TRACE METAL SPECIATION IN SEDIMENTS OF PARACALE BAY

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Total trace metal levels in sediments of Paracale Bay, Camarines Norte were analyzed by flame atomic absorption spectrophotometry and compared with literature values for background, core or baseline metal levels in sediment/soils. The results indicate generally high metal enrichment (specifically Mn, Pb, Cd, Zn, and Cu) in sediments taken from sampling stations near a mining site, and low to moderate metal enrichment in sediments taken from sampling stations distant from the mining site.

Using the Tessier, *et al.* sequential chemical extraction scheme, the order of remobilizability was Mn> Pb> Cd=Hg> Cu> Zn> Fe> Cr. The major association of the metals in sediments were: Cu and Hg with organic matter; Zn, Mn, and Pb with reducible Fe/Mn oxides; and, Fe and Cr with inert fraction (detrital lithogenic minerals). The residual or non-available fraction (relative to the total metal content) in all samples are as follows: Mn, 12%; Pb, 17%; Cd=Hg, 20%; Cu, 33%; Zn, 37%; Fe, 66%; and, Cr, 77%.

INTRODUCTION

Trace metals may be distributed or partitioned between many components of the soil or sediment and may be bonded to them in different ways. Based on the type of bonding site and strength, trace metals association with different components of sediments are broadly classified into five fractions [1] :

F1. Water soluble, weakly adsorbed and exchangeable fractions
F2. Bound to carbonates
F3. Bound to hydrous oxides of Fe, Mn
F4. Bound to organic matter
F5. Inert fraction (detrital lithogenic minerals)

The nature of these associations in the sediment or soil structure has often been referred to as 'speciation" and determines the capacity of the sediment to resupply the water column with the metal when physicochemical conditions are favourable.

Gold mining has been on-going in Paracale, a mineral-rich region of northern Camarines province in the Bicol area, for the past 400 years. The main objective of this project is to assess the extent of a possible metal pollution in Paracale Bay coming from mine tailings or mine waste of a nearby mine site using trace metal speciation of sediments from Paracale.

It is presently recognized that total metal levels do not reflect the real threat posed by the sediments to the aqueous environment. Rather, knowledge of the actual chemical forms of the metal which would have different toxicities [2] would be more useful. In sediments these forms refer to metals associated with discrete phases of the sediment matrix.

For this project, determination of metal speciation or distribution in sediment or soil employed the Tessier *et al.* [3] sequential chemical extraction scheme. This scheme uses reagents that selectively release trace metals which are held in the soil or sediment by different chemical bonds, or dissolve certain mineral phases. Although these reagents are not highly specific in extracting metals from different phases, they provide a useful means for estimating potentially "available" metal concentration.

It can be gleaned from the speciation scheme (Fig. 1) that the metal association in the sediment becomes increasingly stronger as one progresses through the sequence of extractions. In this scheme, the first four fractions may be taken to represent the remobilizable or potentially available
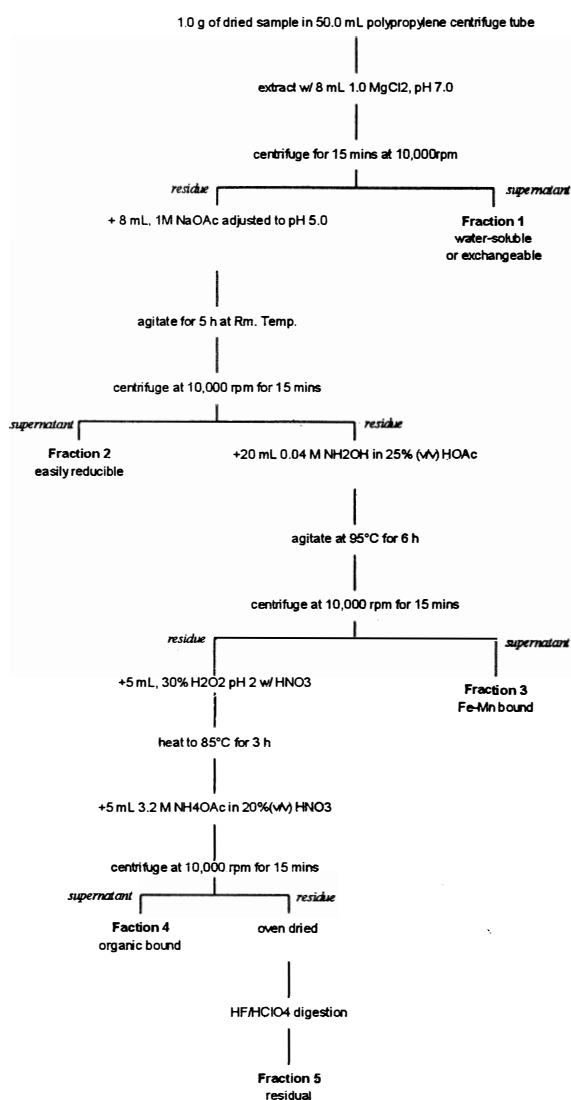
Fig. 1. Sequential extraction scheme for the separation of trace metals [3]

metal levels which may be attributed mainly to anthropogenic sources (contributions from civilizational and human activities). The fifth or inert fractions represents detrital lithogenic minerals (e.g. present in rock debris or released during weathering).

EXPERIMENTAL

Description of Test Sites. The sediment samples were obtained within the proximity of a mining site in Paracale. The ores mined in this area are obtained from a shallow pit near the Paracale bay. A tailings dam is built to impound mine tailings from milling operations. If it is not properly maintained possible dissemination of mine waste can occur.

Figure 2 shows the town of Paracale and the location of the sampling sites with the approximate distance of each station
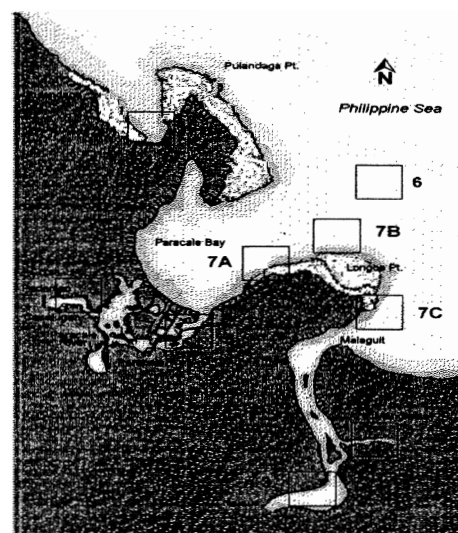

Fig. 2. Sampling sites of sediments from Paracale

from the mine site. A description of sampling sites is given in Table 1.

Sampling and Sample Pretreatment. Bottom (0-15 cm deep) sediments were obtained (using an Eckman dredge grab sampler) from the nine sampling stations (marked 1-7A,B,C) in April and September 1995.

The sediment samples were wet sieved through a 1-mm nylon screen. The sediment was then allowed to settle for 2 days before overlying water was removed by suction and the sample thoroughly mixed before analysis. During settling and between subsequent investigations, samples were stored in tightly sealed polyethylene containers at 4°C.

Metal Analyses. Total metal content of sediments was determined on approximately 0.5 g oven dried sample using single extraction with aqua regia and hydrofluoric acid according to Rantala and Loring's procedure [4]. Mercury analysis [5] used a 1-g (oven dried) at 60°C sample digested in aqua regia for two minutes at 95°C, followed by oxidation with potassium permanganate. Mercury in the digested sample is then measured by the conventional cold vapor technique.

Zinc, Manganese, Copper, Lead, Chromium, Cadmium, Iron, and Mercury were analyzed by flame atomic absorption spectrophotometry (Shimadzu AA-65015S and Varian AA-275). Concentrations were determined by the standard addition method.

Speciation Analysis. Determination of metal speciation or distribution in sediment employed the Tessier et al. [3] sequential chemical extraction scheme (cf. Fig. 1). Wet weight of sample was accurately determined and a separate sample was dried at 110°C to determine moisture content. The results were then calculated on the dry basis and

Table 1. Description of Sampling Sites

Sampling Site	Sample Code	Sites Description
Station 1	S1-PM	Padanlan/Casalugan area; a close river system which ends at the Casalugan (NW of Paracale); good site for fishponds and nurseries.
Station 2	S2-MA	Mangkasay area (Malaguit River) is a close branch of the Malaguit river receiving seawater at the same time with Casalugan/Padanlan. Fewer fishponds are located. The banks are lined with abundant mangroves.
Station 3	S3-NA	Malaguit river area; near residential area, where small-scale miners operate, with occasional fish trapping activity
Station 4	S4-PD	Pulandaga point, bay area distant from the mine site
Station 5	S5-MS	Maligaya area is a residential area near the mouth of Paracale river. The fish port is located 25 meters away. Most of the families are in small-scale mining business with gold extraction by amalgamation. Several temporary ponds for gold panning contribute wastes to the river via small ditches.
Station 6	S6	500 meters away from the mining site is the outer portion of Paracale bay with unstable water column due to wave action
Station 7	S7	The mining area
Station 7A	S7-MA	Near the cyanide treatment plant
Station 7B	S7-MB	Opening of the underground water disposal
Station 7C	S7-MC	Portion of the Longos point which was originally a sandy beach but presently not suitable for swimming because of heavy siltation covering the coral line shores.

Table 2. Total Metal Content of Sediments in µg/g: (a) April 1995; and, (b) September 1995

(a)

Sample ID	Zn	Mn	Cu	Pb	Cr	Cd	Fe	Hg
S1-PM	140	361	283	246	380	35	23,656	0.29
S2-MA	48	241	69	140	412	29	16,916	0.07
S3-NA	61	171	91	386	229	20	14,273	0.15
S4-PD	52	211	71	150	355	25	3,718	0.38
S5-MS	98	792	97	137	398	16	13,375	0.12
S6	90	638	64	155	214	23	25,627	0.28
S7-MA	3758	3,831	1,728	602	3,295	54	13,755	0.57
S7-MB	2010	4,506	844	2,499	270	39	26,812	0.12
S7-MC	38	442	92	95	131	24	3,337	0.16

(b)

Sample ID	Zn	Mn	Cu	Pb	Cr	Cd	Fe
S1-PM	207	170	106	111	773	3.94	26836
S2-MA	53	158	92	57	1428	14	13207
S3-NA	132	556	189	58	1739	0.91	42387
S4-PD	27	166	46	100	235	9.30	10115
S5-MS	268	1834	195	250	1893	1.59	45555
S6	168	650	79	116	552	9.01	25138
S7-MA	868	2556	350	305	1354	15	33263
S7-MB	889	1960	396	962	1999	17	54739
S7-MC	71	1023	151	115	502	14	19411

corrected for loss of volatiles (i.e. water). Extractions on the wet weight of sample were done directly in a 50-ml polypropylene centrifuge tubes and centrifugation was done at ca. 10,000 rpm for 15 minutes. Washings of the residue were combined with supernatant and the total volume of each fraction was made up to 25.0 ml with 0.008 M HNO_3 to preserve the solution.

All solutions were prepared from reagent-grade chemicals and doubly distilled deionized waters. Duplicate trials were performed in all analyses.

RESULTS AND DISCUSSION

Tables 2a and 2b summarize the available data on the total metal content of sediments from the different sampling points. The relative standard deviation (% RSD) of the data in this study were generally 10% or better (for duplicate trials) except for mercury since we were able to do only one trial due to the breakdown of the mercury vapor generation unit of the AAS. For comparison, Table 3 presents some background sediment levels reported in the literature [6-8]. Since many parts of Luzon Islands are geologically

Table 3. Background Trace Metal Levels of Sediments (in µg/g) Reported in the Literature

	Fe	Mn	Cu	Zn	Pb	Hg	Cd	Ref
Mean Sediment	41,000	770	33	95	19	0.19	0.17	6
Shallow water sediments	65,000	850	56	92	22	---	---	6
Luzon sediments[a]	62,000	1230	60	56	25	0.15	0.16	7
Mean crust	41,000	950	50	75	14	0.05	0.11	6
Average shale	47,000	850	45	95	20	0.18	0.22	6
Igneous rocks[b]	14,000	---	15	40	1	<0.1	0.2	8
	94,000	---	90	110	18	---	---	

[a] Baseline level in freshwater sediments from natural waters in Luzon island, Philippines

[b] Minimum and Maximum values are quoted

characterized by basaltic and pyroclastic volcanic rock materials, as well as shales and limestone, the metal levels in igneous rocks and shales are relevant. Because of limited resources, this study was not able to analyze any core sediment/soil samples. The minimum and maximum literature baseline levels for each metal were compared to the corresponding minimum and maximum values obtained in this study.

Total Metal Content Observations. As seen in Tables 2a and 2b, total metal content of sediments from station 7 (near the mining site) are generally very high compared with sediments from stations 1-6 (distant from the mining site) for both the April and September 1995 samples. In general, a comparison of our total metal data with literature background levels in sediments (Table 3) reveals high metal enrichment (specifically Mn, Pb, Cd, Zn and Cu) in sediments from station 7 (near the mining site) for both April and September 1995 samples. Total metal data for stations 1-6 which are distant from the mining area (Station 7) indicate low to moderate metal enrichment specifically for Zn, Cu, Cd and Pb.

The iron level of all sediments (Stations 1-7) for both April and September 1995 samples ranges from 0.4%-8% and are within the background levels found in igneous rocks (1.4%-9.4%).

The geological make-up of Camarines Norte provinces is comprised of ultramafic rocks [9]. The chromium content of this type of rock ranges from 211-5091 µg/g. This study found that the chromium content of Paracale sediments from Stations 1-7 ranges from 214-3295 µg/g and are within the chromium content of ultramafic rocks.

Sediments from Station 7 were found to be contaminated with high levels of cadmium (14-54 µg/g) compared to background levels which ranges from (0.11-0.22 µg/g). The high levels of Cd, Cu (92-1728 µg/g) and Zn (71-3758 µg/g) of these sediments suggests mine tailings as source.

An incredibly high levels of Pb were found in all sediments taken from Stations 1-7 (57- 2,499 µg/g) compared to background levels (1-25 µg/g). Leaded gasoline and diesel fuel used by motor vehicles, motorized boats and barges are diffuse sources of lead in the atmosphere which eventually enter the water systems. Mine tailings could also be a possible source.

Metal Distribution (Speciation). It is observed in Tables 2a and 2b that the total metal content of the sediments at various sampling sites cover a wide range. Hence, for easier comparison of the samples, the distribution of metals in the various fractions are shown in relative amounts in Fig. 3a (distribution graphs for April 1995 samples) and Fig. 3b (distribution graphs for September 1995 samples). Percent (%) extracted or potentially available metal refers to the sum of % extracted in the first four fractions. The values quoted here are averaged values across all samples. The RSD of the mean % extracted across all samples were generally below 20%. The analytical operations involved in the sequential extraction procedure contribute to some loss of precision.

Specific "on the average" observations on the partitioning of the metals in sediments for both April and September samples are given below.

Zinc. On the average across all samples (and for both April and September samples), zinc was found to be associated largely with the reducible Fe/Mn oxides (F3) (~30%) and least with the exchangeable fraction (F1) (6%). The average % extractability was found to be 72% and 28% of total metal content remains in the residual fraction.

Cadmium. On the average across all samples, cadmium seems to be evenly distributed among F1-F3 (~22% each). Average % extractability was found to be 80% and 20% remains in residual fraction.

Chromium. As can be seen in Figs. 3a and 3b, chromium was the least extractable among metals studied. Approximately 77% of the total metal are found in the residual fraction (F5) and almost nil in the exchangeable fraction (F1). Average % extractability was found to be 23%.

Lead. The largest amount of lead was found in F3 (~48%).the average % extractability was found to be 83% and 17% remains in the residual fraction.

Copper. It may be observed from Figs. 3a and 3b that on the average across all sample sites and for both April and September samples, the organically bound fraction (F4) contained the largest amount (~31%). Average % extractability is 67%.

Iron. Among the metals studied, iron is the second least extractable metal next to chromium. Average % extractability is ~34%.
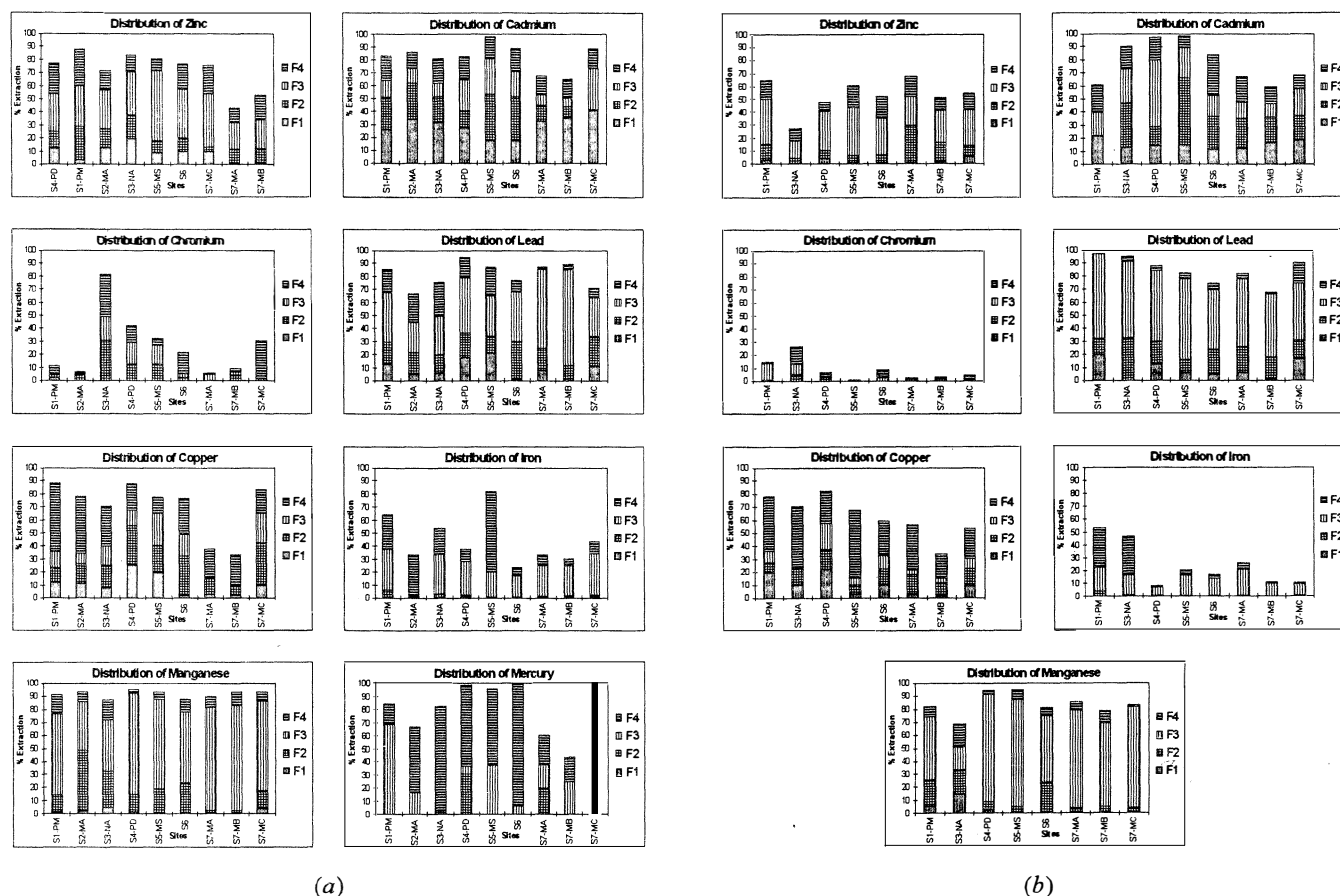
(a)

(b)

Fig. 3. Distribution graphs for: (a) April 1995 samples; and, (b) September 1995 samples

Manganese. In agreement with other studies [6, 7], this was found to be the most extractable metal. The average % extractability of Manganese was found to be 88% and the largest amount is associated with F3 (reducible oxide phase).

Mercury. On the average across all samples, Hg was not detected in the exchangeable fraction. It was found mostly in the organic fraction (~50%). Average % extractability was found to be ~80%.

CONCLUSION

The total metal data of this study as compared to literature background levels in sediments (c.f. Table 3a) reveals high metal enrichment (specifically Mn, Pb, Cd, Zn and Cu) in Paracale Bay sediments near the mining area (Station 7). Total metal data in sediments from Stations 1-6 which are distant from the mining area also indicated low to moderate metal enrichment (specifically Zn, Cu, Cd and Pb).

The speciation results have shown that the order of extractability in Paracale sediments is Mn> Pb > Cd=Hg> Cu> Zn> Fe> Cr. The residual (non-available fraction) was found to be 12% for Mn, 17% for Pb, 20% for both Cd and Hg, 33% for Cu, 37% for Zn, 66% for Fe and 77% for Cr.

The major association of the metals in the sediments were: Cu and Hg with organic, Zn, Mn and Pb with reducible Fe/ Mn oxides and Fe and Cr with inert fraction (detrital lithogenic minerals).

In agreement with other studies, the amount of remobilizable or potentially available metal (as estimated by its chemical extractability) was shown to differ considerably from the total metal content (generally estimated by a single extraction with a strong acid mixture) of the sediment or soil.

The extraction conditions used in this study may not simulate the natural biogeochemical exchange process. Further studies are needed to correlate actual biological uptake levels to the chemical extraction data.

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