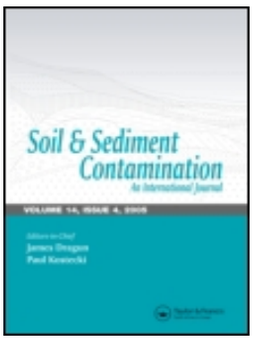

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Levels of Mercury, Cadmium, and Zinc in the Topsoil of Some Selected Towns in the Wassa West District of the Western Region of Ghana

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The Wassa West District of the western region of Ghana is noted for a large deposit of gold ores. As a result, there is a lot of mining activity in the district, which include both legal and illegal miners. A large number of illegal ("galamsey") miners employ mercury in the amalgamation of gold, whereas some of the mining companies use zinc dust (with associated cadmium impurities) in the extraction of gold. Due to the potentially toxic and adverse effect of mercury and cadmium on humans, livestock, and aquatic organisms, this research seeks to determine the concentration of mercury, cadmium, and zinc in the topsoil (up to 30cm), which constitutes the absorption zone of most food crops grown in the district, and compares these levels with literature values as well as control samples taken from other non-mining districts, thus assess the pollution due to these metals. The results for mercury gave a peak average concentration of 2.8 mg/kg around Aboso and decreased to 0.41 mg/kg at Dompem to the south and 0.33 mg/kg at Huni Valley to the north. All these concentrations were higher than those found in the control samples as well as the standard (0.3 mg/kg) found in literature. The contamination of control samples with mercury suggests aerial distribution of the metal. Zinc concentrations, however, did not show any trend that could be due to anthropogenic sources or natural deposition of the metal. However, high concentrations of 387 mg/kg at Aboso, 170 mg/kg at Tarkwa, and 221 mg/kg at Dompem give an indication of the use of zinc dust in the extraction of gold. The research, however, did not detect cadmium above the detection limit of the instrument used.

Keywords cadmium, mercury, Wassa West District, zinc

Introduction

Gold mining in Ghana has been the largest foreign exchange earner apart from cocoa since pre- and post-independent Ghana. According to Obiri et al. (2006), gold export earnings rose from 107.9 million dollars to 744.2 million dollars between 1985 and 1989. This has resulted in an increasing numbers of mining companies operating in the country; the risk of environmental pollution from mining activities is on the increase. The Wassa West District, one of the Districts in the western region of Ghana, is located between Latitude 4° 0′ N and 5° 40′′ N and Longitudes 1° 45′′ W and 2° 10′′ W. It is bounded to the north by the Wassa Amenfi District, the south by the Ahanta West District, the West by the Nzema East

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Municipal, and the East by Mpohor Wassa East District. The district has a total land area of 2354 sq. km and a population (2002) of 232,700. Agriculture is the major economic activity in the district and employs about 85.5% of the people, most of whom are peasant farmers. The major food and cash crops produced in the district are plantain, cassava, cocoyam, rice, cocoa, coffee, and oil palm. The district produces about 20% of the country's cocoa, and production of rice and cassava is about 1.25 tonnes and 9.3 tonnes per hectare, respectively. Both legal and illegal small-scale mining is practiced in the district (Avotri et al., 2002). In the Tarkwa area, small-scale mining is widespread, both in the forest and along the rivers. It is practiced all year and numbers about 20,000 in the Wassa West district. Of these small-scale miners, about 90% are illegal. As of 2003, 168 small-scale mining concessions were valid in the region (Ntibery et al., 2003).

Mercury in artisanal gold mining is used to form an amalgam that binds with gold. The magnitude of loss of mercury and the ways it is released from a specific site are defined by the separation procedures to remove the gold from the amalgam. When mercury is used to amalgamate gold, some escapes directly into water bodies as elemental mercury droplets or as coatings of mercury adsorbed onto sediment grains. The mercury that forms the amalgam with gold is emitted to the atmosphere when the amalgam is heated, unless a fume hood or retort is used (some still escape). In addition to the deliberate use of mercury to extract gold, naturally occurring mercury in soils and sediments that are eroded by sluicing and dredging becomes remobilized and bioavailable in receiving waters (Telmer et al., 2008).

Some mining companies like Tarkwa Goldfields Limited, on the other hand, employ zinc dust instead of mercury for the extraction of gold (Golow and Adzei, 2002). Zinc is less toxic and required for metabolism, reproduction, and healing of wounds. Additionally, toxic effects of large amounts of zinc are increased by impurities of cadmium in zinc (Cook and Morrow, 1995).

Cadmium is toxic at very low concentrations and has been responsible for a number of diseases including the "ouch-ouch" or "itai-itai" disease in Japan (Hill, 1993). High levels of cadmium and arsenic in food crops such as cassava and cocoyam grown in the study area have been reported (Essumang et al., 2007; Obiri et al., 2006), and their cancer-causing risk has been assessed. Levels of cadmium and mercury as high as 43mg/kg and 0.3mg/kg have also been reported in *Xanthosoma sagitifolium*, which is one of the staple food crops grown in the study area. The source of these metals is mostly from the soil (Pereira et al, 2005). Nevertheless, there are no data on the levels of mercury, cadmium, and zinc in soils of the study area. It is with this health concern and the scarcity of data that this research seeks to investigate their levels in the topsoil (up to 30cm). This layer of soil constitutes the absorption zone of the roots of most food crops (e.g. Cassava, cocoyam, pepper, tomatoes, etc.) grown in the study area.

Materials and Methods

Location of the Study Area

The Wassa West District, as shown in Figure 1 below, lies between latitude 4° 0′ N and 5°40′ N and longitudes 1°45′ W and 2°10′ W. The district covers a total land area of 9235 km^2. The gold deposits in the study area lie in the Eburnean Tectonic province in the West African Precambrian shield. The paleoproterozoic rocks that comprise most of the West African craton and host the major gold mineralization in Ghana are subdivided

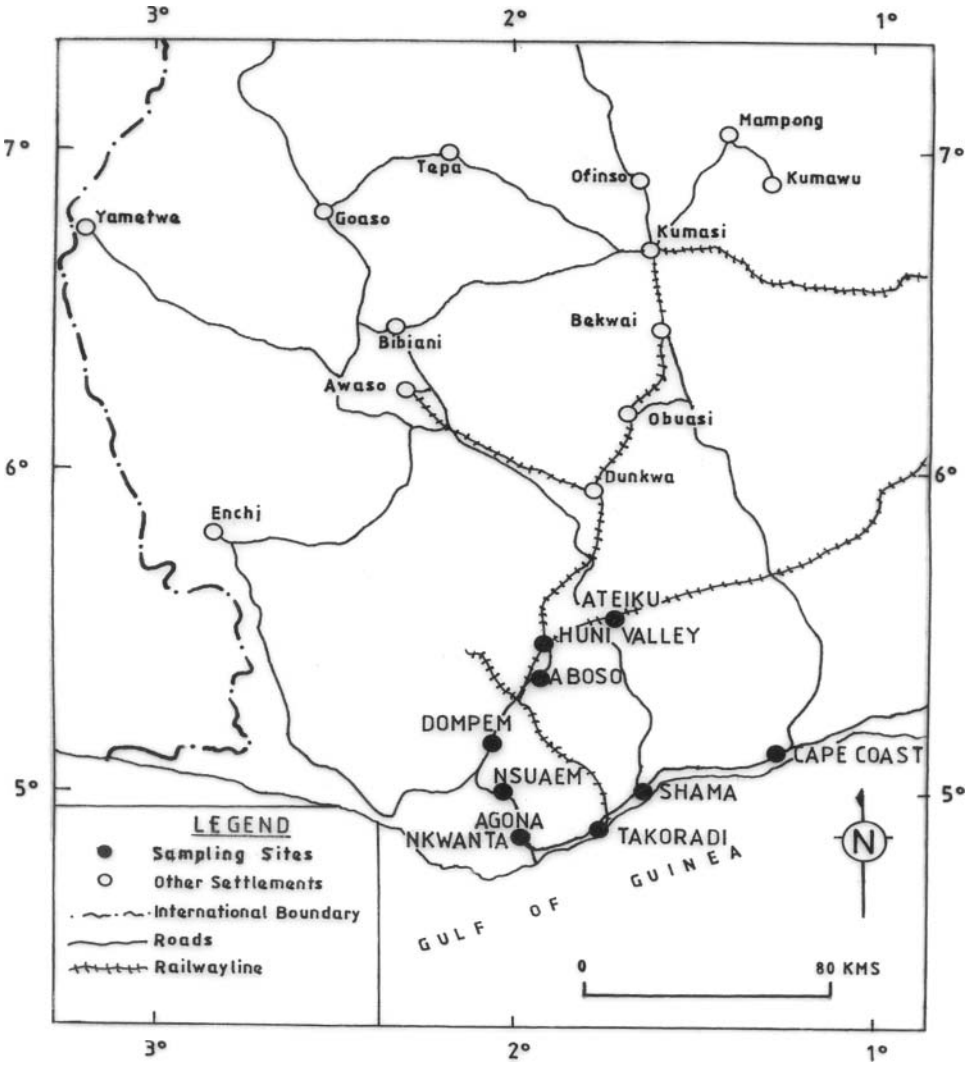

Figure 1. Map of southwestern part of Ghana showing sampling sites.

into metasedimentary and voltaic rock of the Birimian, upper Birimian, and Tarkwaian sequences.

Sample Collection

Triplicate samples were collected from farms in five towns, namely Dompem, Tarkwa, Aboso, Huni Valley, and Atieku, all located within the Wassa West district as shown in Figure 1. Control samples were also collected from Agona Nkwanta, Takoradi, Shama junction, and the agric farm at the University of Cape Coast. The average distance between sample sites was 19 km and sampling was done once monthly between September 2006 and June 2007. Thirty-six (36) samples were collected at each site over the period making a total of 324 samples in all. The soil samples were collected with the aid of a Teflon-coated

soil auger and placed in well washed polyethylene containers and sealed. The samples were collected at depths of 0–5cm, 10–15cm, 25–30cm to cover the plough zone. Nine topsoil samples were in effect collected at each site as followed by Golow and Adzei (2002).

Sample Preparation

In the laboratory, the soil samples were spread out on polyethylene sheets and freed of pieces of roots, pebbles, and other unwanted materials. Large lumps of soil were crushed. The samples were air-dried at room temperature (20–28°C) to a constant weight. The samples were ground and homogenized in a porcelain mortar, sieved with 120 μm size mesh, and made into composite samples. They were finally transferred into polyethylene containers sealed, labelled, and stored at room temperature for digestion.

Mercury Content

One gram each of soil sample was weighed into 100mL beakers. 5 mL double distilled water and 5 mL aqua regia were added to the sample in each beaker. Each was mixed thoroughly and placed in a water bath for 2 minutes at 90°C. The beakers were removed and allowed to cool to room temperature. 50 mL double distilled water was then added, followed by 15 mL of 5% w/v potassium permanganate solution. They were mixed thoroughly again and then placed in a water bath for 30 minutes at 95°C for complete oxidation of mercury in the soil samples. The samples were removed, allowed to cool to room temperature, and 6 mL of 12% hydroxylamine hydrochloride solution added to reduce the excess permanganate in the solution. The resulting solutions were filtered into 100 mL graduated flasks and the filtrate diluted to the mark with double distilled water and stored for analysis. A sample blank was also prepared.

The total mercury was determined using the cold vapor–Atomic Absorption Spectrophotometric technique. The sample blank and the digested samples were each mixed with a carrier solution of 5% H_2SO_4 and 10% $SnCl_2$.2H2O in 3%HCl in a mixing chamber. The mercuric ions were then reduced to elemental mercury. Measurements were made automatically when free mercury atoms in the absorption cell absorbed radiation at 235.7 nm resonance lines. Five mercury standards of between 0.5 and 2.5 μg/L were also analyzed and a calibration curve plotted. The mercury concentrations determined in μg/L were later converted to mg/kg. Analyses were done in triplicate by extracting 5 μL of the blank and digested samples (Golow and Adzei, 2002).

Cadmium and Zinc Content

One gram of soil was each weighed into 100 mL beakers. 20 mL of concentrated HNO_3 were added, thoroughly mixed, and set on a hot plate in a fume chamber. The mixture was heated for 30 minutes, cooled and filtered through Whatman No. 1 filter paper, and stored for analysis. A blank sample was also prepared for the analysis. The flame–atomic absorption spectrophotometer was employed for the analysis of both metals. For the cadmium content, a hollow cathode lamp operating at 8 mA current and 228.8 nm resonance lines was employed, whereas in the analysis of zinc a hollow cathode lamp operating at 213.9 nm resonance lines and 8 mA current was used. Five each of between 0.5 and 2.5 mg/L cadmium and zinc standards were also analyzed and a calibration curve plotted. The cadmium and zinc concentrations determined in mg/L were later converted to mg/kg. Analyses were done in triplicate by extracting 5 μL of the blank and digested samples (Golow and Adzei, 2002).

Recovery and Reproducibility Studies

The automatic mercury analyzer was capable of measuring the mercury atoms to as low as 0.01 ppb with recoveries between 99.3 and 100%. Reproducibility studies using 2.0 μg/L of mercury solution gave 99.5% of the mercury with a coefficient of variation of 0.98, standard error of 0.01, a mean of 1.99, and a standard deviation of 0.021. The Flame-Atomic Absorption Spectrophotometer was also capable of measuring cadmium and zinc to as low as 0.01 mg/L with recoveries between 99.4 and 100% for zinc and 99.4 and 100% for cadmium. Reproducibility studies using 2.0 mg/L of zinc solution gave 99.5% of the zinc with a coefficient of variation of 0.81, standard error of 0.01, mean of 1.99, and a standard deviation of 0.016. Reproducibility studies using 2.0mg/L of cadmium solution also gave 99.9% of the cadmium with a coefficient of variation of 0.62, standard error of 0.01, mean of 2.00, and a standard deviation of 0.01. The above results suggest that the analytical method used was very reliable and credible.

Results and Discussion

Results obtained for the total mercury content of the samples analyzed were found to be significantly higher than those recorded for non-contaminated soils, 0.0005–0.05 mg/kg (Cox, 1995). Also, the average values of mercury concentrations measured in the soil samples from the mining communities generally exceeded the maximum permissible limit (0.3 mg/kg) of mercury in soils (Dobríková and Šalgovičová, 2006; Pereira et al., 2005). As shown in Table 1, samples collected at Aboso recorded the highest total mercury concentration and the levels decreased with distance in the south and north, respectively.

The high concentration of the metal at Aboso could be due to the high number of small–scale mining operators scattered in the region that employ mercury in the amalgamation of gold (Hilson, 2001; Hilson, 2002; Akabzaa and Darimani, 2001). The mercury leaches into the soil where it is alkylated, oxidized or deposited as the metal (Schlüter et al., 1996). The metal is then made available to plant as a result of acid mine drainage as reported by Essumang et al. (2007) and Golow et al. (2009). These trace metals are absorbed by the root systems of plants (Davies, 1980). They are incorporated into the tissues of certain root crops (tubers) such as cassava (*Manihot esculenta),* cocoyam (*Xanthosoma sagititolium*), and the watercocoyam (*Colocasia esculenta*) and subsequently passed on into the food chain and then to those who eat them. The inhabitants of these areas feed on these tuber crops, thereby exposing them to elevated levels of mercury, which pose many health problems through bioaccumulation (Essumang et al., 2007).

Control samples collected from Agona Nkwanta, Takoradi, Shama junction, and Agric farm (University of Cape Coast) contained relatively higher concentrations of mercury though there is no gold mining activities in these sites. The higher levels of mercury in these sites could largely be attributed to the aerial dispersion of the metal from the mining communities due to the high vapor pressure of mercury. Generally, the surface soil (0–5 cm) recorded the least mean mercury concentrations (Table 1). This is attributed to the high vapor pressure of mercury, which causes the deposited metal to evaporate with an increase in atmospheric temperature. The higher concentrations in deeper layers of soil could be due to the leaching of the metal as a result of its weight and being bound to sulfur to form the highly insoluble mercuric sulfide, or bound to soil organic matter. It could be inferred that the mercury concentration of the soil originated from the region of Aboso and spread to other areas as observed by Golow and Adzei (2002). It is possible that the illegal mining operators were more prevalent in Aboso and the whole process originated from

Table 1
Mean levels of mercury in the samples analyzed

Sampling site	Depth (cm)	Mean Hg conc. (mg/kg)	Standard deviation	Standard error
Agric farm (UCC)	0–5	0.08	27	9.0
	10–15	0.08	24	8.0
	25–30	0.06	27	9.1
Shama Junction	0–5	0.12	7.4	2.5
	10–15	0.12	21	7.1
	25–30	0.12	12	4.2
Takoradi	0–5	0.16	24	8.0
	10–15	0.08	3.6	1.2
	25–30	0.19	9.5	3.2
Agona Nkwanta	0–5	0.18	8.9	3.0
	10–15	0.21	9.7	3.2
	25–30	0.21	23	7.8
Dompem	0–5	0.26	20	6.6
	10–15	0.29	14	4.8
	25–30	0.41	119	39
Tarkwa	0–5	0.21	102	34
	10–15	0.48	203	68
	25–30	0.42	175	58
Aboso	0–5	1.7	811	271
	10–15	2.7	1955	652
	25–30	2.8	1554	518
Huni valley	0–5	0.33	59	20
	10–15	0.27	30	10
	25–30	0.26	72	24
Atieku	0–5	0.10	40	13
	10–15	0.13	29	9.6
	25–30	0.13	18	6.0

Aboso and it is possible a census may show that Aboso has the highest population of native illegal gold miners. This calls for a concerted effort to minimize the negative impacts of gold mining in the study area.

Cadmium levels were below the detection limit of 0.01 mg/kg. Though the metal could have been detected at the μg/kg level, its toxicity is evident at the mg/kg level. The non-detectable concentrations also confirm that cadmium is usually present in the environment as minute impurities in zinc (Eggenberger and Waber, 1998). Thus, given the smaller the concentration of zinc, less cadmium will be present.

All of the samples analyzed for zinc (Table 2) fell below the 1000 mg/kg level recorded for normal soil content (Cox, 1995).

This relatively low level of zinc could be the natural background level. The relatively higher concentration of the metal in samples collected from the Agric farm (University of Cape Coast) is attributed to the application of zinc containing fertilizers or pesticides, which have the effect of increasing the zinc levels of the soil. It can also be inferred from

Table 2
Mean zinc concentrations in the samples analyzed

Sampling site	Depth (cm)	Mean Zinc conc. (mg/kg)	Standard deviation	Standard error
Agric farm (UCC)	0–5	186	26	8.9
	10–15	200	40	13
	25–30	150	53	18
Shama Junction	0–5	66	8.1	2.7
	10–15	24	11	3.6
	25–30	37	7.0	2.3
Takoradi	0–5	70	5.4	1.8
	10–15	47	4.9	1.6
	25–30	23	4.6	1.5
Agona Nkwanta	0–5	43	7.6	2.5
	10–15	6.8	2.6	0.86
	25–30	24	4.7	1.6
Dompem	0–5	221	28	9.2
	10–15	113	22	7.1
	25–30	60	14	4.7
Tarkwa	0–5	149	40	13
	10–15	170	37	12
	25–30	170	31	10
Aboso	0–5	194	59	20
	10–15	228	59	20
	25–30	387	75	25
Huni valley	0–5	48	18	5.9
	10–15	34	12	3.9
	25–30	25	7.4	2.5
Atieku	0–5	82	32	11
	10–15	48	17	5.5
	25–30	40	17	5.6

the results (Table 2) that sites such as Aboso, Tarkwa and Dompem recorded relatively high concentrations of zinc. These areas are homes to such mining companies as Anglogold Ashanti, Goldfields Ghana Limited, and Aboso goldfields who employ zinc dust in the extraction of gold (Anamuah-Mensah et al., 1996). The metal is then released into the environment through tailings or effluents from the mining operations. In all the analyses, factors such as the geochemistry of the soil and other anthropogenic sources cannot be ruled out as contributing to the levels of the metals in the soil. The low levels of zinc also show the switch from the use of the metal in gold extraction to the use of cyanide solution in extracting metallic gold from its ores by most of the mining companies, which has resulted in many cyanide spillages. Ghana has recorded over ten officially reported cyanide spillages between 1989 and 2003 (Amegbey and Adimado, 2003).

From the analysis so far, zinc, which is introduced in gold extraction by industrial companies, also displayed similar trends like mercury by showing a peak at Aboso and decreasing gradually to other places.

Conclusion

The results of the study reveal that the topsoil of the study area is heavily contaminated with mercury. This suggests that water bodies in such environments and crops, which absorb nutrients at such depths (up to 30 cm) and have high absorption coefficient for mercury, may also be contaminated. This confirms earlier research by Obiri et al. (2006) that food crops in the study area are heavily contaminated with mercury. It can also be inferred from the results that the concentration of mercury peaked around Tarkwa and Aboso, giving an indication of the high number of illegal mining operations as confirmed by Ntibery et al. (2003). These illegal mining operators use mercury indiscriminately. The roasting of the amalgamated gold releases high concentrations of mercuric oxide and mercury vapor into the atmosphere, which precipitates onto the surface of the soil and later leaches to deeper layers. The research also reveals that the concentration of mercury increased with depth. This suggests that the mode of dispersion of the metal might be aerial, since leaching might have caused accumulation of the metal at deeper soil zones.

This could also be attributed to the high vapor pressure of mercury, which could cause surface deposits to evaporate with changes in atmospheric temperature, whereas leached deposits accumulated as a result of colder temperatures.

Zinc levels in the topsoil showed an irregular trend with distance as well as depth. The results, however, reveal relatively high concentrations of the metal around Aboso and Tarkwa also confirming the use of zinc dust in the extraction of gold, which is subsequently released into the environment.

Cadmium was not detected in the samples analyzed. This is proof that cadmium is usually present as an impurity in zinc and could only be detected at concentrations of zinc higher than those determined in the sample.

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