taken after the samples were crushed in an agate mortar and pestle, sieved, and then quartered. It was thought a smaller grain size would show a more homogeneous state in respect to metal content. Stainless-steel sieves with E-11 specification were used. To establish if there was contamination from the crushing and sieving procedures, fine-grained pure silica samples were treated in the same manner. Five 0.5000-g crushed and sieved portions and five 0.5000-g uncrushed and unsieved portions were taken for chemical analyses.

Each duplicate sediment portion and silica control samples were transferred to centrifuge bottles and 10 ml of 6 N HNO₃ added. This concentration of HNO₃ will separate chemical phases and speciated metals from the sediments but will not effect metals in silicate lattices (Axtman and Luoma 1991). The bottles and contents were shaken in a hot water bath for 18 h at 85°C and centrifuged (Mantei and Foster 1991). The supernate was analyzed directly for all metals except Fe, Mn, and Ca. Micropipetted portions of the aqueous solution were taken and diluted for the determination of these metals.

The Cu, Pb, Zn, Co, Ba, Fe, Mn, and Ca quantities in each duplicate portion of each sediment sample described above were determined using standard atomic absorption procedures. The quantities of the same metals in all silica control samples were also determined. A Varian 1475 atomic absorption spectrophotometer was used.

Results and discussion

The mean content and standard deviation values of duplicate analyses for the eight metals in the very fine sand size unsplit and quartered portions are summarized in Tables 1 and 2, respectively. The same information for the quartered coarse silt size is shown in Table 3. Samples numbered 1–9 represent sediments collected from a stream thought to be unaffected by an emission source. Samples 10–15 are sediments taken from a second stream. Samples 10–13 are sediments collected upstream from an inactive landfill. Sample number 14 is sediment taken adjacent to the landfill. Sample 15 represents sediment collected downstream from the landfill. The mean values of Cu, Pb, Zn, and Ba appear to be much higher in samples 14 and 15 than any of the other samples in the two streams. It is well known that pH of natural waters influences metal solubility. The pH measurements taken along the stream from which the nine samples were collected gave a range of pH of 7.10–7.32 with a mean of 7.23, while that of the second

Table 1. Metal content in unsplit very fine sand size sediment

Sample	Amount (µg/g)					%		
	Cu	Pb	Zn	Co	Ba	Fe	Mn	Ca
1	13.7 ^a 0.7 ^b	130 1	100 1	23.4 0.9	217 5	2.01 0.03	0.255 0.016	1.7 0.035
2	11.9 1.4	92.6 8.9	109 1	23.7 0.5	223 5	1.74 0.04	0.242 0.015	0.341 0.016
3	14.4 0.6	81.2 2.3	106 14	20.9 0.7	209 16	2.13 0.11	0.222 0.009	0.411 0.058
4	8.6 0.7	68.8 5.7	91.5 1.0	20.1 0.4	223 0	2.15 0.03	0.164 0.004	0.296 0.008
5	11.4 0.5	121 3	98.7 0.3	20.7 0.4	200 4	2.08 0.11	0.233 0.027	1.15 0.035
6	8.00 0.14	84.3 1.0	98.6 0.2	21.3 1.3	204 5	2.01 0.05	0.271 0.004	0.615 0.009
7	16.5 1.1	129 7	99.4 0.4	18.9 0.4	240 18	2.00 0.04	0.271 0.018	1.15 0.156
8	10.6 0.2	96.6 3.1	96.5 2.0	21.0 0.9	187 4	2.08 0.04	0.243 0.009	2.42 0.233
9	14.2 1.0	104 8	83.3 6.4	21.6 0.9	258 6	2.05 0.02	0.254 0.008	0.683 0.073
10	9.05 1.63	64.4 2.8	92.3 3.4	28.9 0.2	94.0 0.0	1.94 0.42	0.278 0.051	0.262 0.062
11	7.30 0.71	55.2 1.1	98.9 5.9	27.5 0.6	94.0 3.4	2.31 0.03	0.331 0.009	0.579 0.020
12	7.05 0.21	56.4 0.6	87.0 0.4	28.3 0.6	97.0 4.2	2.18 0.04	0.359 0.016	0.697 0.004
13	5.85 0.07	44.4 5.1	89.9 0.0	16.6 0.3	50.0 4.2	1.71 0.01	0.206 0.004	2.14 0.007
14	31.7 2.1	325 4	385 4	17.4 0.4	482 7	2.39 0.11	0.115 0.005	2.72 0.297
15	26.3 2.1	280 7	360 3	11.0 0.6	427 6	1.58 0.06	0.105 0.004	3.97 0.042

^a Mean content of duplicate analyses^b Standard deviation of duplicate analyses

stream associated with the landfill was 7.23–7.44 and 7.34. Since pH of the streamwaters at all collection sites in both streams did not change significantly, the higher quantities of metals in samples 14 and 15 cannot be attributed to pH differences. The purpose of this study is not to evaluate elevated metal quantities with respect to landfill activity. However, higher metal values in samples 14 and 15 may be attributed to landfill emissions. Two recent studies found elevated quantities of metals in stream sediments affected by landfills. Mantei and Coonrod (1989) report emissions of Ag, Cu, and Zn from a landfill. In a study of two landfills along the same stream, Mantei and Foster (1991) report emissions of Cu, Pb, Cd, and Ag from one landfill and Cu, Cd, Ba, and Ag from the other. Yanful and others (1988) report Cu, Zn, Pb, and Fe migrations from a landfill into a natural clay deposit. It can be inferred from these studies that each landfill may emit a different suite of metals.

Individual relative standard deviation (RSD) values were calculated for each metal in each sample from the numbers in Tables 1–3. Results from each table indicated

Table 2. Metal content in quartered very fine sand size sediment

Sample	Amount (µg/g)					%		
	Cu	Pb	Zn	Co	Ba	Fe	Mn	Ca
1	13.0 ^a 0.6 ^b	117 0	102 1	22.9 0.4	216 9	1.92 0.10	0.230 0.030	0.900 0.141
2	12.3 0.4	103 0	101 0	22.3 1.1	224 2	2.00 0.01	0.227 0.018	0.303 0.019
3	9.65 0.30	69.1 4.6	99.0 1.4	23.7 0.1	212 4	2.10 0.13	0.251 0.009	0.375 0.059
4	8.93 1.11	71.0 0.0	93.5 0.7	21.8 0.4	222 0	2.16 0.14	0.179 0.004	0.282 0.003
5	10.5 0.3	121 1	100 0	21.0 0.8	228 0	2.06 0.06	0.243 0.014	1.10 0.09
6	9.08 0.71	83.9 7.3	99 1	19.3 0.8	221 0	1.83 0.09	0.250 0.001	0.593 0.016
7	15.2 0.3	143 0	102 0	19.3 1.6	254 2	1.99 0.00	0.297 0.062	1.19 0.17
8	9.87 0.62	95.5 1.8	100 0	19.3 3.1	187 6	1.99 0.01	0.238 0.001	2.60 0.16
9	15.0 0.0	91.6 3.7	88.6 1.3	24.8 0.0	268 4	2.18 0.11	0.249 0.023	0.689 0.126
10	8.20 1.27	52.5 0.4	93.1 5.2	28.7 0.0	88.6 2.6	2.25 0.00	0.323 0.006	0.327 0.004
11	7.6 1.1	54.0 0.6	93.1 11.2	27.7 0.3	92.2 2.6	2.21 0.20	0.309 0.030	0.565 0.085
12	6.60 0.00	50.4 1.1	95.2 6.8	27.3 0.3	102 5	2.25 0.01	0.368 0.003	0.739 0.004
13	6.55 0.07	52.4 7.4	97.5 7.8	18.0 1.1	52.4 2.6	1.63 0.13	0.195 0.012	2.01 0.16
14	35.9 1.1	320 0	390 4	17.0 0.3	485 8	2.41 0.18	0.112 0.011	2.75 0.39
15	25.1 2.8	270 6	350 9	10.5 0.6	420 43	1.54 0.08	0.104 0.006	3.71 0.20

^a Mean content of duplicate analyses^b Standard deviation of duplicate analyses

this value did not vary systematically as a function of absolute metal value. Low RSD values were obtained in each table for Cu, Pb, Zn, and Ba in samples 14 and 15, indicating a uniform distribution of these elevated metal quantities. Higher RSD values resulted for some metals in some samples in each table. This was thought to be a normal fluctuation of metal quantities in the speciated metal occurrence. A much higher RSD value for a metal may indicate an occurrence as a fragment or fragments in the sediment, and such samples may be associated with an emission source such as an ore deposit or mining operation.

Table 4 summarizes the mean relative standard deviation values in parts per hundred (pph) for duplicate analyses of metals in the three sediment portions. There is little difference in the mean RSD value for the very fine sand size unsplit and quartered sediments. In comparison, results from the quartered coarse silt size sediment reflect a lower mean RSD value, thus higher metal homogeneity.

Table 5 shows the mean content of metals in sediment portions. The content of each metal in the very fine sand

Table 3. Metal content in quartered coarse silt size sediment

Sample	Amount ($\mu\text{g/g}$)					%		
	Cu	Pb	Zn	Co	Ba	Fe	Mn	Ca
1	40.4 ^a 1.8 ^b	310 2	101 0	17.9 1.1	262 4	2.01 0.04	0.270 0.021	1.71 0.08
2	16.6 0.2	124 1	101 1	16.3 1.2	228 0	1.95 0.11	0.291 0.001	1.37 0.05
3	34.3 0.8	217 3	97.0 1.4	19.3 0.8	225 5	2.16 0.02	0.279 0.004	0.530 0.030
4	12.4 1.5	74 4	80.0 3.4	12.1 0.0	177 7	1.56 0.01	0.340 0.030	0.838 0.072
5	19.8 0.1	157 13	98.0 0.7	15.2 1.2	270 10	2.06 0.06	0.265 0.011	1.94 0.04
6	14.3 1.0	126 1	97.6 0.0	18.5 1.2	224 2	1.98 0.01	0.252 0.016	1.13 0.01
7	21.8 0.3	178 8	101 1	17.7 0.8	286 4	2.17 0.28	0.279 0.004	1.61 0.04
8	17.8 1.12	152 1	101 1	14.9 0.8	243 8	1.98 0.03	0.267 0.003	0.276 0.010
9	24.0 0.5	137 6	90.0 1.4	19.0 1.1	231 4	2.27 0.16	0.250 0.021	1.51 0.13
10	14.0 1.4	122 0	106 1	26.1 1.3	92.8 3.4	2.39 0.01	0.287 0.002	0.192 0.003
11	13.0 0.4	77 4	120 1	28.0 0.0	102 3	2.55 0.15	0.330 0.016	0.320 0.039
12	13.7 0.0	90.4 0.0	121 1	33.1 1.3	115 4	2.80 0.08	0.440 0.009	0.366 0.006
13	12.6 0.6	74 2	131 0	22.5 0.0	74.5 0.7	2.39 0.01	0.276 0.001	1.30 0.04
14	59.4 0.0	530 0	438 6	19.3 0.3	546 11	2.72 0.10	0.129 0.007	3.16 0.14
15	49.9 1.4	525 6	385 4	15.1 0.3	473 4	1.76 0.07	0.119 0.006	4.26 0.28

^a Mean content of duplicate analyses^b Standard deviation of duplicate analyses**Table 4.** Comparison of mean relative standard deviation (RSD) values (%) of metals

Sediment portion	Metal and mean RSD value								RSD mean
	Cu	Pb	Zn	Co	Ba	Fe	Mn	Ca	
Very fine sand, unsplit	6.5	4.3	2.6	3.0	3.0	3.8	5.4	6.4	4.4
Very fine sand, quartered	5.9	2.8	2.8	4.0	2.7	4.1	6.5	8.8	4.7
Coarse silt, quartered	3.9	2.3	1.0	4.0	2.2	3.4	3.9	4.4	3.1

size unsplit and quartered sediments appears quite similar. In contrast, the mean contents for all metals except Co in the quartered coarse silt mesh size are significantly higher. Analyses of the fine-grained silica control samples showed no detectable amounts of these metals before or after crushing and sieving activities. It is believed higher quantities of metals in the crushed and sieved sediments represent

Table 5. Mean content of metals in sediments

Sediment portion	Amount ($\mu\text{g/g}$)					%		
	Cu	Pb	Zn	Co	Ba	Fe	Mn	Ca
Very fine sand, unsplit	13.1	116	133	21.4	214	2.02	0.237	1.28
Very fine sand, quartered	12.9	113	134	21.6	218	2.03	0.238	1.21
Coarse silt, quartered	24.3	193	145	19.7	237	2.18	0.272	1.53

an enrichment of softer chemical phases and associated speciated metals. The higher Fe and Mn values should reflect the presence of higher quantities of Fe and Mn oxide/hydrous oxide phases (Fe and Mn phases). The higher Ca value should represent an increased quantity of carbonate phase.

A ratio was established relating the mean value of Cu, Pb, Zn, and Ba to the mean value of each metal representing the aforementioned chemical phases. This was done for the quartered very fine sand and coarse silt size sediments. It was thought a similar ratio of a metal to phase metal in both sizes may indicate a metal speciation in that phase. Values of metals representing the quartered very fine sand size sediments were chosen for the comparison since both the quartered and unsplit portions of this size reflected similar metal composition. All values used to determine each ratio were taken from Table 5. Table 6 summarizes the ratios. The Zn/Fe, Zn/Mn, and Zn/Ca values representing the very fine sand size sediments are similar to the same ratio values in the coarse silt mesh size. The same result is indicated for Ba/Fe, Ba/Mn, and Ba/Ca values. This would indicate Zn and Ba concentrate in all three chemical phases. Little is known relating heavy metal distributions, concentrations, or affinities for Fe, Mn, and Ca phases in natural stream sediments. Mantei and Foster (1991) report Zn and Ba enrich in these phases. Other studies indicate affinity of these metals in the Fe, Mn, and Ca phases formed under laboratory conditions. Forbes and others (1976) and Kinniburgh and others (1976) indicate Zn displays a relatively high adsorption on iron oxides. Murray (1975) reports a moderate affinity of Zn for hydrous manganese dioxide. Gadde and Laitinen (1974) report relatively high quantities of Zn adsorb on hydrous iron and manganese oxides. Zachara and others (1988) indicate Zn quantities adsorb on calcite and is a function of pH. Copper and Pb do not show a strong relationship with any phase using the above procedure. It is thought these metals may enrich in a phase or phases in the sediments not considered in this study. Higher quantities of these metals are reported in what may be the sulfide and aluminum oxide/hydrous oxide phases (Mantei and Foster 1991). Kinniburgh and others (1976) report Cu and Pb have a very high affinity for aluminum oxide.

There is no clear explanation for the decrease in the mean Co value in the quartered coarse silt size. It is reported Co speciates in the Fe, Mn, and carbonate phases

Table 6. Ratios of mean content of Cu, Pb, Zn, and Ba to Fe, Mn, and Ca

Sediment portion	Iron phase				Manganese phase				Carbonate phase			
	Cu/Fe	Pb/Fe	Zn/Fe	Ba/Fe	Cu/Mn	Pb/Mn	Zn/Mn	Ba/Mn	Cu/Ca	Pb/Ca	Zn/Ca	Ba/Ca
Very fine sand, quartered	6.4	55.8	66	107	54.2	475	563	916	10.7	93.4	110.7	180
Coarse silt, quartered	11.1	88.5	66	109	89.3	710	533	871	15.9	126.1	94.8	155

(Mantei and Foster 1991). Possibly Co concentrates in another phase that is hard enough to resist the crushing and does not enrich during the sieving process, but no specific phase is suggested.

Conclusions

Homogeneity of metals in the very fine sand size sediments appears to be relatively high. Sediments need not be quartered to obtain a better homogeneity because field sieving appears to give a uniform sample. The sediment size used for chemical analyses should be obtained through sieving activities at the collection site. Sediments should not be crushed and sieved prior to chemical analyses. This procedure appears to cause preferential concentration of the Fe, Mn, and carbonate phases and speciated metals. This results in false elevated metal quantities obtained for the sediments.

Presently there is no regulation defining unacceptable or toxic levels of heavy metal quantities in stream sediments. Metal quantities in stream sediments thought to be affected by a landfill may be compared with quantities of the same metals in stream sediments known to be affected by a landfill on the Superfund cleanup list. A knowledge of metal homogeneity in the samples may help in this evaluation. Future studies could include the homogeneity of metal content as a function of stream sediment size fractions and in the isolated individual chemical phases. A study of homogeneity of metals occurring as fragmental particles in stream sediments also may be worthwhile.

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