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Mercury in different environmental compartments of the Pra River Basin, Ghana

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Abstract

Artisanal gold mining (AGM) with metallic mercury has a long history in Ghana. It is believed to be over 2000 years old. Today, AGM has escalated in a new dimension consuming about half of the country where gold lode deposits exist along riverbanks or rivers are alluvial-gold rich. The Pra River in southwestern Ghana is a site of on going application of metallic mercury in prospecting gold, and this paper examines mercury (Hg) contamination in the different environmental compartments in its watershed. Samples of water, sediment, soil and biota (i.e., human hair and fish) were collected from locations along the course of the river during the rainy and dry seasons of 2002 and 2003, respectively. Besides the obvious Hg point sources along the Pra and its tributaries, the obtained results show that Hg levels and speciation in the studied aquatic system are controlled by precipitation, which drives the hydrology and differences in flow regimes versus seasons. The seasonal difference in Hg speciation suggests that methyl mercury (MeHg) found in the aqueous phase and riverine sediments is likely of terrestrial origin where its production is favored during the rainy season by high soil water and organic matter content. The use of the enrichment factor (EF) for the assessment of sediment quality indicated moderate to severe contamination of surface sediments in the rainy season, while in the dry season, the EF index indicates nearly no pollution of surface sediments. Accordingly, most of the Hg introduced into this river system is likely transported to depositional downstream terminal basins (e.g. the river delta and the Gulf of Guinea). With regard to biota, Hg measured in hair in the dry period was higher than data obtained on samples collected during the wet period. This could be explained at least in part by the shift in diet as a result of abundance of fish in the local markets and the concurrent increase and more active fishing during the dry season. Mercury data obtained on a very limited number of fish samples collected during the dry period only are also presented.

Keywords: Ghana; Gold mining; Mercury pollution; Pra River system

1. Introduction

The mining of gold by mercury (Hg) amalgamation technology has been known since ancient times. The inexpensive nature of this amalgamation technique yoked with the easier to use and quite efficient gold recovery makes it to be the method of choice for current small-scale gold mining nations in the developing world. And the socio-economic merits of gold production by this methodology is obvious today; nevertheless, artisanal gold mining (AGM) with Hg faces strong opposition by the international community. This is primarily due to the toxicity of alkyl-Hg

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compounds, namely MeHg, which bio-accumulates and results in deleterious effects on biota and ecosystem functions. Past Hg incidents are the Hg disaster in Minamata, Japan in the 1950s (Klein and Goldberg, 1970; D'Itri and D'Itri, 1977) and Hg food poisoning reported in Iraq, Pakistan, Ghana and Guatemala (Bakir et al., 1973; Derban, 1974; Ehrlich, 2002), which resulted in numerous deaths. Following these fatal incidents, developed countries outlawed and moved on to phase out the use of Hg in both mining and several non-mining industrial activities. However since the advent of the new gold rush in the 1980s, thanks to socio-economic predicaments common to most developing nations, the use of Hg to mine gold has rebound and heightened in spite of the inception of cyanidation technology. This is the situation in Ghana presently; AGM with Hg has escalated in a new dimension consuming about half of the country where riverine sediments and riverbank materials are rich in gold.

In Ghana, gold mining by Hg amalgamation was given a booster in 1989 following its legalization by the government (Addy, 1998; Bonzongo et al., 2004; Donkor et al., in press). This type of mining is believed to be over 2000 years old; with Ghana earning the name "*Gold Coast*" when the Europeans arrived witnessing the land's vast wealth of gold and the indigenous gold industry being manned by Ghanaians in their own simple way (Kesse, 1985). Currently, the bulk of the gold production in Ghana comes from goldfields in the southwestern part of Ghana, which is drained by three main rivers comprising of the Tano, the Ankobra, and the Pra. Inevitably, Hg from process wastes is released to rivers and accumulated in mine tailings along riverbanks. Unfortunately, in Ghana, high annual precipitation and the resulting active fluvial processes are likely to exacerbate the widespread contamination of aquatic systems by Hg. Accordingly, one would expect Hg to be transported from mining sites from river upstream reaches to downstream depositional areas including the river delta and the Gulf of Guinea, which are economically important fishing areas.

In this paper we report on Hg levels, speciation, and distribution along longitudinal transect in the Pra River system. Hg was determined on water, sediment, soil, and biota samples collected during both the wet or rainy and dry seasons. Our findings suggest that for a river system impacted by gold mining by Hg amalgamation for several centuries, Hg levels in different environmental compartment are rather low, although there is a clear evidence of Hg contamination.

2. Materials and methods

2.1. Study area

Ghana is located in the western portion of the African continent, which lies along the Gulf of Guinea. Ghana is bounded in the east by the Republic of Togo, on the west, is Ivory Coast and on the north, is Republic of Burkina Faso. The climate is tropical and humid with temperatures varying between 24 to 28 °C in the south. The study area is the southwestern part of Ghana where most of the gold mines are located, representing an area of 40,000 km^2. In this region, the geology is dominated by the Birimian and Tarkwaian formations (Kesse, 1985; Dumett, 1998). Most of the rocks in this part of Ghana have been formed through re-deposition as placer gold deposits (also known as "alluvial gold"), due to a series of erosional events. These are found in many of the rivers draining the Birimian rocks or the gold belt particularly the three major rivers: Pra and its tributaries, Ankobra, and Tano (Kesse, 1985; Dzigbodi-Adjimah and Bansah, 1995; Oberthur et al., 1997). Accordingly, small-scale gold mining is restricted to these areas. Gold output from this region, according to Addy (1998) accounts for 81% of Ghana's production and AGM contributes only 10% of the annual tonnage of gold in Ghana with the rest coming from commercial ventures (Adimado and Baah, 2002).

Our investigations were conducted along the Pra River, which takes its source from Kwahu Plateau before joining by the main tributaries rivers Offin and Birim to enter the Gulf of Guinea (Fig. 1). Nearly the entire Pra Basin is spotted with active AGM sites.

2.2. Sampling

During the rainy season of 2002 and the dry season of 2003 in Ghana, water, sediments, soils, and human hair were collected along longitudinal transects in the Pra River and its watershed. Samples were collected from a total of 21 sites including locations near past and current AGM sites and locations far up or downstream of current and active mining centers. The 21 sampling sites were selected on the Offin, the Upper Pra, and the Lower Pra (see Fig. 1). From these sites, surface water samples were collected from headwaters upstream of known present and historic mining sites to near the river delta. Sampling sites also included points of connection between streams and canals connecting mining sites/ponds to the Pra. Water samples were collected directly into acid pre-cleaned Teflon® bottles, using the "ultra-clean free-metal sampling" protocol as described

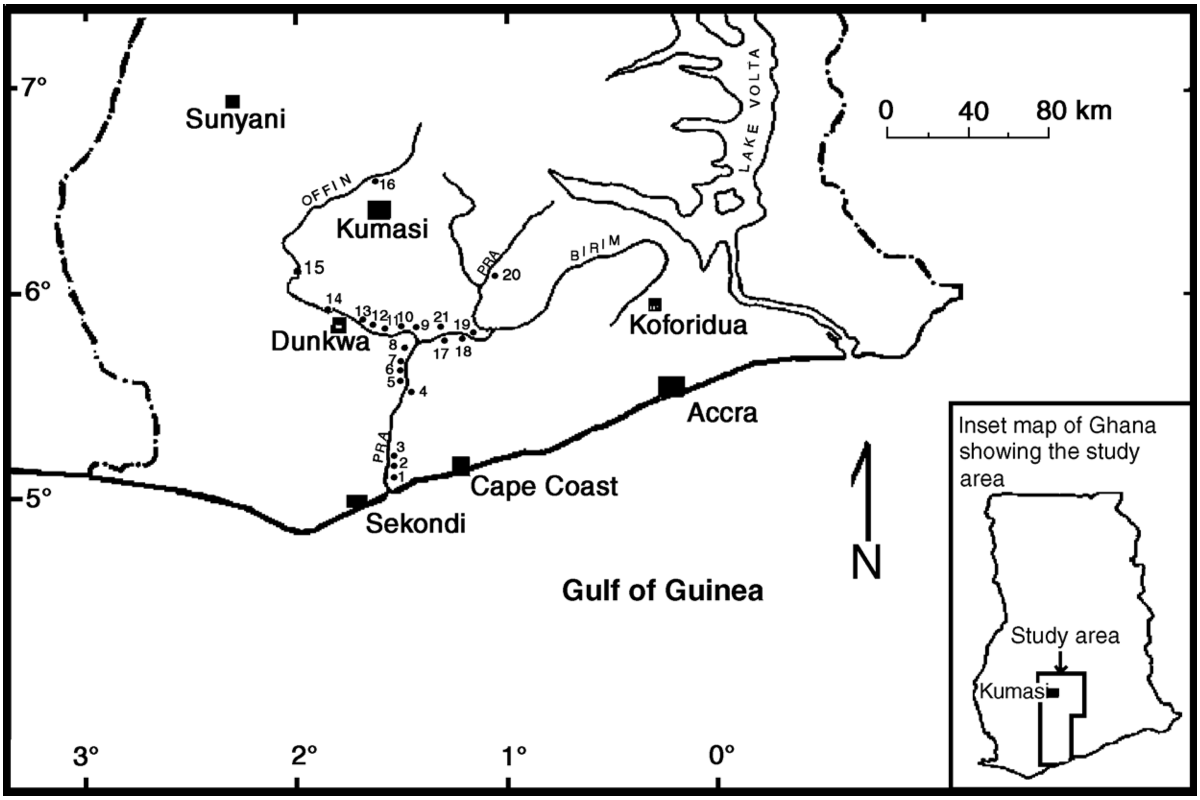

Fig. 1. Map of the gold mining impacted Southwestern Ghana showing sampling locations on the Pra River and its tributaries — site #1 is the farthest downstream with the numbering increasing upward. Sites 1, 2, 3, 4, 6, 16 and 20 have no known direct Hg input sources while sites 5, 7, 8, 9, 10, 11, 12, 13, 14, 15, 17, 18, 19 and 21 are directly impacted by either current or past artisanal mining activities.

in our previous publications on Hg pollution in Ghana (Bonzongo et al., 2003, 2004). Additional water samples were also collected in pre-cleaned polyethylene bottles for the determination of dissolved organic carbon (DOC). In addition, surface sediment samples (0 to ~10 cm) were taken from sites of water collection into acid pre-cleaned polyethylene containers by manual scooping employing Teflon spoon. Soil samples were also taken from some mining and amalgamation sites, amalgam roasting points, and from sites away from mining centers along the river.

Two types of biological samples were collected. First, hair samples were cut close to the rear of the scalp of each individual who volunteered at some sites (Tables 6 and 7). Samples were obtained from 53 people including 2 females during the rainy season, and only 7 in the dry period from one site. The majority of the samples were from the miners whereas the remaining live in riverine villages, having little or no direct contact with gold mining activities. It was extremely difficult to obtain hair samples because of superstition especially in the dry season. Details of age, occupation, and location of residence were also compiled during sampling resulting in easier assessment of occupational and residential exposure. Additional information concerning dietary habits of the volunteers was also collected employing an interview-administered questionnaire. The questions covered fish consumption, stressing on the most frequently consumed fish during high and low flow regimes in the course of the year. Secondly, dry fish samples were purchased directly from local fishermen during the dry season. The choice for dry fish sample was driven by two main reasons. First, in the region under study, fish is commonly consumed after being smoked using wood-fire. This process allows the villagers to store large amount of fish provisions, to be consumed mostly during the long rainy season. Second, it was much easier to transport to the USA. The selected species were the most important in the local population's diet. Obtained fish samples were weighed, and identified (e.g., scientific name) in the biology Department at the University of Ghana. All collected samples were shipped by express courier to our laboratory at the University of Florida, Gainesville where all analyses were conducted.

Table 1
Concentrations of total-Hg (THg), methyl-Hg (MeHg), and dissolved organic carbon (DOC) in water samples collected during both the rainy and dry periods

Pra River system		Total-Hg		Methyl-Hg		DOC	
River sections	Sites #	Rainy ng L^{-1}	Dry ng L^{-1}	Rainy ng L^{-1}	Dry ng L^{-1}	Rainy mg L^{-1}	Dry mg L^{-1}
Lower Pra	1	295.7	171.3	2.59	<0.028	10.48	3.26
	2	233.6	99.0	19.64	0.80	13.39	6.39
	3	52.0	71.7	2.29	<0.028	21.62	6.87
	4	29.1	104.4	1.15	<0.028	11.65	6.70
	5	403.0	100.4	0.69	0.40	5.18	6.79
	6	28.7	92.8	0.95	0.40	13.67	6.50
	7	34.4	nd	1.86	nd	11.45	nd
	8	36.1	57.2	2.65	0.60	11.07	6.67
Offin	9	420.3	169.1	1.57	<0.028	12.58	7.84
	10	91.8	225.6	1.59	0.68	16.79	7.23
	11	348.6	373.3	1.20	<0.028	14.46	7.65
	12	230.1	308.5	3.08	0.71	5.71	6.65
	13	84.6	249.6	1.97	0.82	13.82	7.50
	14	41.6	182.4	1.79	0.49	7.12	7.64
	15	220.5	462.1	1.87	0.51	10.88	3.14
	16	148.9	79.8	1.23	0.47	15.31	6.74
Upper Pra/Birim	17	41.5	188.0	0.88	<0.028	10.08	6.78
	18	69.3	52.7	<0.028	0.59	9.37	6.91
	19	136	45.8	0.93	0.45	4.46	11.61
	20	293.5	118.2	0.99	0.78	10.11	6.74
	21	210.7	84.7	1.03	0.70	8.33	6.17
Average	–	164.28	161.83	2.378	0.420	11.31	6.79
Median	–	136.00	111.30	1.570	0.480	11.07	6.76
Maximum	–	420.30	462.10	19.640	0.820	21.62	11.61
Minimum	–	28.70	45.80	0.000	0.000	4.46	3.14

nd = not determined and detection limit = 0.028 ng L^{-1} .

2.3. Sample analysis

Before analysis, sediment and soil samples were sieved and the <63 μm fraction was used for digestion with a $HCl/HNO_3/HF$ acid mixture (Hossner, 1996; Bertsch and Bloom, 1996; Donkor et al., in press). Following dilution with DI water, aliquots of the digestate were analyzed for total aluminum using ICP-AES, and total Hg by CV-AFS. Total and methyl Hg in water, sediment, soil, and fish samples were determined following analytical procedures already described in our previous publications (e.g., Warner et al., 2003; Bonzongo and Lyons, 2004; Bonzongo et al., 2004). In addition to reagent blanks and standards, QA/QC criteria were met by the use of certified reference materials (IAEA-405 and DORM-2 for sediment/soil and fish tissues, respectively). The percent recoveries on IAEA-405 averaged 98% ± 7% for total-Hg ($n=7$) and 91% ± 4% for methyl Hg ($n=8$). For DORM-2 with certified values of 4.64 ± 0.26 mg/kg for THg and 4.47 ± 0.32 mg MeHg as Hg/kg, recovered averaged values were 4.55 ± 0.16 mg/kg ($n=6$) and 4.38 ± 0.09 mg/kg ($n=6$), respectively.

Hair samples were first washed thoroughly with DI-water and air-dried in a class 100 HEPA hood. For THg determinations, about 50 mg were then digested overnight at 80–90 °C using HNO_3 (Akagi et al., 1995). For MeHg, about 100 mg of hair was added to 2 ml of 5M HNO_3 in a Teflon-bomb and heated at 100 °C for 200 min (Diez and Bayona, 2002; Monturi et al., 2004). An aliquot of cooled digestate was transferred to a Teflon bubbler with 60 ml nanopure® water. The mixture was buffered with an acetate buffer solution ($pH=4.5$) and ethylated using sodium tetraethylborate (Bloom, 1989). MeHg was determined after GC-separation and thermo-decomposition by atomic fluorescence spectrometer. For hair samples, a human hair certified reference material (IAEA-086) with a THg concentration of 0.573 mg/kg and MeHg average concentration of 0.258 mg/kg was analyzed in conjunction with the samples. Average recoveries were 98% ± 8% and 93% ± 3% for THg and MeHg, respectively.

In addition to major ions (not presented in this paper), water samples were also analyzed for the dissolved organic carbon (DOC), measured by high temperature catalytic combustion using a Tekmar-Dohrmann Apollo 9000 HS Combustion TOC Analyzer. Finally, the total organic carbon content of soil and sediment samples was measured as loss on ignition (LOI) by ashing at 550 °C for 2 h.

3. Results and discussion

3.1. Mercury in the aqueous phase

Concentrations of THg and MeHg determined on samples collected during both the rainy and dry seasons are presented in Table 1. In both seasons, trends in THg concentrations show peak values corresponding primarily to points of Hg inputs by active and past mining activities. Based on the lack of signs of either current or past mining activities in the headwaters of the studied system, we anticipated a background low value from site 16 on the Offin River (Fig. 1). Surprisingly, in both the rainy and dry seasons, THg data obtained from this specific site were among the highest measured values, a clear evidence of contamination that is likely attributable to historic mining. In our previous investigation of the wider southwestern Ghana (Bonzongo et al., 2004), water samples collected from a control site (i.e. not directly impacted by mining activities) had a THg concentration of 3.22 ng L^{-1}, which is within the range of most reported baseline values from different non-con-

Table 2
Total and methyl-Hg concentrations in mg kg^{-1} in sediments samples collected during the rainy and dry periods

Pra River system		Total-Hg		Methyl-Hg		Organic matter as LOI	
River sections	Sites #	Rainy mg kg^{-1}	Dry mg kg^{-1}	Rainy mg kg^{-1}	Dry mg kg^{-1}	Rainy %	Dry %
Lower Pra	1	0.076	0.003	0.040	<0.001	2.08	0.46
	2	0.076	0.008	0.046	<0.001	5.55	3.15
	3	2.917	0.002	0.023	<0.001	9.98	1.68
	4	0.018	0.017	0.007	<0.001	11.50	4.74
	5	0.046	0.005	0.018	<0.001	1.30	0.25
	6	0.103	0.043	0.010	0.001	4.92	0.96
	7	0.022	0.009	0.015	nd	1.67	nd
	8	0.310	0.002	0.015	0.001	7.61	3.01
Offin	9	0.032	0.008	0.002	0.001	0.59	0.46
	10	0.022	0.007	0.003	<0.001	0.28	0.40
	11	0.132	0.118	0.048	<0.001	1.50	0.47
	12	0.329	0.026	0.009	<0.001	2.62	2.48
	13	0.032	0.007	0.015	<0.001	0.62	0.53
	14	0.121	0.018	0.040	<0.001	1.79	0.47
	15	0.072	0.036	0.009	<0.001	6.53	2.79
	16	0.189	0.010	0.075	<0.001	6.85	4.39
Upper Pra/Birim	17	0.079	0.002	0.018	<0.001	1.91	1.74
	18	0.678	0.002	0.028	<0.001	2.89	0.52
	19	0.071	0.005	0.007	<0.001	1.56	0.39
	20	0.180	0.030	0.003	0.005	7.91	0.84
	21	0.070	0.043	0.005	0.005	3.47	2.91
Average	–	0.265	0.019	0.021	0.001	3.96	1.63
Median	–	0.077	0.008	0.015	0.000	2.62	0.84
Maximum	–	2.917	0.118	0.075	0.005	11.50	4.74
Minimum	–	0.018	0.002	0.002	0.000	0.280	0.25

Detection limit = 0.001 mg kg^{-1}, nd = not determined and BDL = below detection limit.

taminated aquatic systems (e.g., Gill and Bruland, 1990; Bonzongo et al., 1996; Lyons et al., 1999). In fact, all sampled sections of the Pra River system in this study are obviously contaminated with Hg and the mean THg concentrations in this river system are 1 to 2 orders of magnitude higher than those found in most uncontaminated rivers. Measured THg concentrations in the Pra River waters ranged from 28.7 to 420.3 ng L^{-1} in the rainy season and from 45.2 xto 462.1 ng L^{-1} in the dry season (Table 1). When sites are considered individually, THg values decrease or increase with the shift from rainy to dry season. Without total suspended solid (TSS) data (not measured), we can only speculate that peak values in the rainy season are likely due to inputs of Hg-contaminated particles as reflected by the observed highly turbid surface waters, while during the dry season, high THg levels are sustained by the increase in mining activities, that are usually less intensive in the rainy season due to frequent flooding.

Unlike the THg values discussed above, MeHg concentrations show a clear decline from the rainy to the dry season, and during the dry season a few samples had MeHg levels below our analytical detection limit of ~0.028 ng L^{-1}. We believe that MeHg measured in surface waters during the rainy season is predominantly from terrestrial sources, and introduced into surface river waters via soil erosion and runoffs. However in the dry season, the terrestrial source either ceases or minimizes and measured MeHg probably originates predominantly from in-river production, supplemented by any other potential sources such as groundwater inputs. This observation is supported in part by our DOC data (Table 1). During the rainy season, DOC concentrations are higher than in the dry season presumably due to terrestrial organic matter inputs from the heavily vegetated watershed of the studied river system. The latter then translates into high DOC in the aqueous phase despite the high dilution effect caused by torrential rains characteristics of Southern Ghana. Overall, DOC values decrease at nearly all sites during the dry season, supporting the above-stated hypothetical explanation. It is worthy to note that MeHg determined on our water samples is not the total extractable MeHg. Since neither distillation nor a chemical extraction was conducted prior to sample ethylation, measured MeHg is operationally defined here as labile MeHg. This avoids the recently reported analytical artifacts associated with MeHg separation from the sample matrix with high inorganic Hg and organic matter concentrations (e.g. Bloom et al., 1997). Therefore, values listed as BDL in Table 1 could simply correspond to the lack of labile MeHg.

Further, our Hg when compared with available safe guidelines for water consumption on one hand and THg levels in tropical river systems impacted by similar AGM activities on the other hand, the following trends are observed: first, THg levels in waters of the Pra River system do not exceed the 1000 ng L^{-1} or the 2000 ng L^{-1} levels for drinking water set by the World Health Organization (WHO, 1976) and the USEPA, respectively. However, all obtained values exceed the 12 ng L^{-1} standard set by the USEPA for the protection against chronic effects to aquatic wildlife (USEPA, 1985). Second, THg concentrations determined in the Pra River waters are higher than values reported for most Hg-contaminated sites in the Brazilian Amazon and Indonesia. For instance, while THg values in the Pra River system average 164.28 and 161.83 ng L^{-1} for the wet and dry seasons, respectively, far lower values have been reported for the Madeira and the Tapajos rivers in Brazil, averaging 9.51 and 3.4 ng L^{-1}, respectively (Cleary and Thornton, 1994; Malm et al., 1990; Lechler et al., 2000; Bonzongo et al., 2002). A similar trend is observed with data reported for some Indonesian sites, averaging 6.03 ng L^{-1} (Aspinall, 2001). In contrast, THg values reported from AGM-impacted sites in the Mindanao Island, in the Philippines are several orders of magnitude higher than numbers obtained from any of the above-mentioned sites and average 75,400 ng L^{-1} (Appleton et al., 1999; Akagi et al., 2000; Drasch et al., 2001). The observed differences between the Ghanaian river basin and the other AGM sites could be attributed to several reasons as discussed in our earlier publication (Bonzongo et al., 2004). In the case of MeHg, contrasting with the well studied Hg-impacted Madeira and Tapajós Rivers, concentrations measured in samples collected from the Pra River Basin are far higher. Finally, with regard to the longitudinal distribution of both THg and MeHg, unlike most impacted river systems which show a general decrease downstream from main points of Hg introduction to the river (Bonzongo et al., 2002), the Pra River and its tributaries have several and unequally distributed past and current mining sites resulting in a rather peculiar Hg distribution from headwaters to the most downstream reaches.

3.2. Mercury in sediments

Total and methyl Hg concentrations determined on surface sediment samples collected during both the rainy and dry seasons from the 21 sites along the Pra River system are presented in Table 2. With the exception of four samples collected during the rainy season from sites 3, 8, 12, and 18, none of the other measured Hg concentrations exceeded the USEPA quality guideline of 0.2 mg kg^{-1}. Generally, THg values were higher in samples collected during the rainy season, when inputs of Hg-contaminated particles into the river are high, resulting in increased sediment Hg-levels. In addition, high river flow regimes characteristics of the rainy seasons in this tropical region produce sediment re-suspension resulting in downstream transport of Hg-contaminated fine sediment particles. This loss of Hg-contaminated fine particles to downstream depositional river reaches results in the decrease in THg concentrations observed along the same river transect during the dry season. Sediment organic matter content follows approximately a similar trend, in that high OM content is associated with the rainy season and low values with the dry season. Of interest is the trend of MeHg concentrations between seasons. While THg in

Table 3
Total aluminum (Al) and total mercury (THg) data used in the determination of the enrichment factor[a] (EF) for sediment collected in the rainy and dry seasons

Site #	Rainy season			Dry season		
	THg mg kg^{-1}	Al mg kg^{-1}	EF	THg mg kg^{-1}	Al mg kg^{-1}	EF
1	0.076	278.10	55	0.003	90.0	7
2	0.076	267.50	57	0.008	308.0	5
3	2.917	236.90	2463	0.002	406.0	1
4	0.018	146.20	25	0.017	570.0	6
5	0.046	174.70	53	0.005	117.0	9
6	0.103	195.10	106	0.043	198.0	43
7	0.022	223.60	20	0.009	287.0	6
8	0.310	348.90	178	0.002	245.0	2
9	0.032	172.20	37	0.008	315.0	5
10	0.022	55.90	79	0.007	320.0	4
11	0.132	236.80	111	0.118	660.0	36
12	0.329	317.60	207	0.026	323.0	16
13	0.032	178.00	36	0.007	462.0	3
14	0.121	262.90	92	0.018	1449.0	2
15	0.072	361.40	40	0.036	699.0	10
16	0.189	544.80	69	0.010	420.0	5
17	0.079	226.80	70	0.002	407.0	1
18	0.678	158.10	858	0.002	318.0	1
19	0.071	273.70	52	0.005	509.0	2
20	0.180	736.90	49	0.030	288.0	21
21	0.070	236.80	59	0.043	247.0	35

Reported shale values for Al and THg were used as reference background concentrations (see text).

[a] 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).

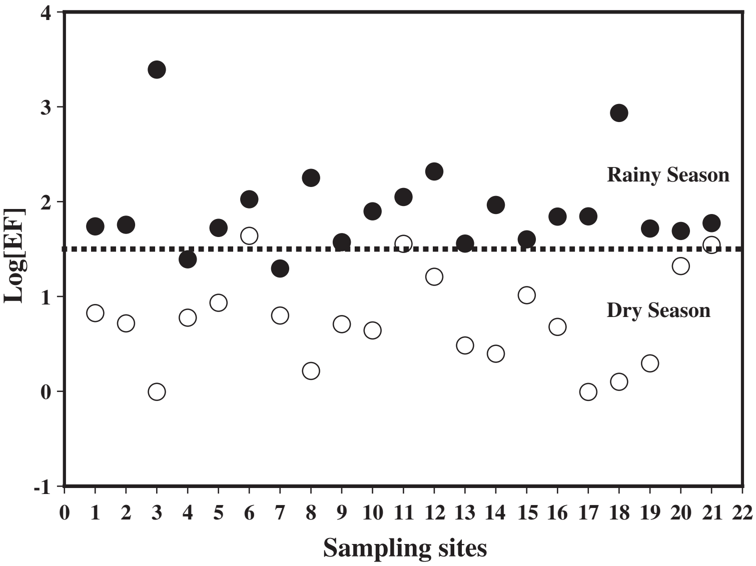

Fig. 2. Trends of the enrichment factor (EF) in the rainy (full circles) and dry (empty circles) seasons. The dotted horizontal line shows the point of quasi separation of rainy and dry seasons.

samples collected during the wet season contained ~1% to >68% MeHg, the methylated Hg fraction was barely detectable in most of the samples collected during the dry period. Similar to the water data discussed earlier, we believe that the higher MeHg concentrations observed in surface sediments during the wet period are mostly due to terrestrial inputs, perhaps in combination with in-river sediment production.

Measured THg levels in the top 0–10 cm were rather low as only 4 samples exhibited THg concentrations >0.2 mg kg^{-1}, the above-mentioned USEPA sediment quality guideline. One possibility could be that the local THg background in geological material is naturally very low. This is supported by our very limited number of THg data on soil from sites not directly impacted by mining activities. In such cases, to assess the deviation of measured THg concentrations in sediments from background values, several approaches can be used ranging from simple metal/normalizer ratios (Singh et al., 1997; Datta and Subramanian, 1998; Birch et al., 2001), to more complex methods based on regression analyses (e.g. Rowlatt and Lovell, 1994). Metal to normalizer ratio approaches include the determination of the enrichment factor (EF) (e.g., Sutherland, 2000) and the geo-accumulation index (I_{geo}), which was proposed originally by Muller (1969). In the normalization approaches, used background concentrations are usually values reported for shale or the earth's upper crust. But, in a few specific cases, the use of local background values, when available, seems more appropriate, particularly when the latter is order of magnitude lower than the shale and/or the crust reference values (e.g. Ram et al., 2003; Woitke et al., 2003). In this study, we choose to normalize our THg data using aluminum as a tracer and proxy for grain size. And based on reported background shale values for metals of interest (i.e., THg = 0.40 mg kg^{-1} and Al = 80,000 mg kg^{-1}; Turekian and Wedepohl, 1961; Mason and Chapman, 1982), the sediment enrichment factor (EF) was calculated using THg and Al data obtained from the <63 μm sediment fraction (Subramanian and Mohanachandran, 1990; Sahu and Bhosale, 1991; Rodrogues-Filho and Maddock, 1997). The following equation was used to calculate the EF:

$$\mathrm{EF} = \left(\frac{\mathrm{Hg}}{\mathrm{Al}}\right)_{\mathrm{sample}} \Big/ \left(\frac{\mathrm{Hg}}{\mathrm{Al}}\right)_{\mathrm{shale}}$$

where $(\mathrm{Hg/Al})_{\mathrm{sample}}$ is the ratio of THg to total aluminum concentrations determined on the sediment sample and $(\mathrm{Hg/Al})_{\mathrm{shale}}$ is a similar ratio based on shale reference data. Obtained EF values are shown comparatively in Table 3 and Fig. 2 for both seasons. Fig. 2 shows a clear separation of EF values, with the rainy season plotting above the dry season. The range of EF values obtained during the rainy season is indicative of contamination, with extremely severe contamination at two of the 21 sites. In contrast, EF values obtained in the dry season show much cleaner sediments. Using this approach, it appears that riverine sediments in the Pra River system receive high loads of Hg on a cyclic basis and these inputs temporally increase THg levels above

Table 4
Total and methyl-Hg concentrations and percent organic matter (% OM) in soil samples collected during the rainy and dry periods

Pra River River sections	Site numbers	Site characteristics	THg (mg kg^{-1})		MeHg (mg kg^{-1})		% OM	
			Wet season	Dry season	Wet season	Dry season	Wet season	Dry season
Lower Pra	1	Non-mining	0.008	0.012	0.003	<0.001	0.75	0.36
	2	Non-mining	0.042	0.010	0.010	<0.001	4.27	1.01
	3	Non-mining	0.011	0.007	0.005	<0.001	0.50	0.51
	4	Non-mining	0.027	0.015	0.007	<0.001	2.08	1.05
	5	Mining site	0.011	0.006	0.004	<0.001	0.86	0.37
	6	Non-mining	0.260	1.106	0.048	<0.001	4.38	2.30
	7	Past-mining	4.876	nd	0.128	nd	1.78	nd
	8	Mining site	0.089	0.015	0.030	<0.001	0.90	2.09
Offin	9	Tailings impacted	0.015	0.010	0.004	<0.001	0.45	0.47
		Amalgamation	0.052	nd	0.008	nd	1.59	nd
		*100 m	0.066	nd	0.034	nd	4.51	nd
		*500 m	0.140	nd	0.008	nd	6.04	nd
	10	Mining	0.036	0.028	0.020	<0.001	2.24	17.56
	11	Tailings impacted	0.025	nd	0.015	nd	0.17	nd
		Mining site	0.034	0.023	0.016	<0.001	0.49	0.38
	12	Mining site	0.057	0.016	0.004	<0.001	1.58	0.65
		*100 m	0.543	nd	0.141	nd	1.22	nd
		*300 m	0.062	nd	0.020	nd	2.92	nd
		*500 m	0.022	nd	0.010	nd	1.11	nd
	13	Mining site	nd	0.028	nd	<0.001	nd	0.56
		Roasting site	5.547	nd	0.162	nd	1.32	nd
		*100 m	0.168	nd	0.003	nd	0.23	nd
		*300 m	0.060	nd	0.005	nd	1.34	nd
		*500 m	0.015	nd	0.010	nd	4.18	nd
	14	Mining site	0.272	0.022	0.008	<0.001	9.92	0.37
		*300 m	0.036	nd	0.005	nd	0.56	nd
		*500 m	0.074	nd	0.002	nd	1.82	nd
	15	Tailings impacted	0.029	0.025	0.002	<0.001	3.86	nd
		Roasting site	0.052	nd	0.013	nd	1.89	5.42
		*100 m	0.028	nd	0.010	nd	1.26	nd
		*300 m	0.070	nd	0.028	nd	2.92	nd
		*500 m	0.027	nd	0.020	nd	5.41	nd
Upper Pra/Birim	16	Non-mining	0.149	0.031	0.054	<0.001	1.47	2.10
	17	Non-mining	0.197	0.012	0.042	<0.001	3.06	2.15
	18	Mining site	0.138	0.010	0.050	<0.001	1.97	0.65
	19	Mining site	0.079	0.031	0.030	<0.001	4.94	5.11
	20	Mining site	0.093	0.037	0.020	<0.001	1.54	2.88
	21	Mining site	0.091	0.009	0.018	<0.001	1.90	1.11

*Distance from mining site, detection limit = 0.001 mg kg^{-1}, nd = not determined.

background concentrations (i.e., higher inputs of Hg-contaminated particles in the rainy season). In the dry season however, the contamination is reduced and lower EF values are obtained; thanks to the efficient downstream transport of fine Hg-contaminated particles which are likely discharged into the Gulf of Guinea, the terminal basin for the Pra River. If true, this could then have long-term implications with regard to the local fishing industry since the Gulf of Guinea serves as an important fishing site for both local inhabitants and commercial fishing.

Finally, comparing our sediment THg data with those obtained from some of the well-studied AGM-impacted sites discussed earlier (Section 3.1.) the average THg concentrations of 0.265 and 0.019 mg kg^{-1} for wet and dry seasons, respectively, in the Pra River system are far lower than the reported 21.03 mg kg^{-1} for the Philippines' sites. Nevertheless, the Ghanaian mean values compare quite well with some of the numbers reported for the Maidera River (average: 0.04 mg kg^{-1}) and the Tapajós River (average: 0.29 mg kg^{-1}) in the Brazilian Amazon (e.g. Malm et al., 1990; Malm, 1998; Lodenius and Malm, 1998). Moreover, these data from the Pra River seem to be on the low end for sites that have been supposedly exposed to AGM by Hg amalgamation for centuries; a few previous studies (e.g. Bonzongo et al., 2004) recently conducted in the same watershed found broader ranges

Table 5
Average total and methyl-Hg concentrations in tissues (dry weight) in mg kg^{-1}, average weight in grams and average length in centimeters from four different fish species that are common in local people's diet collected along Pra River during January 2003 dry season

Species' scientific name	Common name	Diet habit	*n*	Average weight	Average length	Average THg	Average MeHg
Synodontis sp.	Cat fish	Bottom feeder	4	17.58 ± 16.48	14.45 ± 8.94	0.69 ± 0.57	0.0035 ± 0.0012
Hepsetus odoe	Kafue pike	Piscivorous	2	66.01 ± 1.41	26.0 ± 1.41	4.473 ± 0.42	0.0072 ± 0.0014
Clarias sp.	Mud fish	Bottom feeder	2	40.60 ± 28.43	22.25 ± 6.72	1.04 ± 0.05	0.0019 ± 0.0001
Sarotherodon melantheron	Tilapia	Planktivorous	4	22.75 ± 8.19	15.0 ± 1.58	0.08 ± 0.01	<0.001

Detection limit = 0.001 mg kg^{-1}.

and higher levels of THg in water, sediments, and soils, when samples collected from mining ponds and canals connecting these ponds to rivers were included. Lastly, and similar to the trend observed in the aqueous phase, MeHg levels in sediments were higher than most values reported for sites with similar climate and impacted by artisanal gold mining.

3.3. Mercury in soils

Soil samples were obtained from locations near sites of water and sediment sample collection (Fig. 1). At sites 9, 12, 13, 14, and 15, additional soil samples were collected along outward transects from mining centers in the wet season only. Measured THg and MeHg concentrations as well as the organic matter content of these soil samples are presented in Table 4. Besides three peak values obtained in samples collected from sites #7 (4.87 mg kg^{-1}) and #13 (5.55 mg kg^{-1}) in the rainy season, and site #6 (1.1 mg kg^{-1}) in the dry season, no marked differences was observed in THg levels from mining versus non-mining sites. Hg was detected in both the wet and dry seasons without major changes in concentration trends. However, MeHg was undetectable in soil samples collected in the dry season. This is likely due to the low water content of these dry soils, and we believe this to be a limiting factor for microbial driven MeHg production when compared to the nearly wet at field capacity for soil samples collected in the rainy season. Further MeHg levels observed in the soils followed a quite similar trend as observed in the aqueous phase (Table 1); in that higher values were recorded during the high flow period and lower concentrations including several values below our analytical detection limit were found in the dry period. Although no statistically significant relationship was observed between the two parameters, the striking similarity in MeHg trends in the two compartments presupposes a non-linear linkage between the two. As hypothesized earlier, these trends tend to suggest that terrestrial sources could account for a good portion of MeHg found in the river channel. In consequence, the potential of both soils and sediments to produce MeHg versus seasons calls for further investigations. Finally, our investigation of the distribution of Hg concentrations away from points of different mining activities in the rainy season (Table 4) showed no consistent increasing or decreasing trends, and overall, the mean THg soil values from the Pra River system are lower than those reported for river systems used for comparison in earlier sections of this paper.

3.4. Mercury in biological tissues

THg and MeHg were also determined in fish tissues and human hair samples collected from the Pra River Basin, and obtained results are discussed below.

3.4.1. Mercury in fish tissues

During our trips to the sampling sites and due to limited fish availability, only a total of 12 fishes were purchased from fishermen in villages along the river Pra. Due to this limited number of samples, the obtained data are presented here to simply illustrate the average concentrations of Hg versus the fish trophic levels (Table 5). The two bottom feeders (*Claria* sp. and *Synodontis* sp.) and the piscivorous fish (*Hepsetus odoe*) had average THg concentrations above the WHO's safe consumption guideline of 0.5 mg kg^{-1}. In contrast, the tilapia (*Sarotherodon melantheron*) showed THg concentrations below the above-mentioned guideline. Curiously, and unlike in most reports on Hg fish data determined on fresh tissues, the fraction of THg occurring as MeHg represented <1% in all fish samples analyzed in this study. Our efficient recoveries on tested reference material (DORM-2) described in the analytical section of this paper suggested that this was not an analytical problem. However, the technique of fish dehydration via smoking used by villagers for long-term conservation purposes could explain the observed low MeHg. One could speculate that heat driven MeHg degradation during the smoking process was responsible for the observed low MeHg values. How-

Table 6
THg and MeHg concentrations in mg kg^{-1} in head hair samples collected from indigenous people along the river Pra during the rainy period of 2002

Sampling site #	*n*	Age	Sex	Occupation	THg	MeHg
1	5	43	M	Farming	1.58	0.11
		20	M	Student	0.40	0.11
		17	M	Student	0.41	<0.01
		45	M	Fishing	1.66	0.03
		50	M	Farming	4.13	0.12
2	5	46	M	Farming	0.77	0.19
		21	M	Farming	1.19	0.10
		55	M	Storekeeper	0.39	<0.01
		32	M	Farming	1.02	0.20
		35	M	Farming	0.48	0.06
3	2	22	M	Trader	1.37	0.59
		15	M	Farming	0.43	0.03
4	10	18	M	Unemployed	1.16	0.89
		25	F	Trader	0.71	0.07
		27	M	Mechanic	0.69	<0.01
		60	M	Farming	1.29	0.83
		26	F	Housewife	0.63	0.37
		22	M	Laborer	1.00	0.32
		40	M	Sanitary job	0.85	0.07
		23	M	Unemployed	0.85	0.07
		27	M	Farming	0.97	0.04
		24	M	Farming	0.54	0.12
5	2	32	M	Farming	1.56	0.36
		26	M	Farming	0.55	0.17
9	7	32	M	Mining	0.87	0.13
		55	M	Mining	0.60	0.10
		22	M	Mining	0.70	0.13
		29	M	Mining	1.09	0.08
		36	M	Mining	0.93	0.23
		30	M	Mining	0.82	0.44
		32	M	Mining	0.58	0.06
11	4	26	M	Mining	0.79	<0.01
		30	M	Mining	1.39	0.25
		27	M	Mining	1.83	0.06
		29	M	Mining	1.38	0.22
12	8	15	M	Mining	0.99	<0.01
		47	M	Mining	0.96	0.33
		25	M	Mining	0.69	0.01
		28	M	Mining	1.12	<0.01
		12	M	Mining	0.85	<0.01
		28	M	Mining	0.96	0.01
		16	M	Mining	2.73	0.07
		38	M	Mining	1.44	<0.01
14	12	29	M	Mining	2.41	0.21
		15	M	Mining	0.68	<0.01
		22	M	Mining	1.27	<0.01
		40	M	Mining	1.42	0.07
		32	M	Mining	1.50	0.20
		20	M	Mining	0.75	<0.01
		20	M	Mining	0.98	0.19
		19	M	Mining	1.81	0.40
		39	M	Mining	1.22	0.25
		25	M	Mining	1.34	<0.01
		22	M	Mining	1.41	0.19
		34	M	Mining	1.17	0.02

Table 7
THg and MeHg concentrations in mg kg^{-1} in head hair samples collected from indigenous people at the sampling location number 6 during the dry period of 2003

Sampling site	*n*	Age	Sex	Occupation	THg	MeHg
6	7	23	M	Mining	3.42	0.138
		34	M	Mining	6.50	0.278
		36	M	Mining	2.65	<0.01
		39	M	Mining	5.26	0.060
		33	M	Mining	0.89	0.211
		33	M	Mining	2.19	<0.01
		33	M	Mining	1.51	0.661

Detection limit = 0.01 mg kg^{-1}.

ever, since no fresh fish tissues were analyzed in this study, it was therefore impossible to conclude without reservation on the cause of the observed low MeHg levels. Since smoked fish is the main form of fish consumed predominantly during the long rainy season, the smoking practice might reduce the exposure to significant amount of MeHg. It is clear that a more comprehensive investigation of Hg in fish tissues (dry and fresh) encompassing spatial and temporal variations and more trophic levels are needed.

3.4.2. Mercury in human hair

Hair samples came from 53 subjects in the rainy period from a total of 9 sites (Table 6) and only 7 individuals volunteered in the dry season, all from site #6 (Table 7). The miners contributed the majority of obtained hair samples. The highest THg levels were found in the dry season (Table 7), likewise MeHg. Overall, high levels of Hg were observed in the upper river reaches, active mining areas (sites #5, 6, 9, 11, 12 and 14) than the lower reaches non-mining centers (sites #1, 2, 3, and 4). With reference to age and THg, no significant relation was found ($r^2=0.02$; $p>0.05$) particularly in the rainy period. Thus THg concentrations in the adult and the young hairs did not indicate any consistent trends. The females on the other hand, were small in number, two, nevertheless the hair Hg value observed in the two donors were lower than many of the hair Hg in the male counterparts. And in all the cases examined the miners were greatly exposed to Hg than any other professionals with reference to THg (Tables 6 and 7). In general, the proportion of MeHg in head hair to THg in individuals were below 50% of the THg with

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Notes to Table 6:
Detection limit = 0.01 mg kg^{-1} . Samples were collected from villages corresponding to the listed site numbers. The number of individuals per site is listed in column 2. Detection limit = 0.01 mg kg^{-1}.

the exception of few individuals among the riverine population downstream (sites #3 and 4, Table 7), indicating that inorganic Hg was the predominant form of Hg in the hair samples. Besides, most miners interviewed confessed eating fish at least four times a week. In the Pra River Basin, it appears that gold mining by Hg-amalgamation technique leads to excessive leaching and dispersal of Hg, which contaminates non-mining downstream reaches of the river system. The consequence is the accumulation of Hg in aquatic organisms as evidenced in the most patronized fish species (Table 5). As such the exposure of these miners to Hg is likely due to both direct inhalation of Hg vapor during the gold extraction processes and ingestion of Hg-contaminated fish. Whereas, the probable route for the riparian population downstream to Hg exposure is primarily through the intake of Hg-contaminated fish. Finally, the differences in number of head hair in the two seasons are huge (Tables 6 and 7), yet the mean THg concentrations in hair do confirm findings reported previously from the Amazon, in that hair samples collected during the dry period are richer in Hg than those obtained during the rainy season.

In spite of all, Hg levels measured in hair samples obtained from both miners and non-miners were on the low end and far below the 50 mg kg^{-1} guideline recommended by the World Health Organization (WHO, 1976). Overall, the average Hg values measured in Ghanaian hair samples were much lower than those documented in the literature for Brazil (8.89 mg kg^{-1}, Madeira River and 16.2 mg kg^{-1}, Tapajós River) and the Philippines 4.14 mg kg^{-1}), two countries where similar mining operations prevail. These trends could be explained at least partly, by differences in diet habits in these locations during the time of sample collection. Nevertheless, these findings of Hg in hair from Ghana did confirm the seasonal variations of previous studies carried out in the Brazilian Amazon (Akagi et al., 1995; Kehrig et al., 1997; Dolbec et al., 2001; Maurice-Bourgoin et al., 2003; Coquery et al., 2003), where high levels of Hg in hair in the dry period was linked to the consumption of fish abundant at that time unlike the wet period (Malm et al., 1995; Barbosa et al., 1995; Bidone et al., 1997) characterized with minimal fish catch.

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References

Addy SN. Ghana: revival of the mineral sector. Resour Policy 1998;24:229–39.

Adimado AA, Baah DA. Mercury in human blood, urine, hair, nail, and fish from the Ankobra and Tano River Basins in southwestern Ghana. Bull Environ Contam Toxicol 2002;68:339–46.

Akagi H, Malm O, Kinjo Y, Harada M, Branches FJP, Pfeiffer WC, et al. Methylmercury pollution in the Amazon, Brazil. Sci Total Environ 1995;175:85–95.

Akagi H, Castillo ES, Cortes-Maramba N, Francisco-Rivera AT, Timbang TD. Health assessment for mercury exposure among schoolchildren residing near a gold processing and refining plant in Apokon, Tagum Davao del norte, Philippines. Sci Total Environ 2000;259:31–43.

Appleton JD, Williams TM, Breward N, Apostol A, Miguel J, Miranda C. Mercury contamination associated with artisanal gold mining on the island of Mindanao, the Philippines. Sci Total Environ 1999;228:95–109.

Aspinall, C. Small-Scale Mining in Indonesia. Publishers: International Institute for Environment and Development (IIED) and World Business Council for Sustainable Development (WSCSD), England, MMSD 2001; 79 2–30.

Bakir F, Damluji SF, Amin-Zaki L, Murtadha M, Khalidi A, Al-Rawi NY, et al. Methylmercury poisoning in Iraq. Science 1973;181:230–41.

Barbosa AC, Boischio AA, East GA, Ferrai I, Goncalves A, Silva PRM, et al. Mercury contamination in the Brazilian Amazon Environmental and occupational aspects. Water Air Soil Pollut 1995;80:109–21.

Bertsch PM, Bloom PR. Aluminum. In: Sparks DL, editor. Methods of soil analysis, Part 3, vol. 5. Chemical methods-SSSA book series. Madison, WI: Soil Science Society of America and American Society of Agronomy; 1996. p. 517–49 [Chp. 18].

Bidone ED, Castilhos ZC, Santos TJS, Souza TMC, Larceda LD. Fish contamination and human exposure to mercury in Tartarugalzinho River, Amapa State, Northern Amazon, Brazil A Screening Approach. Water Air Soil Pollut 1997;97:9–15.

Birch G, Siaka M, Owens C. The source of anthropogenic heavy metals in fluvial sediments of a rural catchment: Coxs river, Australia. WaterAir Soil Pollut 2001;126:13–35.

Bloom NS. Determination of picogram levels of methylmercury by aqueous phase ethylation, followed by cryogenic gas chromatography with Cold vapour atomic fluorescence detection. Can J Fish Aquat Sci 1989;46:1131–40.

Bloom NS, Coleman JA, Barber L. Artifact formation of methyl mercury during aqueous distillation and alternative techniques for the extraction of methyl mercury from environmental samples. Fresenius' J Anal Chem 1997;658:372–7.

Bonzongo JCJ, Lyons WB. Impact of land use and physicochemical settings on aqueous methylmercury levels in the mobile-Alabama River system. Ambio 2004;33(6):329–33.

Bonzongo JC, Ojiambo BS, Lyons WB, Wilder S, Welch K. Mercury concentrations in waters of Lake Naivsha watershed, Kenya. Geophys Res Lett 1996;23:1581–4.

Bonzongo JC, Lyons WB, Hines ME, Warwick JJ, Faganeli J, Hovart M, et al. Mercury in surface waters of three mine-dominated river systems: Idrija River, Slovenia; Carson River, Nevada; and Madeira River, Brazillian Amazon. Geochem, Explor Environ Anal 2002;2:111–9.

Bonzongo JC, Donkor AK, Nartey VK. Environmental Impacts of Mercury related to Artisanal Gold Mining in Ghana. J Phys IV France 2003;107:217–20.

Bonzongo JC, Donkor AK, Nartey VK, Lacerda LD. Mercury pollution in Ghana: a case study of environmental impacts of artisanal gold mining in sub-Saharan Africa. In: Lacerda LD, Santelli RE, editors. Facets of environmental geochemistry in tropical and sub-tropical environments. Berlin: Springer Verlag; 2004. p. 135–53.

Cleary D, Thornton I. The environmental impact of gold mining in the Brazilian Amazon. In: Hester RE, Harrison RMIssues in environmental science and technology. Cambridge: Royal Society of Chemistry; 1994. p. 17–47.

Coquery M, Cossa D, Azemard S, Peretyazhko T, Charlet L. Methylmercury formation in the anoxic waters of the petit-saut reservior (French Guiana and its spreading in the adjacent Sinnamary river). J Phys IV France 2003;107 [327–321].

Datta DK, Subramanian V. Distribution and fractionation of heavy metals in the surface sediments of the Ganges–Brahmaputra–Meghna river system in the Bengal basin. Environ Geol 1998; 36:93–101.

Derban LKA. Outbreak of food poisoning due to alkyl-mercury fungicide on Southern Ghana State Farm. Arch Environ Health 1974;28:49–52.

Diez S, Bayona JM. Determination of methylmercury in human hair by ethylation followed phase solid-phase microextraction-gas chromatography-cold-vapor atomic fluorescence spectrometry. J Chromatogr, A 2002;963:345–51.

D'Itri PA, D'Itri FM, 1977. Mercury contamination: a human tragedy. New York: John Willey; 1977. p. 1–311.

Dolbec J, Mergler D, Larribe F, Roulet M, Lebel J, Lucotte M. Sequential analysis of hair mercury levels in relation to fish diet of an Amazonian population, Brazil. Sci Total Environ 2001; 271:87–97.

Donkor AK, Bonzongo JC, Nartey VK, Adotey DK. Heavy metals in sediments of gold mining impacted Ghanaian Pra River Basin, West Africa. International Journal of soil and sediment contamination 2005;14:1–25.

Drasch G, Böse-O'Reilly S, Beinhoff C, Roider G, Maydl S. The Mt Diwata study on Philippines 1999—assessing mercury intoxication of the population by small scale gold mining. Sci Total Environ 2001;267:151–68.

Dumett RE, 1998. El Dorado in West Africa. Athens, Ohio: Ohio University Press; 1998. p. 1–396.

Dzigbodi-Adjimah K, Bansah S. Current developments in placer gold exploration in Ghana: time and financial considerations. Explor Min Geol 1995;4(3):297–306.

Ehrlich HL, 2002. Geomicrobiology, 4th ed. Marcel Dekker Inc. p. 327–43.

Gill GA, Bruland KW. Mercury speciation in freshwater systems in California and other areas. Environ Sci Technol 1990;24: 1392–1400.

Hossner LR. Dissolution for total elemental analysis. In: Sparks DL, editor. Methods of soil analysis, Part 3, vol. 5. Chemical Methods-ASA and SSSA book series. Madison, WI: Soil Science Society of America and American Society of Agronomy; 1996. p. 49–64 [Chp. 3].

Kehrig HA, Malm O, Akagi H. Methylmercury in hair samples from different riverine groups, Amazon, Brazil. Water Air Soil Pollut 1997;97:17–29.

Kesse GO, 1985. The mineral and rocks resources of Ghana. Rotterdam/Boston: A.A. Balkema Publishers; 1985. p. 6–208.

Klein DH, Goldberg ED. Mercury in the marine environment. Environ Sci Technol 1970;4(9):765–8.

Lechler PJ, Miller JR, Lacerda LD, Vinson D, Bonzongo J-C, Lyons WB, et al. Elevated mercury concentrations in soils, sediments, water, and fish of the Madeira River basin, Brazilian Amazon: a function of natural enrichments? Sci Total Environ 2000; 260:87–96.

Lodenius L, Malm O. Mercury in the Amazon. Rev Environ Contam Toxicol 1998;152:25–52.

Loska K, Wiechuala D, Korus I. Metal contamination of farming soils affected by industry. Environ Int 2004;30:159–65.

Lyons WB, Welch KA, Bonzongo JC. Mercury in aquatic systems in Antarctica. Geophys Res Lett 1999;26:2235–8.

Malm O. Gold mining as a source of mercury exposure in the Brazilian Amazon. Environ Res Section A 1998;77: 73–8.

Malm O, Pfeiffer WO, Souza CMM, Reuther R. Mercury pollution due to gold mining in the Madeira river basin, Brazil. Ambio 1990;19(1):11–5.

Malm O, Branches FJP, Akagi H, Castro MB, Pfeiffer WC, Harada M, et al. Mercury and methylmercury in fish and human hair from the Tapajos river basin, Brazil. Sci Total Environ 1995;175(2): 141–50.

Mason, B, Chapman, CB. Principles of Geochemistry. Wiley, New York, 1982. p. 46–7 and 176–7.

Maurice-Bourgoin L, Alanoca L, Fraizy P, Vauchel P. Sources of mercury in surface waters of the upper Madeira erosive basins, Bolivia. J Phys IV France 2003;107:855–8.

Monturi P, Jover E, Alzaga R, Diez S, Bayona JM. Improvements in the methylmercury extraction from human hair by headspace solid-phase microextraction followed by gas-chromatography cold-vapor atomic fluorescence spectrometry. J Chromatogr, A 2004;1025:71–5.

Muller G. Index of geoaccumulation in sediments of the Rhine River. GeoJournal 1969;2:108–18.

Oberthur T, Weiser T, Amanor JA, Chryssoulis SL. Mineralogical siting and distribution of gold in quartz veins and sulfide ores of the Ashanti mine and other deposits in the Ashanti belt of Ghana: genetic implications. Miner Depos 1997;32:2–15.

Ram A, Rokade MA, Borole DV, Zingde MD. Mercury in sediments of Ulhas estuary. Mar Pollut Bull 2003;46:846–57.

Rodrogues-Filho S, Maddock JEL. Mercury pollution in two gold mining areas of the Brazilian Amazon. J Geochem Explor 1997;58:231–40.

Rowlatt SW, Lovell DR. Lead, zinc, and chromium in sediments around England and Wales. Mar Pollut Bull 1994;28:324–9.

Sahu, KC, Bhosale, U. Heavy metal pollution around the island city of Bombay, India. Part I: quantification of heavy metal pollution of aquatic sediments and recognition of environmental discriminants. Chemical Geology 1991; 91 263–283.

Singh M, Ansari AA, Muller G, Singh IB. Heavy metals in freshly deposited sediments of the Gomati River (a tributary to the Ganga River): effect of human activities. Environ Geol 1997; 29:246–52.

Subramanian V, Mohanachandran G. Heavy metals distribution and enrichment in sediments of southern east coast of India. Mar Pollut Bull 1990;2:324–30.

Sutherland RA. Depth variation in copper, lead and zinc concentrations and mass enrichment ratios in soils of urban watershed. J Environ Qual 2000;29(5):1414–24.

Turekian KK, Wedepohl KH. Distribution of the elements in some major units of the earth's crust. Geol Soc Amer Bull 1961;72:186–92.

USEPA. Water quality for Mercury 440/5/84–026. Washington, DC: Office of Water, US Environmental Protection Agency; 1985.

Warner KA, Roden EE, Bonzongo JC. Microbial mercury transformation in anoxic freshwater sediments under iron-reducing and other electron-accepting conditions. Environ Sci Technol 2003;37:2159–65.

WHO. Environmental Health Criteria Document 1: Mercury. Geneva: World Health Organization; 1976.

Woitke P, Wellmitz J, Helm D, Kube P, Lepom P, Litheraty P. Analysis and assessment of heavy metal pollution in suspended solids and sediments of the river Danube. Chemosphere 2003;51:633–42.