

Heavy Metals in Sediments of the Gold Mining Impacted Pra River Basin, Ghana, West Africa

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Total concentrations of Hg, Al, Fe, As, Pb, Cu, Cr, Ni, Mn, Co, V, and Zn were determined in surface sediments collected from 21 locations within the gold mining impacted Pra River basin in southwestern Ghana. Samples were collected during both the rainy and dry seasons. We hypothesized that in the rural southwestern portion of Ghana, the lack of industrial activities makes artisanal gold mining (AGM) by Hg amalgamation the main source of water resource contamination with heavy metals. Therefore, metals showing concentration trends similar to that of Hg in the studied system are likely impacted by AGM. We found that total-Hg (THg) concentrations in riverine sediments are rather low as compared to other aquatic systems that are impacted by similar mining activities. Measured THg concentrations ranged from 0.018 to 2.917 mg/kg in samples collected in the rainy season and from about 0.01 to 0.043 mg/kg in those collected during the dry season. However, the determination of the enrichment factor (EF) calculated using shale data as reference background values showed signs of severe contamination in most of the sampled sites. In the dry season, THg concentrations correlated positively and significantly to the concentrations of As ($r = 0.864$, $p < 0.01$), Cu ($r = 0.691$, $p < 0.05$), and Ni ($r = 0.579$, $p < 0.05$). Based on our previously stated hypothesis, this could then be an indication of the impact of AGM on ambient levels of these 3 elements. However, the determined concentrations of Cu, and Ni co-varied significantly with Al, suggesting that natural sources do account for the observed levels. Accordingly, both AGM and metal inputs from weathered natural deposits are likely co-responsible for the observed levels of Cu and Ni. In contrast, the lack of correlation between As and Al tends to suggest an impact of AGM on As levels. Overall, our data suggest that besides Hg and to some extent As, the impact of AGM on ambient levels of investigated metals in the gold mining impacted Pra River remains negligible. Finally, the increase in metal concentrations from the dry to the rainy season underlines the impact of changes in hydrologic conditions on levels and fate of metals in this tropical aquatic system.

Keywords Heavy metals, mercury, gold mining, sediment contamination, Ghana, West Africa

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1. Introduction

Trace metals found in different environmental compartments can be derived from natural sources and from either non-point and/or point sources associated with anthropogenic activities (Bonzongo *et al.*, 2002). In the developed world, metal pollution is primarily due to fossil fuel combustion, waste incineration, historic mine wastes, etc., whereas in most developing nations this is attributable chiefly to mining, particularly gold mining, which uses metallic mercury (Hg^0) to extract gold from crude ores coupled with the release of mine wastes and tailings enriched with toxic heavy metals. Despite the alarming findings on the negative impacts of Hg on human health and the environment, small-scale gold mining by Hg amalgamation in gold-rich countries of South America, Asia, and Africa is a growing and widespread economic activity. Therefore, the contamination of soils, sediments, water and biota by heavy metals has become a primary concern in these new mining sites because of their toxicity, persistence, and accumulation in food chains. These concerns arise from prior findings obtained from studies conducted in both historic and current gold mining sites by Hg-amalgamation (Förstner and Wittman, 1983). Nevertheless, this type of mining now occurs in most nations in the tropics (Larceda *et al.*, 1995; Villas Boas *et al.*, 2001), as it is a highly important source of income for many individuals in the nations where it is practiced (ILO, 1999). Further, the mining of ore and placer gold deposits has been identified as one of the most ecologically damaging aspects of the gold mining industry (Davidson, 1993; Hangi, 1996; Amegbey *et al.*, 1997; Tarras-Wahlberg *et al.*, 2001; Tarras-Wahlberg, 2002).

In Ghana, artisanal gold mining (AGM) has been practiced as early as the 4th century, and since that time, gold has been extracted by the Hg amalgamation technique from alluvial deposits in rivers and waterways and from denuded outcrops and subsurface sediments along the side of dried-up valleys (Dumett, 1998; Hilson, 2001). The use of Hg in gold extraction heightened and became widespread in Ghana after May 1989 when AGM was legalized by the local government. In Ghana, most of the gold produced by Hg-amalgamation process comes from goldfields located in the southwestern part of the country (Adimado and Baah, 2002), which is drained by three main rivers including the Pra River, which is the focus of this study. In these river systems, metal pollution comes primarily from the processing of ores and disposal of tailings and wastewaters around mines, resulting in negative impacts on both the biogeochemistry and ecology of receiving water bodies (Adriano, 1986; Grimalt *et al.*, 1999).

The fate of different heavy metals introduced into waterways by AGM or other anthropogenic activities depends on their specific characteristics including the ionic potential, the oxidation state, the affinity for specific ligands, the ability to form oxyanions, etc. In most natural surface waters, often characterized by circum neutral pH values, positively charged metal ions (e.g. Pb^{2+} , Cu^{2+} , Ni^{2+} , V^{3+} , and Zn^{2+}) tend to adsorb onto negatively charged solid surfaces such as oxyhydroxides of Fe- and Mn-colloids and fines dominated by silt and clay particles ($<20\ \mu\text{m}$). Oxyanion forming elements (e.g. As and Se) on the other hand have more complex adsorption behaviors, which vary with both the water pH and the element's oxidation state. With regard to the data presented in this paper, the main anthropogenic disturbance in the watershed under study is gold mining. In this case, and in addition to background Hg naturally present in soils/sediments, metallic Hg (Hg^0) used in gold amalgamation is introduced into soil, water, sediment, and the atmosphere through the different steps of gold extraction and purification processes. In these environmental compartments, Hg undergoes transformations which increase its bioavailability, resulting in Hg accumulation and biomagnification in aquatic food chains. In contrast, the levels of the other metals considered in this study are primarily from natural sources (i.e. local

geology) and the impact of AGM in this case is expected to be the combination of exposure of reduced minerals and mobilization of metals associated with such exposed minerals. Overall, metal ions adsorbed onto solid surfaces will ultimately become removed from the water column via sedimentation. Therefore, sediments behave as a sink for most metals that are introduced into aquatic systems and can therefore be used to assess the quality and pollution state of aquatic systems (Salomons and Förstner, 1984; Larsen and Jensen, 1989; Baker and Harris, 1991; Andersen, 1992; Balls *et al.*, 1997). It is worthy to note that this accumulation of metals in sediments could be a dynamic process in that a significant fraction of deposited contaminated fine sediment particles can be re-suspended and transported downstream during high flow regimes. Finally, to assess the contamination of sediments by metals, various geochemical approaches have been used including the use of a tracer, which is an element that is not or only slightly impacted by anthropogenic activities. The most common approach is the use of aluminum (Al) as a normalizer to assess the contamination of soils/sediments by trace metals (Bruland *et al.*, 1974; Windom *et al.*, 1989; Daskalakis and O'Connor, 1995; Shine *et al.*, 1995).

In the Pra River basin, besides AGM, there are no industrial activities to serve as point source for trace metal inputs. The river supports subsistence fishing activities and serves as drinking water supply to communities along its course. To this effect, heavy metal inputs and transport in the river basin as well as the ecological significance owing to the presence of aquatic organisms and waterfowls that use the basin and its delta as feeding grounds may have great impact. However, unlike AGM sites found in the Brazilian Amazon (Larceda and Salomons, 1998; Roulet *et al.*, 2000; Larceda *et al.*, 2004) and other parts of the world (Lin *et al.*, 1997; Nriagu and Wong, 1997; Laperdina, 2002; Kishe and Machiwa, 2003; Limborg *et al.*, 2003), the severity of trace metal contamination in sediments of the Ghanaian Pra River has not been thoroughly examined to ascertain the extent of metal contamination of sediments, as well as the biogeochemical fate of released metals. We hypothesized that in the rural southwestern portion of Ghana, which is drained primarily by the Pra River and its tributaries, the lack of industrial activities makes artisanal gold mining by mercury amalgamation the main source of water resource contamination with heavy metals. Therefore, metals showing concentration trends similar to that of Hg in the studied system are likely impacted by artisanal gold mining. In this paper, we report on our findings on levels and the distribution of trace metals in the fine fraction ($<64\ \mu\text{m}$) of surface sediment samples collected from the Pra River basin in Ghana, and the use of normalization on the obtained data to examine the extent of contamination along the studied river system.

2. Materials and Methods

Ghana is located in the western portion of the African continent and lies along the Gulf of Guinea. Most of Ghana gold mines are located in the southwestern portion of the country, which represents an area of about 40,000 Km². Our investigations were conducted along the Pra River Basin, which takes its source from the Kwahu Plateau before joining by the main tributaries rivers Offin and Birim (Figure 1) to enter the Gulf of Guinea at the south of Ghana. Almost the entire Pra basin is known to be a very active artisanal mining area. During the rainy season of 2002 and the dry season of 2003 in Ghana, sediments were collected along longitudinal transects in the Pra River and its tributaries. The location of sampling sites is marked in numerals in Figure 1. Samples were collected near sites of either past or current AGM (sites 5–15, 17, 18, 19, and 21 upstream) and from locations remote from mining centers (sites 1–4, downstream) such as headwaters (sites 16 and 20) to assess the

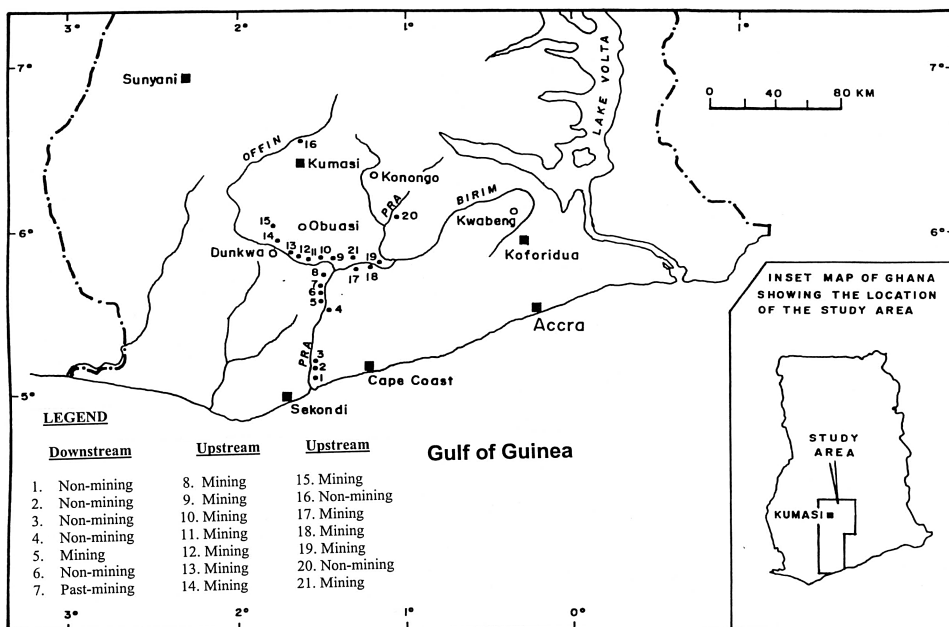


Figure 1. Map of the gold mining impacted Southwestern Ghana showing sampling locations on the Pra River and its tributaries—site 1 is the farthest downstream with the numbering increasing upward.

extent and levels of trace metal contamination related to this activity. Surface sediments were collected from the top 5 to 10 cm using acid pre-cleaned polyethylene scoops. Samples were immediately transferred into acid pre-cleaned polyethylene containers and kept in coolers at all times during collection and transportation. Samples were frozen at the University of Ghana, Accra, and shipped by overnight courier to our laboratory at the University of Florida, Gainesville.

In the laboratory sediment samples were first freeze-dried and then sieved to separate the $<64 \mu\text{m}$ size fraction which normally has the higher metal content. The organic carbon content was determined after loss on ignition (LOI) by combustion at 550°C for 2 hours. For total metal analysis, about 0.5 g of dry fine sample from each site was digested in duplicate with $\text{HCl-HNO}_3\text{-HF}$ mixtures in a closed Teflon vessel overnight at 110°C . The mixture on cooling was diluted with saturated solution of H_3BO_3 to dissolve the fluorides and filtered ($0.45 \mu\text{m}$). Samples were then analyzed for total concentrations of Al, Fe, As, Pb, Cu, Cr, Ni, Mn, Co, V, and Zn by inductively coupled plasma-atomic emission spectrometer (ICP-AES). The reported data are averages of duplicate digestion/analysis of a single sample. Total Hg (THg) was determined by cold vapor atomic fluorescence spectrometry (CVAFS) after SnCl_2 reduction. Analytical QA/QC criteria were met by running, reagent blanks, standard solutions, and certified reference materials. For the determination of total mercury, the reference material IAEA-405 for estuarine sediments containing an average of 0.81 mg/kg THg was used. The percent recovery on the IAEA-405 averaged $95 \pm 11\%$ ($n = 10$) for THg. Finally, simple linear regressions and 95% confidence intervals were used to (i) identify sites with metal concentrations above background values based on co-variation with aluminum, and (ii) examine the relationship between any two of the investigated metals.

Table 1
Total metal concentrations in mg/kg dry weight (ppm) and organic matter content determined as loss on ignition (LOI) on river sediments collected from the Pra River basin during the “rainy season”

River section	Site #	Hg	Al	Fe	As	Pb	Cu	Mn	Co	Ni	V	Cr	Zn	% OM
Lower Pra	1	0.066	278.1	301.2	0.414	0.238	0.263	6.790	0.053	0.439	0.777	0.905	1.418	2.08
	2	0.076	267.5	328.1	0.411	0.043	0.226	8.955	0.134	0.370	0.791	0.819	1.531	5.55
	3	2.917	236.9	168.7	0.213	0.179	0.252	2.387	0.130	0.271	0.706	0.724	1.553	9.98
	4	0.018	146.2	134.8	0.184	0.064	0.127	3.516	0.063	0.308	0.392	0.47	0.742	11.50
	5	0.046	174.7	225.3	0.360	0.096	0.221	6.518	0.188	0.362	0.758	0.825	1.214	1.30
	6	0.103	195.1	155.6	0.384	0.041	0.158	4.384	0.078	0.318	0.518	0.586	0.754	4.92
	7	0.022	223.6	220.7	0.488	0.022	0.221	6.297	0.166	0.348	0.652	0.744	1.072	1.67
	8	0.310	348.9	370.4	0.691	0.078	0.333	8.595	0.272	0.493	1.098	1.321	1.285	7.61
	9	0.032	172.2	224.9	0.12	0.051	0.206	1.174	0.335	0.406	0.693	0.640	5.906	0.59
	10	0.022	55.9	103.4	0.395	0.071	0.153	1.488	0.062	0.249	0.349	0.396	1.685	0.28
Offin	11	0.132	236.8	190.9	0.714	0.017	0.227	0.940	0.230	0.346	0.749	0.775	4.199	1.50
	12	0.329	317.6	328.1	4.31	0.038	0.877	1.401	0.288	0.489	1.274	1.261	5.486	2.62
	13	0.032	178.0	143.9	0.100	0.112	0.162	0.903	0.050	0.361	0.587	0.638	1.756	0.62
	14	0.121	262.9	194.5	0.220	0.076	0.202	1.406	0.197	0.311	0.818	0.842	2.531	1.79
	15	0.072	361.4	715.2	0.453	0.110	1.155	2.196	0.515	1.177	3.338	3.614	5.665	6.53
	16	0.189	544.8	510.1	0.125	0.012	0.316	2.930	0.128	0.450	1.281	1.088	0.886	6.85
	17	0.079	226.8	432.9	0.180	0.060	0.386	4.883	0.112	0.356	3.378	1.176	1.526	1.91
	18	0.678	158.1	166.2	0.079	0.214	0.169	2.658	0.023	0.300	0.594	0.620	0.802	2.89
	19	0.071	273.7	376.1	0.115	0.014	0.323	5.002	0.249	0.441	1.252	1.273	1.201	1.56
	20	0.180	736.9	1266.3	0.133	0.160	1.010	10.704	0.517	0.874	0.861	2.401	1.603	7.91
Upper Pra	21	0.070	236.8	290.2	0.165	2.441	0.299	3.546	0.138	0.342	0.834	1.100	1.286	3.47

3. Results and Discussion

3.1. Concentrations of Hg and Other Metals in Analyzed Sediments

Concentrations of THg in samples collected during both the wet (July 2002) and dry (January 2003) seasons are given in Tables 1 and 2 and presented comparatively in Figure 2.

Overall, THg concentrations were higher in samples collected during the rainy season as compared to the dry season. Elevated concentrations of Hg were observed in samples collected from sites downstream of active mining centers, located a few or several miles away from mining centers (sites 1 through 4 and 6). THg peaks observed primarily near mining areas (Figures 1 and 2) reveal the impact of AGM activity on sediment quality. The highest value in the rainy season was recorded at site number 3 (2.917 mg/kg). As one moves away from the heightened AGM area either upstream or downstream to a lesser one, Hg concentration diminishes, suggesting that Hg contaminated particles are preferentially deposited close to the source of contamination (Figure 2). A case in point compares site 8 and sites 7 and 9 in the rainy period (Figure 2). The non-mining centers also show a similar pattern. Therefore increased run-off during the rainy season may accelerate the transport of Hg contaminated particles into the stream bed, resulting in the observed higher values downstream (sites 1–3). In the dry season, sediments are less enriched with fines. This is likely due to the intense re-suspension and downstream transport of fines that follow tropical rains. As a consequence, much lower THg values are observed in samples collected during the dry season. When compared with well known contaminated historic mining sites (e.g. the Carson River in Nevada with a reported range of 2.0 to 156 mg/kg in riverine sediments) and current AGM areas (e.g. the Philippines, with an average THg value of 21.03 mg/kg), the obtained average values of 0.02 mg/kg in dry season and 0.27 mg/kg in wet season in the Ghanaian Pra River system are lower. Nevertheless, these Ghanaian average

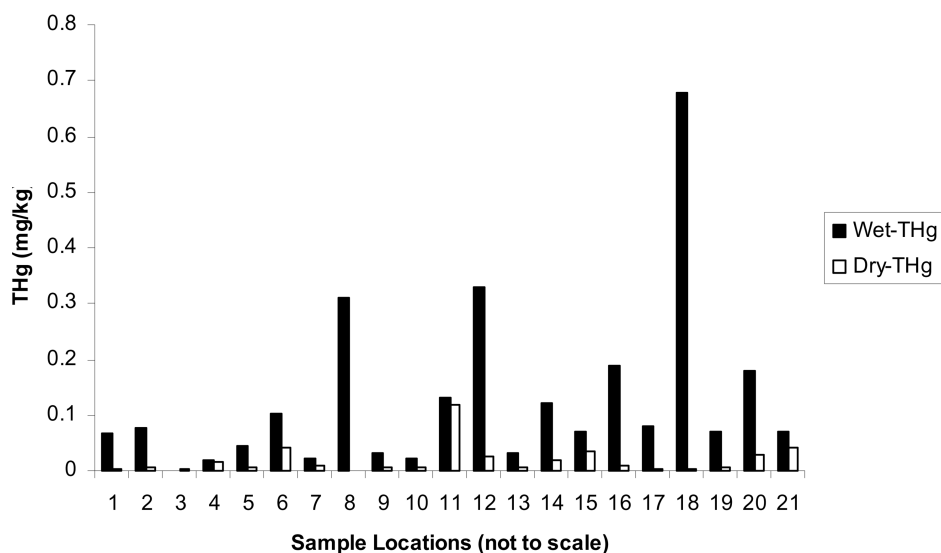


Figure 2. Longitudinal distribution of total-Hg concentrations (ppm) in surface sediments collected from the Pra River Basin during wet and dry seasons.

Table 2

Total metal concentrations in mg/kg dry weight (ppm) and organic matter content determined as loss on ignition (LOI) on river sediments collected from the Pra River basin during the “dry season.” *BDL = Below Detection Limit (0.003 ppm for Pb and 0.00075 ppm for Co)

River section	Site #	Hg	Al	Fe	As	Pb	Cu	Mn	Co	Ni	V	Cr	Zn	% OM
Lower Pra	1	0.003	90.0	141.0	0.216	BDL	0.018	3.031	*BDL	0.252	0.204	0.203	0.569	0.46
	2	0.008	308.0	214.0	0.146	BDL	0.089	2.828	BDL	0.400	0.484	0.523	1.199	3.15
	3	0.002	406.0	236.0	0.281	BDL	0.153	5.102	BDL	0.457	0.645	0.732	0.704	1.68
	4	0.017	570.0	283.0	0.355	BDL	0.207	4.461	BDL	0.457	0.878	0.985	1.280	4.74
	5	0.005	117.0	68.0	0.218	BDL	0.029	1.470	BDL	0.301	0.145	0.267	0.746	0.25
	6	0.043	198.0	271.0	0.370	BDL	0.192	7.890	BDL	0.453	0.619	0.579	1.152	0.96
	7	0.009	287.0	135.0	0.158	BDL	0.091	2.573	BDL	0.343	0.475	0.575	0.557	0.00
	8	0.002	245.0	247.0	0.458	BDL	0.133	8.221	BDL	0.574	0.548	0.537	0.756	3.01
	9	0.008	315.0	202.0	0.230	BDL	0.153	4.140	BDL	0.450	0.525	0.964	1.004	0.46
	10	0.007	320.0	189.0	0.181	BDL	0.105	5.825	BDL	0.428	0.528	0.516	0.964	0.40
Offin	11	0.118	660.0	393.0	5.076	BDL	1.112	7.034	BDL	1.015	1.326	1.305	1.274	0.47
	12	0.026	323.0	178.0	0.940	BDL	0.185	3.157	BDL	0.542	0.606	0.588	1.065	2.48
	13	0.007	462.0	219.0	0.759	BDL	0.257	3.850	BDL	0.554	0.794	0.831	0.819	0.53
	14	0.018	1449.0	1077.0	0.613	BDL	0.992	5.609	BDL	1.088	3.750	4.322	2.013	0.47
	15	0.036	699.0	1228	0.235	BDL	0.574	7.904	BDL	1.058	3.082	2.756	1.833	2.79
	16	0.010	420.0	248.0	0.139	BDL	0.134	5.241	BDL	0.511	0.621	0.781	0.933	4.39
	17	0.002	407.0	497.0	0.125	BDL	0.150	5.016	BDL	0.437	0.867	1.030	1.027	1.74
	18	0.002	318.0	116.0	0.088	BDL	0.072	2.195	BDL	0.429	0.461	0.522	0.728	0.52
	19	0.005	509.0	356.0	0.124	BDL	0.196	9.781	BDL	0.568	0.885	1.031	1.171	0.39
	20	0.030	288.0	378.0	0.103	BDL	0.261	4.480	BDL	0.429	1.219	1.755	0.666	0.84
Upper Pra	21	0.043	247.0	243.0	0.369	BDL	0.049	2.495	BDL	0.569	0.349	0.333	0.881	2.91

Table 3a
Pearson correlation coefficients for sediment data collected during the dry season. Lead (Pb) and cobalt (Co) are not included as their concentrations were below instrument analytical detection in samples collected in the dry season

	Hg	Al	Fe	As	Cu	Mn	Ni	V	Cr	Zn	%OM
Hg	1.000										
Al	0.226	1.000									
Fe	0.231	0.783*	1.000								
As	0.864*	0.255	0.069	1.000							
Cu	0.691**	0.809*	0.681	0.716**	1.000						
Mn	0.252	0.330	0.461	0.209	0.405	1.000					
Ni	0.579**	0.817*	0.825*	0.526	0.899*	0.504	1.000				
V	0.257	0.894*	0.958*	0.149	0.783*	0.397	0.858*	1.000			
Cr	0.199	0.908*	0.906*	0.107	0.764*	0.340	0.793*	0.978*	1.000		
Zn	0.328	0.822*	0.842*	0.204	0.710**	0.449	0.814*	0.848*	0.797*	1.000	
%OM	-0.034	0.008	0.091	-0.148	-0.150	0.054	0.057	-0.007	-0.064	0.195	1.000

* $p < 0.01$; ** $p < 0.05$.

Table 3b
Pearson Correlation coefficients for sediment data collected during the wet season

	Hg	Al	Fe	As	Pb	Cu	Mn	Co	Ni	V	Cr	Zn	%OM
Hg	1.000												
Al	-0.009	1.000											
Fe	-0.119	0.896*	1.000										
As	-0.003	0.058	-0.023	1.000									
Pb	-0.020	-0.040	-0.013	-0.107	1.000								
Cu	-0.042	0.660*	0.801*	0.414	-0.024	1.000							
Mn	-0.137	0.476	0.523	-0.169	-0.026	0.167	1.000						
Co	-0.100	0.622**	0.749*	0.191	-0.092	0.819*	0.204	1.000					
Ni	-0.163	0.640**	0.803*	0.083	-0.074	0.899*	0.229	0.834*	1.000				
V	-0.099	0.241	0.423	0.071	-0.066	0.586**	-0.006	0.408	0.582	1.000			
Cr	-0.096	0.629	0.796*	0.081	0.028	0.908*	0.220	0.815*	0.971*	0.690**	1.000		
Zn	-0.082	0.029	0.117	0.488	-0.132	0.508**	-0.462	0.610	0.445	0.334	0.399	1.000	
%OM	0.432	0.415	0.330	-0.095	-0.014	0.243	0.296	0.162	0.277	0.034	0.275	-0.224	1

* $p < 0.01$; ** $p = 0.05$.

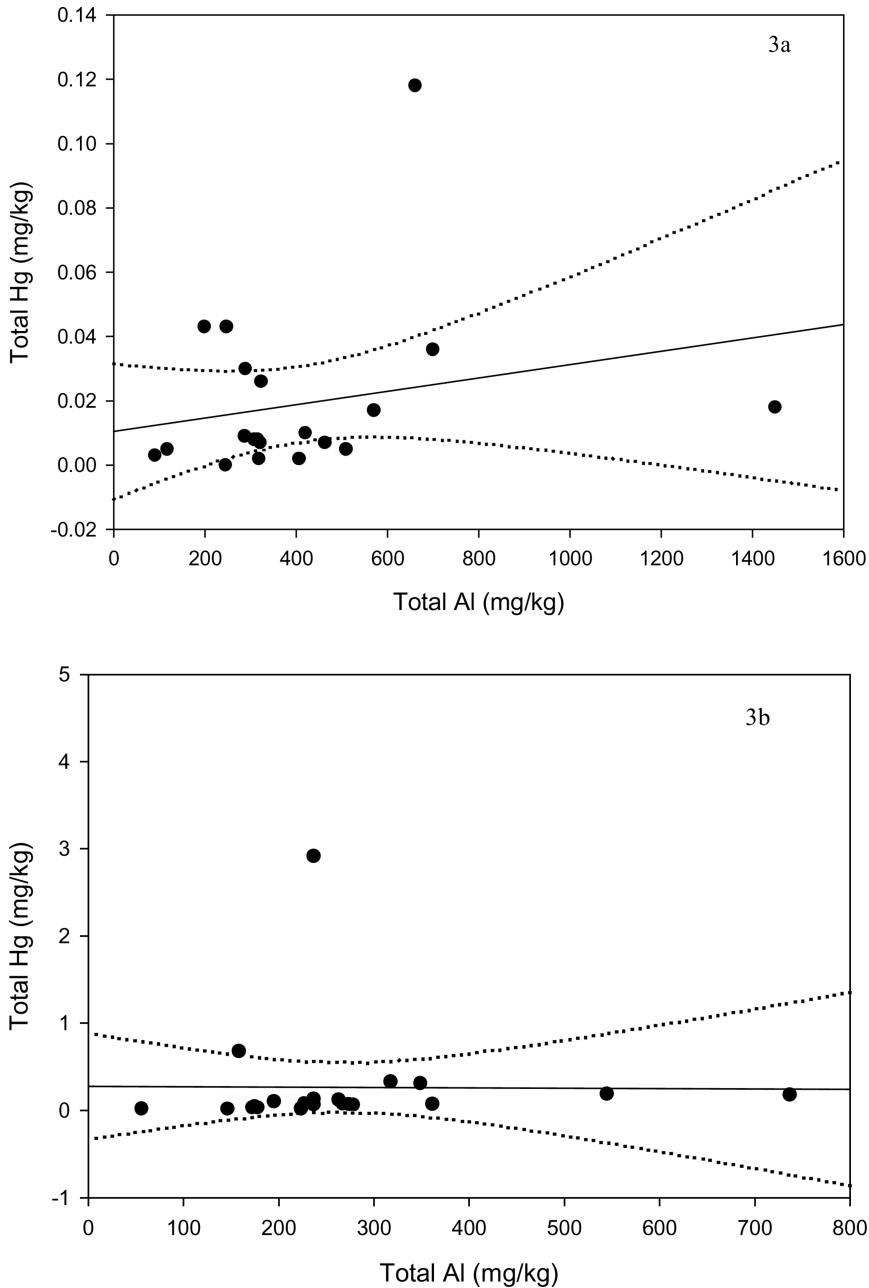


Figure 3. Hg: Al scatter plot for sediments of the Pra River basin: 3a = dry season and 3b = rainy season. The dotted lines represent the 95% confidence interval.

values are comparable to the values reported for the Madera River (average 0.04 mg/kg) and the Tapajós River (average 0.29 mg/kg) in the Brazilian Amazon (Malm *et al.*, 1990; Malm *et al.*, 1995; Malm, 1998; Lodenius and Malm, 1998; Roulet *et al.*, 2001). Factors affecting the THg concentration may include the magnitude of AGM activities, season, location of

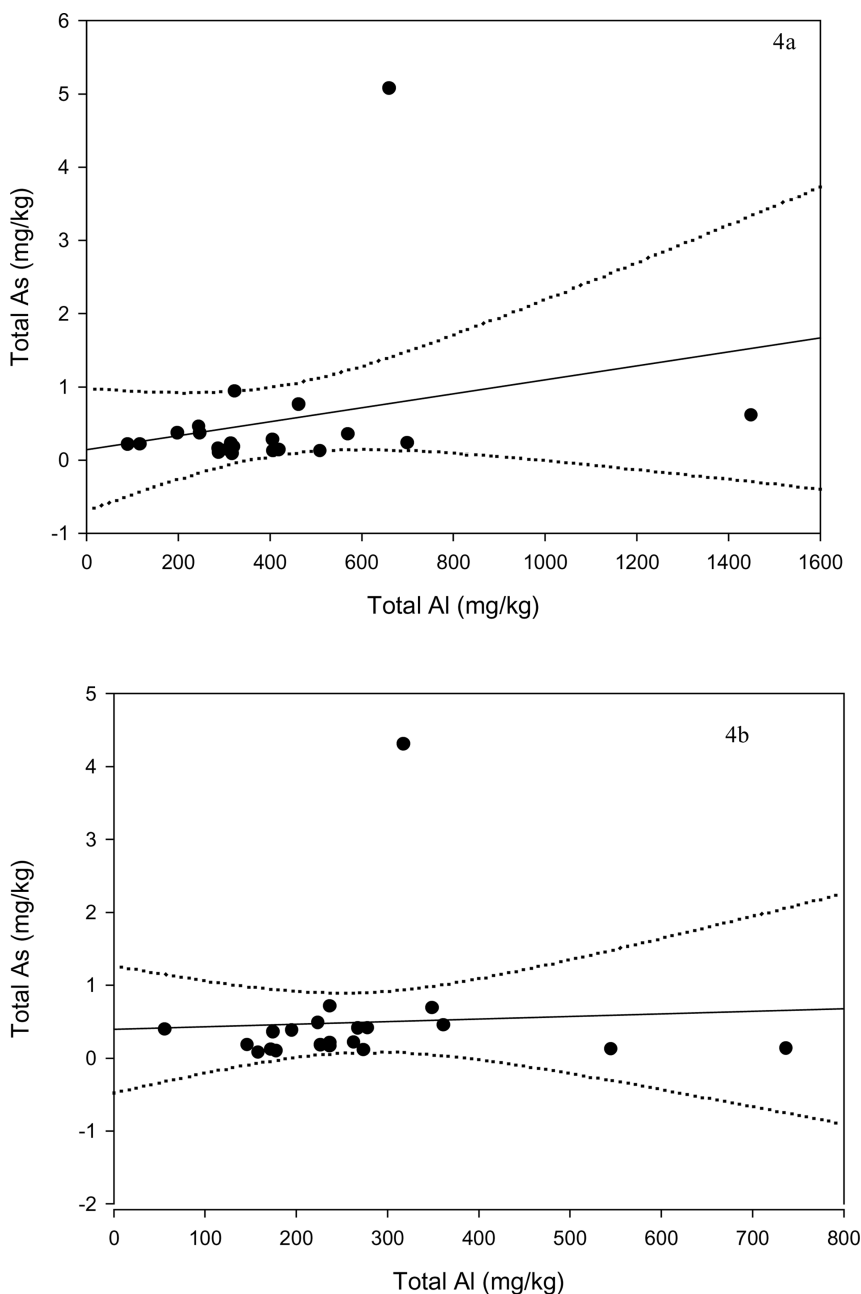


Figure 4. As: Al scatter plot for sediments of the Pra River basin: 4a = dry season and 4b = rainy season. The dotted lines represent the 95% confidence interval.

sampling site from mining centers, volume and flux of waterways, sediment grain size, etc. (Larceda and Salmons, 1998). THg concentrations in most of the sampled sites in the Pra River basin in both seasons were lower than the 0.2 ppm guideline of US-EPA (1985) with the exception of sites 3, 12 and 18 in the wet season (see Table 1).

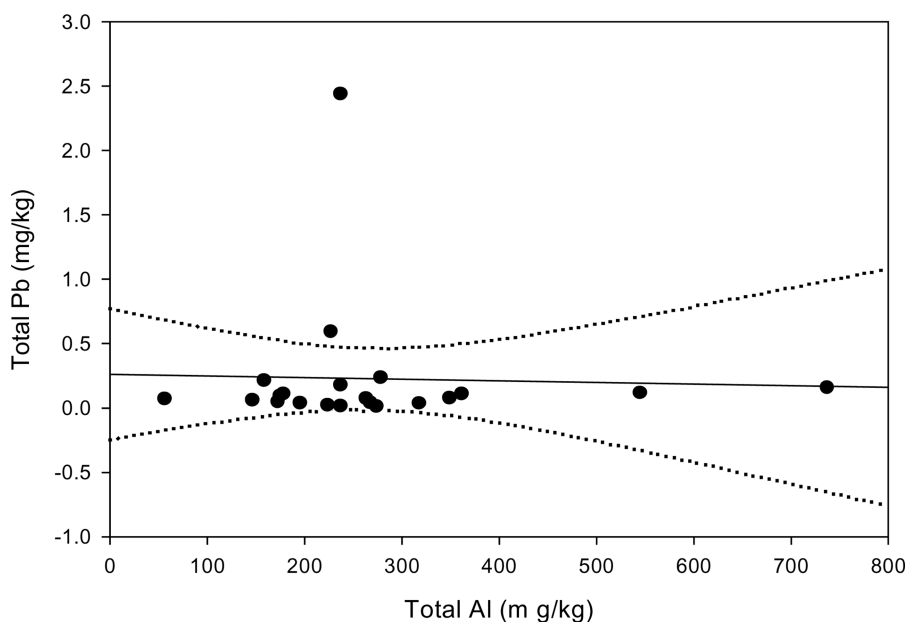


Figure 5. Pb: Al scatter plot for sediments of the Pra River basin: rainy season. The dotted lines represent the 95% confidence interval.

Seasonal variations of the total concentrations of the other metals are summarized in Tables 1 (wet season) and 2 (dry season). Al, Fe, and Mn show higher concentrations than the rest of the elements. Zn, Cu, Co, Ni, V and Cr exhibited their highest concentrations in the sediment during the high flow regime, while levels of Co and Pb were below the instrument detection limit (see Table 2) in all samples collected during the dry season. The correlation coefficients amongst sediment parameters are shown in Tables 3a and 3b. These tables point to: (i) the lack of relationship between organic matter (%OM) and all analyzed metals in both the dry and wet seasons; (ii) strong and significant correlations between Al and Fe, Cu, Ni, V, Cr, and Zn in the dry season; (iii) weaker but significant relationships between Al and Fe, Cu, Mn, Co, Ni, and Cr in the rainy season; and (iv) As, Cu and Ni show positive and significant relationships with Hg, but only during the dry season. The lack of strong correlation between OM and any of the analyzed metals is an indication that a significant fraction of analyzed metals in these sediments is rather associated with fine inorganic particles. This observation supports the use of Al as a normalizer for the determination of the contamination state of the Pra River sediments as discussed below.

3.2. Assessing the Contamination Level of the Pra River Sediments

To assess the impact of AGM on levels of heavy metals investigated in this study, we used a combination of two approaches. First, we used the co-variation of metals of interest with Al to determine for each of these metals the level of sediment contamination, or the concentration above what would naturally occur. Second, we calculated the enrichment factor (EF) for each of the elements using Al as a tracer and the reported metal concentrations in shales (Turekian and Widepohl, 1961) as reference background levels.

Variability in trace metal concentrations in sediments could be driven by natural and/or anthropogenic sources, and in sediment matrices metals are usually associated chiefly with

the fine-grained sediment fractions. There is no generally accepted protocol for selecting a sediment constituent to be used for normalization, and several approaches/elements have been used. Prominent among them are aluminum, iron, lithium, total organic carbon and grain size (e.g. Windom *et al.*, 1989; Loring, 1990; Loring and Rantala, 1992; Daskalakis and O'Connor, 1995; Aloupi and Angelidis, 2001a, 2001b). Based on published information, it is apparent that Al has been the most commonly used tracer element in normalization calculations/models. Several reasons explain the choice of Al over others. Al is a major component of fine-grained aluminosilicate minerals. As an essential component of these smallest sized particles, Al is a good surrogate for clay particles (Windom *et al.*, 1989; Daskalakis and O'Connor, 1995), which constitute the bulk of adsorption sites for metals on sediment particles. In contrast, the use of organic carbon content as a normalizer has been proved to show weaker correlations than Al (Windom *et al.*, 1989; Horowitz, 1991). Iron is not as good a matrix element as Al because it is chemically active in both oxic and anoxic environments, hence it is always associated with surfaces (Daskalakis and O'Connor, 1995). Based on these observations, Al was chosen as normalizer in this study. Scatter plots of metals versus normalizer were used to decipher signs of anthropogenic impacts on concentrations of metals of interest. The regression of each metal on Al in the natural

Table 4a

Calculated enrichment factors* (EF) for analyzed elements in sediment samples collected in the rainy season. Shale reference values were taken from Turekian and Wedepohl (1961)

River section	Site #	Hg	Fe	As	Pb	Cu	Mn	Co	Ni	V	Cr	Zn
Lower Pra	1	47	2	9	3	2	2	1	2	2	3	4
	2	57	2	9	1	2	3	2	2	2	3	5
	3	2463	1	6	3	2	1	2	1	2	3	6
	4	25	2	8	2	2	2	2	2	2	3	4
	5	53	2	13	2	2	4	5	2	3	4	6
	6	106	1	12	1	1	2	2	2	2	3	3
	7	20	2	13	0	2	3	3	2	2	3	4
	8	178	2	12	1	2	2	3	2	2	3	3
Offin	9	37	2	4	1	2	1	8	3	2	3	29
	10	79	3	43	5	5	3	5	5	4	6	25
	11	111	1	19	0	2	0	4	2	2	3	15
	12	207	2	84	0	5	0	4	2	2	4	15
	13	36	1	3	3	2	0	1	2	2	3	8
	14	92	1	5	1	1	1	3	1	2	3	8
	15	40	3	8	1	6	1	6	4	6	9	13
Upper Pra	16	69	2	1	0	1	1	1	1	1	2	1
	17	70	3	5	1	3	2	2	2	9	5	6
	18	858	2	3	5	2	2	1	2	2	3	4
	19	52	2	3	0	2	2	4	2	3	4	4
	20	49	3	1	1	2	1	3	1	1	3	2
	21	59	2	4	41	2	1	2	2	2	4	5

*EF defined as: EF < 2 deficient to minimal enrichment; EF = 2–5 moderate enrichment; EF = 5–20 significant enrichment; EF = 20–40 very high enrichment, and EF > 40 extremely high enrichment (Loska *et al.*, 2004).

sediment was calculated using the data from Table 1 and 2, and possible contaminated sites were identified using previously published procedures (see Loring, 1991; Loring and Rantala, 1992; Aloupi and Angelidis, 2001a,b). All points within the 95% confidence band were classified as natural or background levels, while points out of the 95% confidence interval were considered enriched due to AGM activities and/or inputs from weathering of natural deposits. The graphs produced using this approach are presented in Figures 3 through 13 and are discussed below.

3.2.1. Mercury (Hg), Arsenic (As), Lead (Pb) and Zinc (Zn). Based on the above described approach, Hg and As (in both the wet and dry seasons), and Pb and Zn (in the dry season only) give a rather similar distribution when plotted against Al concentrations (Figures 3, 4, 5, and 13b). Although most data points in these graphs fall within the 95% confidence interval, the observed lack of relationships is a likely indication of anthropogenic impact on initially very low concentrations. This observation is validated by the determination of the enrichment factor (EF) calculated as:

$$EF = \frac{\left(\frac{Me}{Al}\right)_{\text{sample}}}{\left(\frac{Me}{Al}\right)_{\text{background}}},$$

Table 4b

Calculated enrichment factors (EF) for analyzed elements in sediment samples collected during the dry season. Shale reference values were taken from Turekian and Wedepohl (1961). *ND = not detected

River section	Site #	Hg	Fe	As	Pb	Cu	Mn	Co	Ni	V	Cr	Zn
Lower Pra	1	7	3	15	*ND	0	3	ND	3	1	2	5
	2	5	1	3	ND	1	1	ND	2	1	2	1
	3	1	1	4	ND	1	1	ND	1	1	2	2
	4	6	1	4	ND	1	1	ND	1	1	2	3
	5	9	1	11	ND	0	1	ND	3	1	2	5
	6	43	2	11	ND	2	4	ND	3	2	3	5
	7	6	1	3	ND	1	1	ND	1	1	2	2
	8	2	2	12	ND	1	3	ND	3	1	2	3
Offin	9	5	1	4	ND	1	1	ND	2	1	3	3
	10	4	1	3	ND	1	2	ND	2	1	1	3
	11	36	1	47	ND	3	1	ND	2	1	2	2
	12	16	1	18	ND	1	1	ND	2	1	2	3
	13	3	1	10	ND	1	1	ND	1	1	2	1
	14	2	1	3	ND	1	0	ND	1	2	3	1
	15	10	3	2	ND	1	1	ND	2	3	4	2
	16	5	1	2	ND	1	1	ND	1	1	2	2
Upper Pra	17	1	2	2	ND	1	1	ND	1	1	2	2
	18	1	1	2	ND	0	1	ND	2	1	1	2
	19	2	1	1	ND	1	2	ND	1	1	2	2
	20	21	2	2	ND	2	1	ND	2	3	5	2
	21	35	2	9	ND	0	1	ND	3	1	1	3

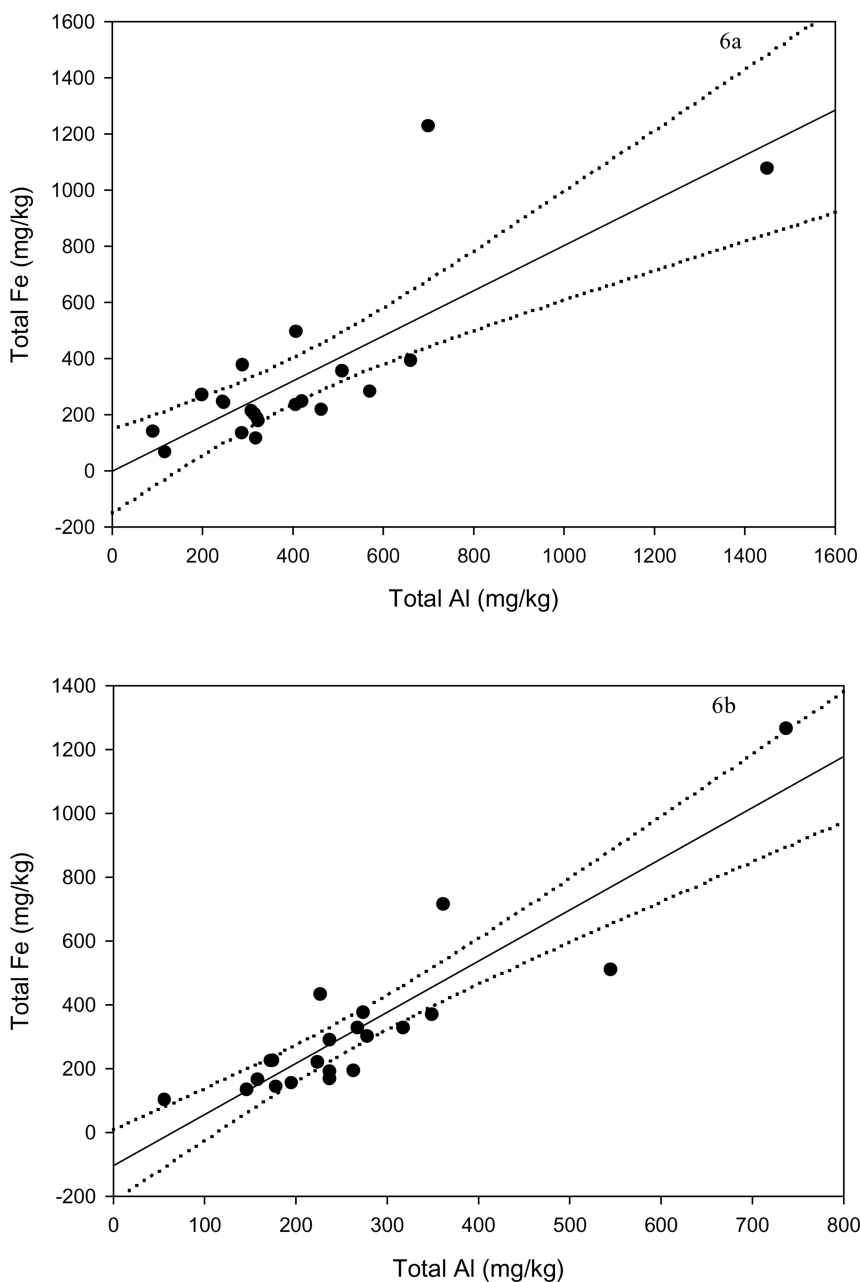


Figure 6. Fe: Al scatter plot for sediments of the Pra River basin: 6a = dry season and 6b = rainy season. The dotted lines represent the 95% confidence interval.

where Me and Al are the concentrations of the metal of interest and Al in the sample and in shale used for background determination. In this study, shale reference values were taken from Turekian and Wedepohl (1961), and the calculated EF values for each of the analyzed metals are presented in Table 4a (wet season) and 4b (dry season). It appears that Hg, As,

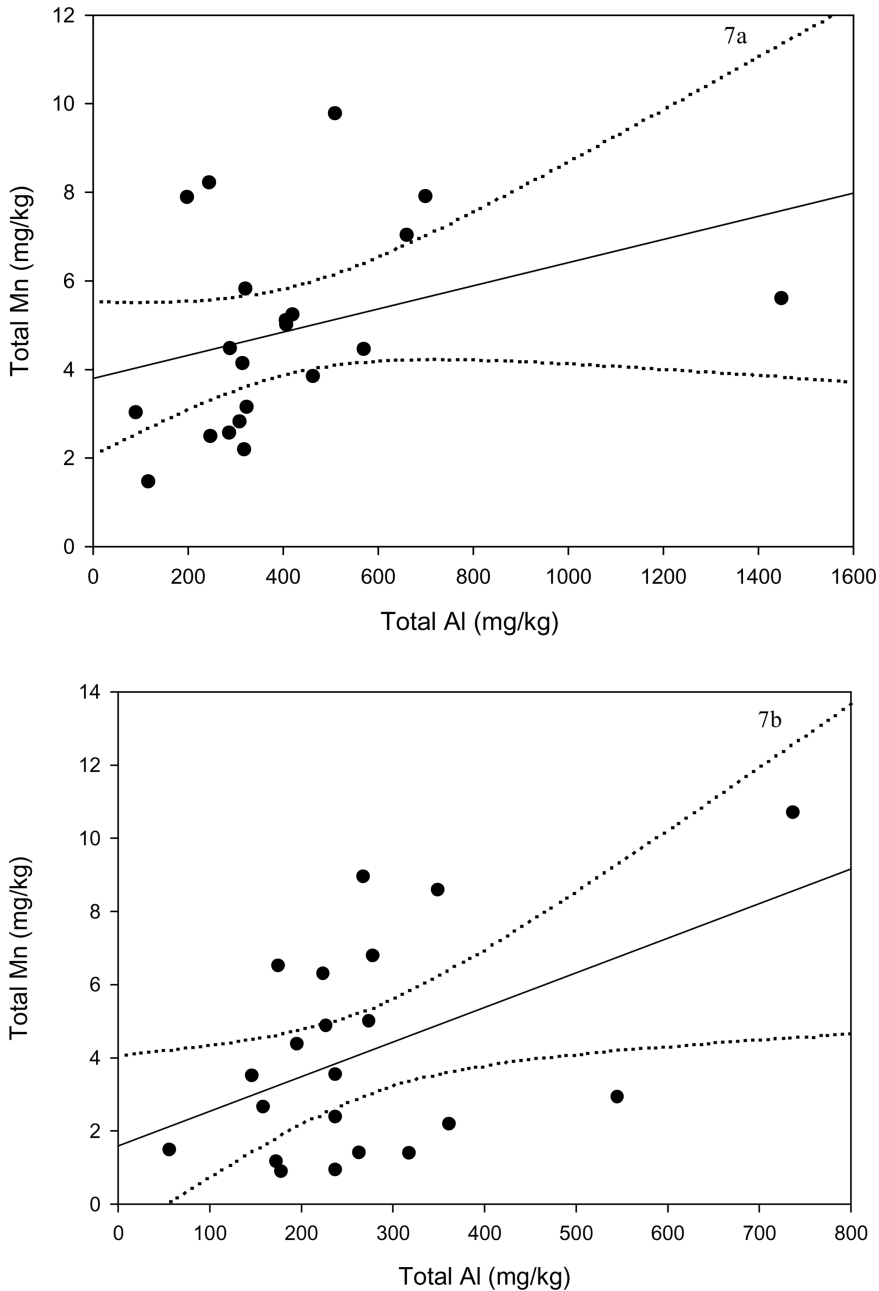


Figure 7. Mn: Al scatter plot for sediments of the Pra River basin: 7a = dry season and 7b = rainy season. The dotted lines represent the 95% confidence interval.

and to some extent Zn are the only elements to show high enrichment above background. In addition to the strong relationship between Hg and As mentioned earlier, these data support the suggestion that the increase in Hg and As concentrations above background values in this river system is likely driven by AGM activities. However, the lack of correlation

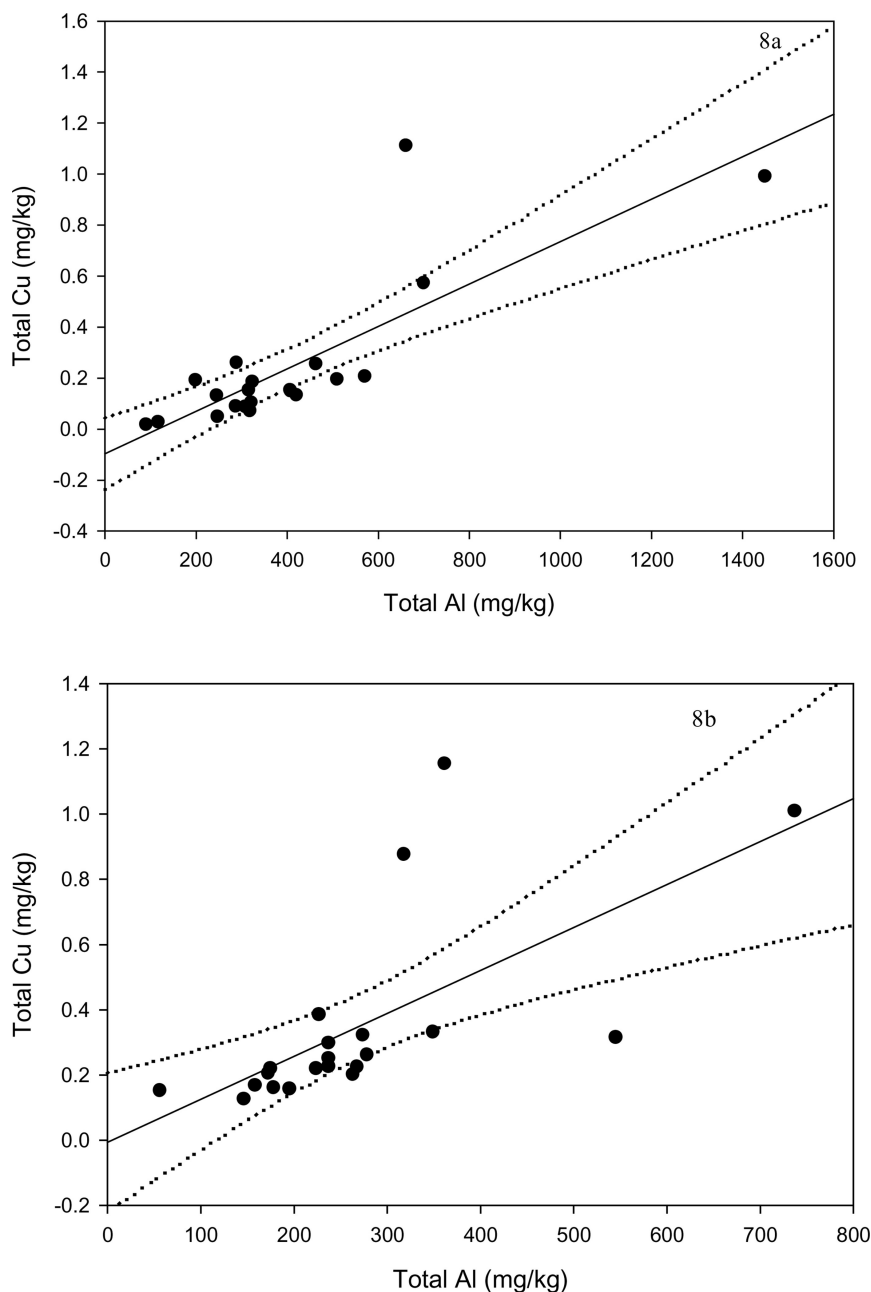


Figure 8. Cu: Al scatter plot for sediments of the Pra River basin: 8a = dry season and 8b = rainy season. The dotted lines represent the 95% confidence interval.

between Hg and As, Cu, and Ni in the rainy season shows the importance of changes in hydrologic conditions on levels and the fate of metals in this tropical aquatic system. Overall, our data (Tables 1 and 2) suggest that the levels of all examined metals increase from the dry to the rainy season. This is probably due to increased inputs of metal-contaminated

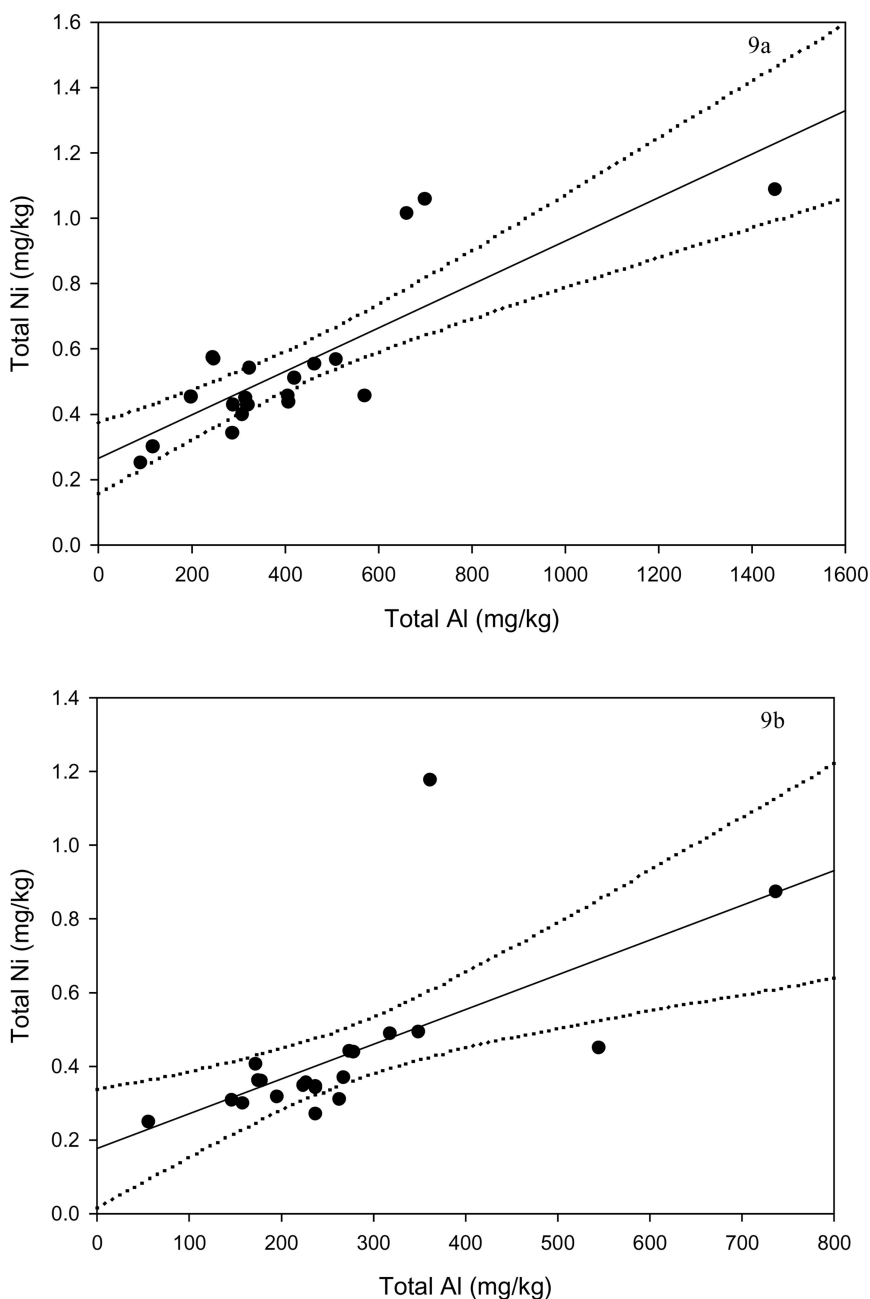


Figure 9. Ni: Al scatter plot for sediments of the Pra River basin: 9a = dry season and 9b = rainy season. The dotted lines represent the 95% confidence interval.

particles eroded from soils and mine tailings, which are carried into waterways by storm water runoffs. Despite this common increasing trend from dry to wet seasons, the lack of correlation between Hg and the other metals (except for As, Cu, and Ni in the dry season) can be explained by the fact that the fate of metallic Hg manually added to soil/sediments

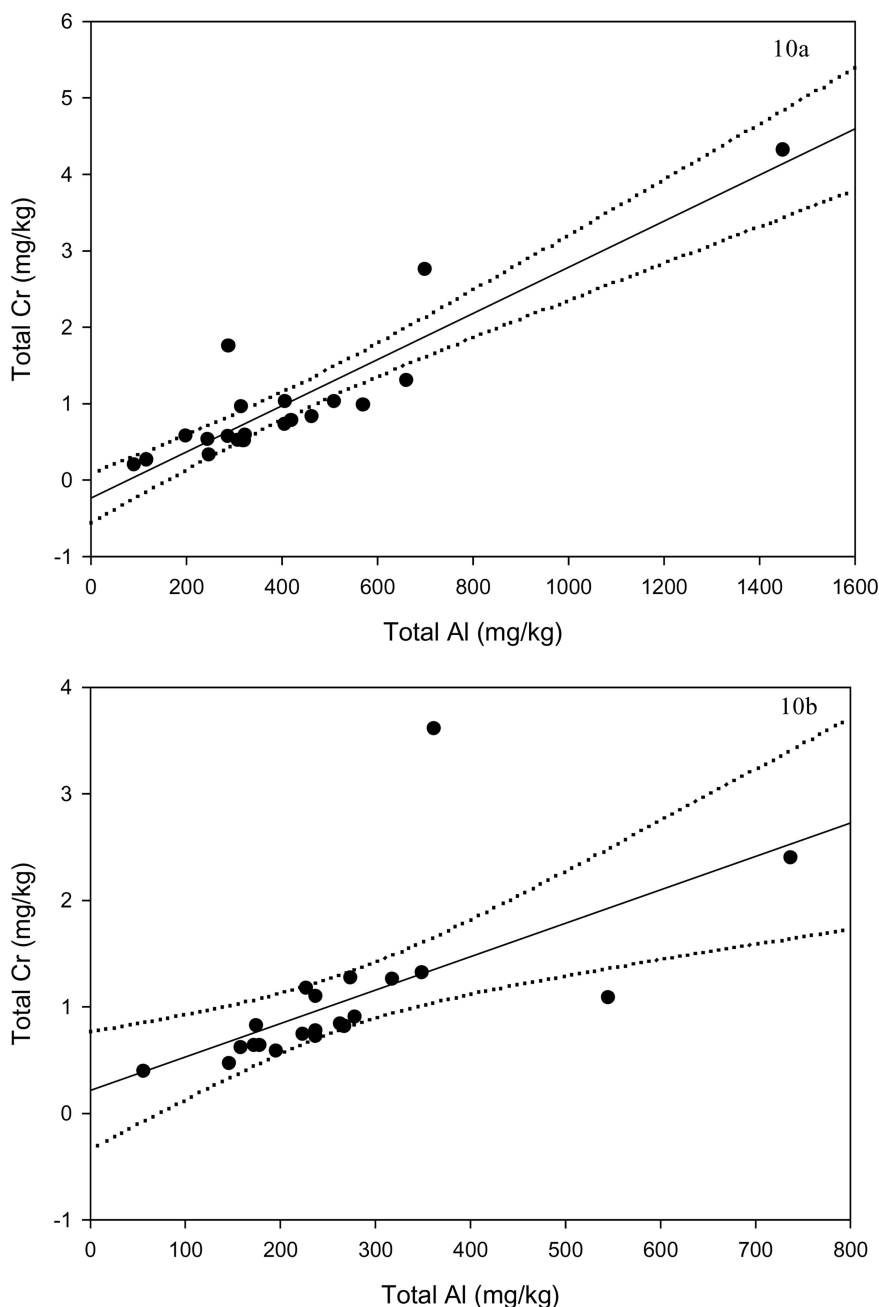


Figure 10. Cr: Al scatter plot for sediments of the Pra River basin: 10a = dry season and 10b = rainy season. The dotted lines represent the 95% confidence interval.

during gold extraction processes does not necessarily follow that of the elements already present in geological matrices and which become mobilized with soil/sediment dredging and digging activities. This is supported by the observed strong and significant correlations between Al (structural element of the fine clay particles) and most of the non-added elements

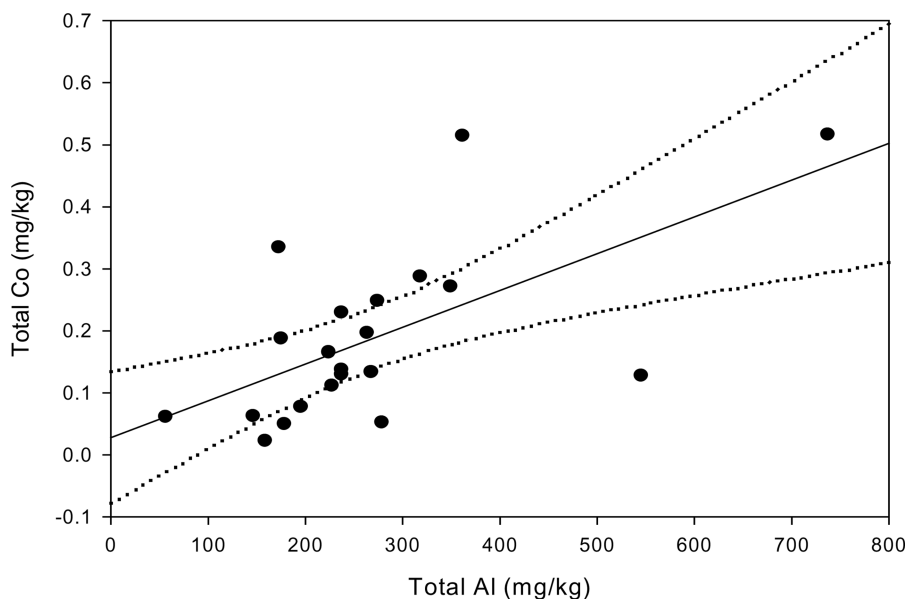


Figure 11. Co: Al scatter plot for sediments of the Pra River basin: rainy season. The dotted lines represent the 95% confidence interval.

(e.g. Cu, Ni, V, Cr, Zn, Co) in addition to a few strong and significant relationships amongst some of these metals (e.g. Ni with V, Cr, or Zn; V with Cr or Zn, Cu with Ni, V, Cr or Zn, etc.) (see Tables 3a and 3b). If THg alone may not be used as strong tracer of environmental perturbation in the Pra River system based on simple linear regressions between Hg and the other metals, the combination of approaches used in this study allows us to conclude that besides the addition of Hg in the investigated river system, the impact of AGM on ambient levels of the other trace metals varies from none (e.g. V, Co, Pb, Cr, Fe and Mn) to very limited (e.g. As).

3.2.2. Iron (Fe) and Manganese (Mn). The naturally abundant metals Fe and Mn whose concentrations in the sediments are normally not greatly affected by AGM co-varied with Al (Figures 6 and 7), with Fe showing stronger relationships with Al, regardless of the season. Mn shows much weaker relationships with Al and signs of anthropogenic impacts are illustrated by a much higher number of outliers in Figure 7a and 7b as compared to Fe, which shows a positive and significant relationship with Al in both the rainy and dry seasons (Table 3). One possibility could be the introduction of Mn into waterways by erosion/runoff following exposure and oxidation of reduced minerals.

3.2.3. Copper (Cu), Nickel (Ni), Chromium (Cr), Cobalt (Co), and Vanadium (V). These elements (Figures 8–12) give good and often significant relationships with aluminum (Table 3), suggesting that with the exception of a very few outliers, the determined levels correspond to values at or near background concentrations. Overall, the relationship between any of the metals and Al is stronger during the dry season and tends to be less so in the wet season. Also, most of these elements show positive and significant relationships

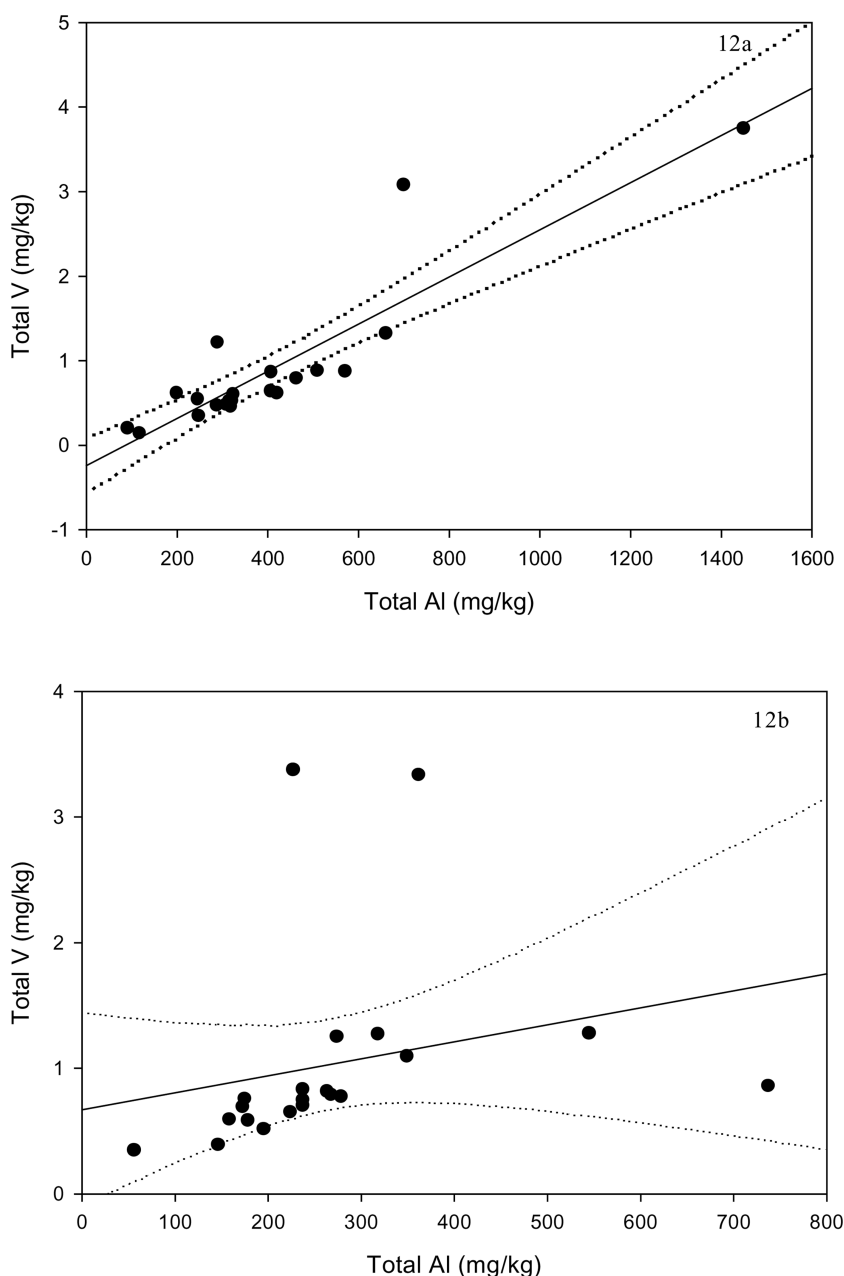


Figure 12. V: Al scatter plot for sediments of the Pra River basin: 12a = dry season and 12b = rainy season. The dotted lines represent the 95% confidence interval.

with Zn (Table 3), but no relationship with Hg. It is likely that some of these elements are associated primarily with sulfide minerals of Zn and are of natural origin. Based on our hypothesis stated in the introduction, the levels of these metals are likely not impacted by AGM.

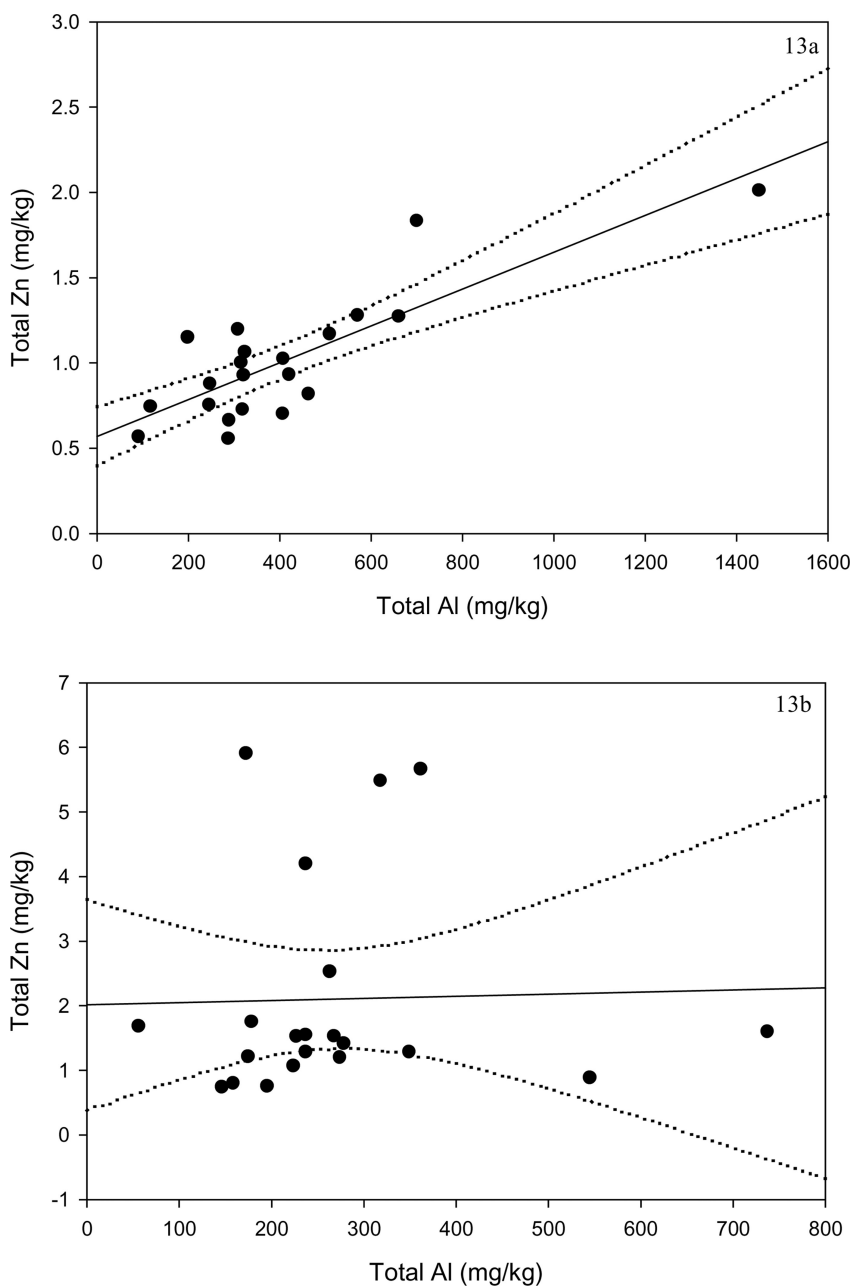


Figure 13. Zn: Al scatter plot for sediments of the Pra River basin: 13a = dry season and 13b = rainy season. The dotted lines represent the 95% confidence interval.

4. Conclusion

The widespread and intensive AGM activities are quite recent in Ghana, after its legalization in 1989. Yet this activity is believed to have occurred earlier in the 19th century before being made illegal in 1933 by the British. However its legalization in 1989 by the government

gave birth to the new *gold rush* with increased use of Hg in gold extraction. The major conclusions of our study are threefold. First, despite the long-term use of Hg in gold mining in the studied Ghanaian river system, sediment Hg levels remain low and often below most safe guidelines for sediment contamination. Though these Hg values may seem low, especially when compared with other well-known gold mining sites, the Hg transfer to the food chain could still be a problem since the extent of Hg bioaccumulation and biomagnification seems to depend primarily on the amount of Hg occurring as methyl-Hg (Pickhardt *et al.*, 2005). Second, the use of a normalizer and calculation of enrichment factors suggest none to moderate enrichment of the sediment for most of the metals investigated in this study. However, Hg, with EF > 40 in most sampled sites in the rainy season seems to be highly enriched. Third, seasonal variability in total concentrations of metals with lows in the dry season and highs in the rainy season is suggestive of metal export to depositional downstream reaches, namely the river delta and ultimately the estuary. If true, the collection of sediment cores in non-dredged lower portions of the river/estuary could help track down Hg pulses associated with seasons. In fact, AGM in Ghana tends to expand with droughts as farmers switch from the “rain-fed” agriculture to gold mining. Since AGM activities in Ghana take place primarily in the river banks and flood plains and not directly within the river itself, the accumulation of Hg-contaminated tailings/soils during the dry seasons is always followed by rain-driven erosion and export of Hg-contaminated particles. Such climate driven shifts in land use types could provide an opportunity to assess the impact of climate change on land use and the resulting impacts on water quality and human health.

References

- Adimado, A.A. and Baah, D.A. 2002. Mercury in human blood, urine, hair, nail, and fish from the Ankobra and Tano River basins in southwestern Ghana, *Bull. Environ. Contam. Toxicol.* **68**, 339–346.
- Adriano, D.C. 1986. *Trace Elements in Terrestrial Environment*, Springer-Verlag, New York.
- Aloupi, M. and Angelidis, M.O. 2001a. Normalization to lithium for the assessment of metal contamination in coastal sediment cores from the Aegean Sea, Greece. *Marine Environmental Research* **52**, 1–12.
- Aloupi, M. and Angelidis, M.O. 2001b. Geochemistry of natural and anthropogenic metals in the coastal sediments of the island of Lesbos, Aegean Sea, *Environmental Pollution* **113**, 211–219.
- Amegbey, N.A., Dankwa, J.B.K., and Al-Hasson, S. 1997. Small scale mining in Ghana—techniques and environmental considerations. *International Journal of Surface Mining, Reclamation and Environment* **11**, 135–138.
- Andersen, H.E. 1992. The expansion of mercury contamination, five years after discovery, *Marine Pollution Bulletin* **24**, 367–369.
- Baker, E.K. and Harris, P.T. 1991. Copper, lead and zinc distribution in the sediments of the Fly River Delta and Torres Strait. *Marine Pollution Bulletin* **22**, 614–618.
- Balls, P.W., Hull, S., Miller, B.S., Pirie, J.M., and Proctor, W. 1997. Trace metal in Scottish estuarine and coastal sediments. *Marine Pollution Bulletin*, **34**, 42–50.
- Bonzongo, J.C., Lyons, W.B., Hines, M.E., Warwick, J.J., Faganeli, J., Horvat, M., Lechler, P.J., and Miller, J.R. 2002. Mercury in surface waters of three mine-dominated aquatic systems: Idrija River, Slovenia; Carson River, Nevada, USA; and Madeira River, Brazil. *Geochem. Explor. Environ. Anal.* **2**, 111–120.
- Bruland, K.W., Bertine, K., Koide, M., and Goldberg, E. 1974. History of metal pollution in southern California coastal zone. *Environ. Sci. Technol.* **8**, 425–432.
- Daskalakis, K.D. and O'Connor, T.P. 1995. Normalization and elemental sediment contamination in the coastal United States. *Environ. Sci. Technol.* **29**, 470–477.

- Davidson, J. 1993. The transformation and successful development of small-scale mining enterprises in developing countries. *Natural Resources Forum* 315–326.
- Dumett, R.E. 1998. *El Dorado in West Africa*. Ohio University Press, Athens, Ohio.
- Förstner, U. and Wittman, G.T.W. 1983. *Metal Pollution in the Aquatic Environment*. Springer-Verlag, Berlin.
- Grimalt, J.O., Ferres, M., and Macpherson, E. 1999. The mine tailing accident in Aznalcolla. *Sci. Tot. Environ.* **242**, 3–11.
- Hangi, A.Y. 1996. *Environmental Impacts of Small Scale Mining: A Case Study of Merelani, Kahama, Nzega, Geita and Musoma*. The Center for Energy, Environment, Science and Technology (CEEST) Research Report Series Number 1, Tanzania.
- Hilson, G. 2001. *A Contextual Review of the Ghanaian Small-Scale Mining Industry*. International Institute for Environment and Development (IIED) and World Business Council for Sustainable Development (WCSDD), England.
- Horowitz, A.J. 1991. *A Primer on Sediments-Trace Element Chemistry*, 2nd Edition, Lewis Publishers, Michigan.
- Kishe, M.A. and Machiwa, J.F. 2003. Distribution of heavy metals in sediments of Mwanza Gulf of Lake Victoria, Tanzania. *Environmental International* **28**, 619–625.
- I.L.O. 1999. *Social and Labor Issues in Small-scale Mines*. Report for discussion at the Tripartite Meeting on Social and Labor Issues in Small-scale Mines, International Labor Organization (ILO), Sectoral Activities Program, International Labor Office, Geneva.
- Laperdina, T.G. 2002. Estimation of mercury and other heavy metal contamination in traditional gold-mining areas of Transbaikalia. *Geochemistry, Exploration, Environment, Analysis* **2**, 219–223.
- Larceda, L.D., Marins, R.V., Barcellos, C., and Molisani, M.M. 2004. Sepetiba Bay: A case study of the environmental geochemistry of heavy metals in subtropical coastal lagoon, In: *Environmental Geochemistry in Tropical and Subtropical Environments*, 293–318 (de Larceda, L.D., Santelli, R.E., Duruursm, E.K., and Abrao, J.J., eds), Berlin, Springer-Verlag Publishers.
- Larceda, L.D., Malm, O., Guimaraes, J.R.D., Salomons, W., and Wilken, R. D. 1995. Mercury and the new gold rush in the South. In: *Biogeodynamics of Pollutants in Soils and Sediments*, 213–245 (Salomons, W. and Stigliani, W., eds), Berlin, Springer-Verlag Publishers.
- Lacerda L.D. and Salomons, W. 1998. *Mercury from Gold and Silver Mining: A Chemical Time Bomb?* Springer-Verlag, New York.
- Larsen, B. and Jensen, A. 1989. Evaluation of the sensitivity of sediment monitoring stationary in pollution monitoring stationary in pollution monitoring. *Marine Pollution Bulletin* **20**, 556–560.
- Limbong, D., Kumampung, J., Rimper, R., Arai, T., and Miyazaki, N. 2003. Emissions and environmental implications of mercury from artisanal gold mining in north Sulawesi, Indonesia. *Sci. Tot. Environ.* **302**, 227–236.
- Lin, Y., Guo, M., and Gan, W. 1997. Mercury pollution from small gold mines in China. *Water Air Soil Pollut.* **97**, 233–239.
- Lodenius, M. and Malm, O. 1998. Mercury in the Amazon. *Rev. Environ Contam. Toxicol.* **157**, 25–52.
- Loring, D.H. 1990. Lithium—a new approach for the granulometric normalization of trace metal data. *Marine Chemistry* **29**, 155–168.
- Loring, D.H. 1991. Normalization of heavy metal data from estuarine and coastal sediments. *ICES Journal of Marine Science* **48**, 101–115.
- Loring, D.H. and Rantala, R.T.T. 1992. Manual for the geochemical analysis of marine sediments and suspended particulate matter. *Earth Sci. Rev.* **32**, 235–283.
- Loska, K., Wiechuala, D., and Korus, I. 2004. Metal contamination of farming soils affected by industry. *Environmental International* **30**, 159–165.
- Malm, O. 1998. Gold mining as a source of mercury exposure in the Brazilian Amazon. *Environ. Res Sect A* **77**, 73–78.
- Malm, O., Pfeiffer, W.O., Souza, C.M.M., and Reuther, R. 1990. Mercury pollution due to gold mining in the Madeira river basin, Brazil. *Ambio* **19**, 11.

- Malm, O., Castro, M.B., Bastos, W.R., Branches, F.J.P., Guimaraes, J.R.D., Zuffo, C.E., and Pfeiffer, W.C. 1995. An assessment of Hg pollution in different gold mining areas, Amazon Brazil. *Sci. Tot. Environ.* **175**, 127–140.
- Nriagu, J.O. and Wong, H.K.T. 1997. Gold rushes and mercury pollution. In: *Metal Ions in Biological Systems*, Vol. **34**, pp. 131–160. (Siegel, A. and Siegel, H., eds), New York, Marcel Dekker Inc.
- Pickhardt, P.C., Folt, C.L., Chen, C.Y., Klaue, B., and Blum, J.D. 2005. Impacts of zooplankton composition and algal enrichment on the accumulation of mercury in an experimental freshwater food web. *Science of the Total Environment* **339**, 89–101.
- Roulet, M., Lucotte, M., Canuel, R., Farella, N., Courcelles, M., Guimarães, J.-R.D., Mergler, D., and Amorim, M. 2000. Increase in mercury contamination recorded in lacustrine sediments following deforestation in central Amazon. *Chemical Geology* **165**, 243–266.
- Roulet, M., Lucotte, M., Canuel, R., Farella, N., De Freitas Goch, Y.G., PachecoPeleja, J.R., Guimarães, J.-R.D., Mergler, D., and Amorin, M. 2001. Spatio-temporal geochemistry of mercury in waters of the Tapajós and Amazon rivers. Brazil. *Limnol. Oceanogr.* **46**, 1141–1157.
- Salomons, W. and Förstner, W. 1984. *Metals in Hydrocycle*. Springer-Verlag, Berlin.
- Shine, J.P., Ika, R.V., and Ford, T.E. 1995. Multivariate statistical examination of spatial and temporal patterns of heavy metal contamination in New Bedford Harbor Marine Sediments. *Environ. Sci. Technol.* **29**, 1781–1788.
- Tarras-Wahlberg, N.H., Flachier, A., Lane, S.N., and Sangfors, O. 2001. Environmental impacts and metal exposure of aquatic ecosystems in rivers contaminated by small scale gold mining: Puyango River basin, southern Ecuador. *Sci. Tot. Environ.* **278**, 239–261.
- Tarras-Wahlberg, N.H. 2002. Environmental management small-scale gold and artisanal mining: Portovelo-Zaruma gold mining area, southern Ecuador. *Journal of Environmental Management* **65**, 165–179.
- Turekian, K.K. and Wedepohl, K.H. 1961. Distribution of the elements in some major units of the earth's crust. *Geol. Soc. America Bull.* **72**, 186–192.
- Windom, H.L., Schropp, S.T., Calder, F.D., Ryan, J.D., Smith, R.G., Burney, L.C., Lewis, F.G., and Rawlinson, C.H. 1989. Natural trace metal concentrations in estuarine and coastal marine sediments of the Southeastern United States. *Environ. Sci. Technol.* **23**, 314–320.
- USEPA. 1985. *Water Quality for Mercury*. 440/5/84-026, Office of Water, US Environmental Protection Agency, Washington, DC.
- Villas Boas, R.C., Beinhoff, C., and da Silva, A.R. December 2001. *Mercury in the Tapajos Basin*. UNIDO Workshop in Belem, Para, Brazil.