

## Levels of Cadmium in Soil, Sediment and Water Samples from Tarkwa and Its Environs

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### Abstract:

Soil, sediment and water samples collected from the catchment areas of some selected rivers and streams in Tarkwa and its environs were investigated for the levels of cadmium using the Atomic Absorption spectrophotometric technique. From the results, it was observed that cadmium levels were generally higher than the WHO (1993) recommended level of  $2.0 \text{ mgkg}^{-1}$ . Cadmium levels in soil ranged from  $1.23 \pm 0.21 \text{ mgKg}^{-1}$  at N<sub>3</sub> to  $4.63 \pm 1.13 \text{ mgkg}^{-1}$  at K<sub>1</sub>. Soil pHw ranged from  $4.99 \pm 1.16 \text{ mgKg}^{-1}$  at Bn<sub>2</sub> to  $6.60 \pm 1.39 \text{ mgKg}^{-1}$  at K<sub>4</sub>. Cadmium in sediments were generally very high. It ranged from  $2.40 \pm 0.06 \text{ mgkg}^{-1}$  at Bn<sub>1</sub> to  $8.64 \pm 1.76 \text{ mgkg}^{-1}$  at K<sub>4</sub>. Sediment pHw ranged from  $4.59 \pm 2.49$  at N<sub>2</sub> to  $5.87 \pm 0.23$  at K<sub>4</sub>. Cadmium levels in water were also higher than the WHO (1993) standard value of  $0.003 \text{ mgL}^{-1}$ . However, the pHs of the water samples were very close to the minimum standard value of 6.5.

### Introduction

Gold, a precious metal occurs in the various regions of Ghana, especially the Wassa traditional area. Both small companies (i.e. locally referred to as '*galamsey*') and large companies compete for the mining of this metal. Preliminary studies had shown that Goldfield Ghana Limited uses zinc dust to precipitate gold from the gold cyanide solutions. Although these poisonous cyanide solutions are controlled or prevented from entering the environment, there are some accidental spillages into the environment. For example, on June 18, 1996, after days of torrential rains, the embankment of one of the solution ponds at Teberebie Goldfield limited collapsed, sending poisonous torrents of cyanide and other harmful chemicals into a river on which nine communities depend for drinking and domestic use (Lassey, 1999). As a result, over fifty (50) acres of farmland were turned into wastelands of scorched plants.

Moreover, Cadmium is always an impurity in zinc and zinc related compounds, hence where zinc is suspected to be a major pollutant, the possibility of the presence of cadmium cannot be ruled out. Tarkwa also has rich soil for agricultural activities. In an attempt to increase food supply to meet the growing population, various types of chemical fertilizers are applied to the crops for good yield. Again hazardous substances like Cadmium which is an impurity in phosphate fertilizers also find their way into the environment as a result of the use of the phosphate fertilizer. The agricultural application of phosphate fertilizers represents a direct impute of cadmium to arable soils. Acidification of soils and lakes may result in enhanced mobilization of cadmium from soil and sediments and lead to increase levels in surface and groundwater's.

Soil cadmium contamination is a characteristic feature around non-ferrous metal mines and smelters, particularly in the case of those handling zinc ores. Increase in soil cadmium content results in an increase in the uptake of cadmium by plants, the pathway to human exposure from agricultural crops (WHO, 1990). These sources may cause higher crop cadmium levels, which in turn may lead to an increase in dietary cadmium exposure. The tobacco plant naturally accumulates relatively high cadmium concentration in its leaves from soil. As a

result, this material represents an important source of exposure for smokers. It has been reported that one cigarette contains about 1-2 $\mu\text{g}$  Cadmium and that about 10% of the cadmium content is inhaled when the cigarette is smoked. One study has suggested that, modifications in cigarette preparation and the increasing popularity of filters in cigarette have reduced cadmium exposure from this source in recent years (WHO, 1990). Regional differences exist in the cadmium concentration of cigarettes, and lower values of 0.1-0.5 $\mu\text{g}$  have been found in samples from Argentina, India and Zambia (WHO, 1990). Mobility and bioavailability of soil cadmium is affected by soil moisture, the composition of the soil solution, pH, redox potential and abundance and distribution of surfaces capable of adsorbing metal ion. These factors may vary over short distances, affecting the concentration and bioavailability of the cadmium in both soil and sediments. Cadmium is toxic and has been responsible for poisoning calamities in Japan (Forstner and Wittmann, 1983). Data from experimental animals and humans have shown that pulmonary absorption is higher than gastrointestinal absorption. There is a maternal-foetal gradient of cadmium. Although cadmium accumulates in the placenta, transfer to the foetus is low. Long-term occupational exposure to cadmium has caused severe chronic effects predominately in the lungs and kidneys. Among other effects are disturbances in calcium (Ca) metabolism (WHO, 1990).

Since cadmium is toxic to life processes and air pollutants may not have a defined boundary for its dispersal, it will be of interest to measure how this metal is distributed in the environs. The report presented here is part of such studies.

## Materials and Methods

Soil samples were collected three times from the catchment areas of some selected rivers and streams in Tarkwa and its environs. The soil samples were taken preferably from places where agricultural activities were in progress. A Teflon-coated soil auger was used to collect the soil samples from four different points at the same site at an average depth of 30.0 cm to cover the plough zone. The samples were put into clean plastic containers and sealed. The plastic containers were given identification codes.

Sediment samples were also taken from four different points at each sampling site, bulked together, from which a representative sample was taken. The sediment samples were collected by hand using disposable gloves at each sampling site to avoid sample contamination. The sediment samples were also put into white transparent labelled polythene bags.

Water samples were collected from the same rivers and streams at four different points at each sampling site. The pH of the water was determined at each sampling site before the water was sampled. All the water samples were acidified using 2.0 mL of 5.0M HCl per liter of sample immediately after sampling. This acidification process was necessary in order to minimize the precipitation of metal ions (Figure 1, map).

In the laboratory, the soil and sediment sample were freed of pieces of roots, leaves and other foreign objects. The samples were next dried in an oven at 110 $^{\circ}\text{C}$  to a constant weight. The dried samples were ground and homogenized in a porcelain mortar, sieved to 40 mesh size and packed into a clean labelled polythene bags.

Duplicate weights of 2.0 $\pm$ 0.01g were put into a beaker. 10.0 mL of hydrogenperoxide ( $\text{H}_2\text{O}_2$ ) were added to each beaker and then evaporated to near dryness at 90 $^{\circ}\text{C}$  on water bath. Additional  $\text{H}_2\text{O}_2$  were added until the sample no longer effervesced on addition of  $\text{H}_2\text{O}_2$ . To each sample, 2.0 mL of concentrated sulphuric acid ( $\text{H}_2\text{SO}_4$ ), 15.0mL concentrated nitric acid ( $\text{HNO}_3$ ) and 5.0mL concentrated perchloric acid ( $\text{HClO}_4$ ) were then added successively to each beaker.

The beakers were then transferred to a hot plate where the temperature was slowly raised to 200 $^{\circ}\text{C}$ . The heating continued until strong fumes of  $\text{SO}_3$  were produced, depicting the end of the digestion. The beakers were then cooled and 25.0ml of redistilled water were added to

each beaker rinsing down the sides of the beaker. The digested soil samples were then filtered using Whatman No 1 filter paper into a 50.0 mL volumetric flask and made up to the mark using redistilled water (Methods of soil Analysis part 2, 1982). The sediment samples were similarly treated like the soil samples. Working standards and a blank were prepared. The calibration standards and the blank were used to determine cadmium levels in the digested soil and sediment samples using Perkin-Elmer 5100 PC Atomic Absorption Spectrometer at 240.7nm wavelength.

Weights of  $5.0 \pm 0.01$ g of dried soil samples were weighed into plastic tubes containing 5.0 mL ( 5.0g of water) of redistilled water and well shaken, and centrifuged at a speed of 3000.0 revolutions per minute for 5.0 seconds. The sample mixture (soil suspension) was allowed to stand for 10 minutes and pH of the soil solution was taken and recorded as soil pH in water (pHw). The same procedure was used for the sediment samples.

Duplicate 100.0 mL of each water sample was taken, concentrated and digested with 5.0 mL of concentrated  $\text{HNO}_3$ . As the volume of the sample solution reduced to about half during the digestion process, an additional 2.0 mL of concentrated  $\text{HNO}_3$  was added and the digestion allowed to continue until the volume of the sample solution reduced to about 20. The digestion is complete when the solution is light coloured. The solution was then filtered where appropriate using the Whatman No 1 filter paper into a 100.mL volumetric flask and made up to the mark with redistilled water. A blank was also prepared and the cadmium in the water sample was determined using the same machine at 240.7nm wavelength. The reproducibility of the AAS method was determined by a recovery test. Recoveries ranged from 84.1% to 86.8% with a mean recovery of 85.1%. The relative standard deviation ranged from 0.416% to 1.17% with a mean of 0.68% at 95% confidence level. The relative error averaged 14.7%.

## Results and Discussion

Table 1 shows mean cadmium levels in soil, sediment and water samples and their respective pHs in the catchment areas of some rivers and streams in Tarkwa and its Environs.

**Table 1 Mean cadmium levels in soil, sediment and water samples and their respective pHs in the catchment areas of some rivers and streams in Tarkwa and its Environs.**

1

River	Soil Cd mgkg <sup>-1</sup> Dry weight basis	pHw	Sediment Cd mgkg <sup>-1</sup> Dry weight basis	pHw	Water pH
Nsukese (N <sub>1</sub> )	3.11± 0.28	5.68 ± 1.60	3.58 ± 0.68	4.64 ± 1.95	0.004± 0
N <sub>2</sub>	3.54 ± 0.93	5.79 ± 1.77	4.74 ± 0.52	4.59 ± 2.49	0.032± 0
N <sub>3</sub>	1.23 ± 0.21	5.14 ± 2.31	4.49 ± 0.80	4.73 ± 2.54	0.033± 0
Kawire (K <sub>1</sub> )	4.63 ± 1.13	5.45 ± 0.10	8.31 ± 1.46	5.78 ± 0.06	0.014± 0
K <sub>2</sub>	2.10 ± 0.23	5.37 ± 0.36	6.68 ± 1.49	5.80 ± 0.29	0.106±0.04
K <sub>3</sub>	3.13 ± 0.49	6.10 ± 0.84	7.88 ± 1.72	5.84 ± 0.32	0.036±0.02
K <sub>4</sub>	4.05 ± 0.43	6.60 ± 1.39	8.64 ± 1.76	5.87 ± 0.23	0.014± 0
Bonsa Bn <sub>1</sub>	3.08 ± 0.33	5.24 ± 2.48	2.40 ± 0.06	5.52 ± 1.79	0.051±0.03
Bn <sub>2</sub>	1.28 ± 0.19	4.99 ± 1.16	3.14 ± 1.09	4.99 ± 1.66	0.051±0.02
Bn <sub>3</sub>	2.29 ± 0.34	5.70 ± 0.66	4.03 v 0.37	5.33 ± 1.22	0.02±0.01
WHO 1993 Standard Value	2.0		0.6		6.5-8.5

Cadmium levels in soil from the catchment areas of Nsukese were generally higher than the WHO 1993 standard Value of 2.0 mgkg<sup>-1</sup>. It ranged from  $1.23 \pm 0.21$  mgkg<sup>-1</sup> at N<sub>3</sub> to  $3.54 \pm 0.93$  mgkg<sup>-1</sup> at N<sub>2</sub>. The corresponding levels of cadmium in sediments were however higher than that of soils. These levels of cadmium in sediments far exceeded the acceptable limit of 0.6 mgkg<sup>-1</sup>. The difference between cadmium level at N<sub>3</sub> in soil and their corresponding sediment N<sub>3</sub> is so significant to suggest human influences. However, N<sub>3</sub> is at downstream, and the flow of water at downstream is generally very low, hence suspended solids tend to

accumulate or settle more at the downstream compared to the upstream. The pH<sub>w</sub> of sediments were generally lower than that of soils. Hence the benthic organisms are likely to bioconcentrate the cadmium metal at a higher concentrations. The level of cadmium in water increases from 0.004 mgL<sup>-1</sup> at N<sub>1</sub> to 0.033 ± 0 mgk<sup>-1</sup> at N<sub>3</sub> (downstream). The cadmium level in water at N<sub>3</sub> is about 10 times the recommended WHO 1993 value. The pH of the water is closer to the minimum recommended value of 6.5. Cadmium levels in soil from the catchment areas of Kawire showed a general increase above the recommended WHO 1993 value of 2.0 mgkg<sup>-1</sup>. It ranged from 2.10 ± 0.23 mgkg<sup>-1</sup> at K<sub>2</sub> (Akyem) to 4.63 ± 1.13 mgkg<sup>-1</sup> at (Akyem). The levels of cadmium in sediments however showed a marked increase. It ranged from 2.40 ± 0.06 mgkg<sup>-1</sup> at Bn<sub>1</sub> to 8.64 ± 1.76mgkg<sup>-1</sup> at K<sub>4</sub>. Sediment pH<sub>w</sub> ranged from 4.59 ± 2.49 at N<sub>2</sub> to 5.87 ± 0.23 at K<sub>4</sub>.

Cadmium levels in water were also higher than the WHO 1993 standard value of 0.003 mgL<sup>-1</sup>. However the pHs of the water samples were very close to the minimum standard value of 6.5. These levels of cadmium in sediments were about twice that of the corresponding soils. These higher levels of cadmium in sediment suggest some human influences in the locality.

Also, this river receives effluents from Ghana Manganese Company Limited during the crushing and washing process of the manganese ores. The sediment pH<sub>w</sub> were quite high compared to the values obtained from the catchment areas of Nsukese river. Cadmium levels in water samples were also higher than the acceptable limit of 0.003 mgL<sup>-1</sup>. The pH of the water however, fell within the recommended level.

River Bonsu (Bn) is the main river from which the people of Tarkwa and Bonsaso get their supply of treated water. Cadmium levels in soil from this catchment area were however higher except at Bn<sub>2</sub>, where it recorded a value of 1.28 ± 0.19 mgkg<sup>-1</sup> compared to the standard value of 2.0 mgkg<sup>-1</sup>. Cadmium levels in sediments were generally higher than the recommended maximum level of 0.6 mgkg<sup>-1</sup>. The pH<sub>w</sub> of both soils and sediments were quite higher except Bn<sub>2</sub> where both samples recorded a pH<sub>w</sub> value of 4.99. The levels of cadmium in water samples were extremely high. However the high pH of the water may not favour the dissolution of the metal in the water

## Conclusions

Cadmium levels in the study area in both soil and sediment samples were found to be relatively high. Although the levels of cadmium in samples from the catchment areas of Kawire were higher than those from Bonsa, the levels in Bonsa were of much interest since this river is the main source of water supply to the people of Tarkwa and Bonsasu. These levels of cadmium in the sediment samples from the Bonsa river were too high although the water from this river is treated before distribution.

## Recommendations

From this study, it is suggested that

1. further studies be carried out on the fishes from these rivers and streams.
2. biological fluids such as urine, blood and faeces be analysed for Cadmium levels among the people living in these catchment areas.
3. the palm kernel oil produced from Tarkwa should be investigated for the level of cadmium since such small scale industries are normally sited along these stream and rivers, and water from these rivers are used in the production of the oil without pre-treatment
4. more routine analysis of trace metals in Tarkwa and her environs is suggested in order to control trace metal pollution in the area.

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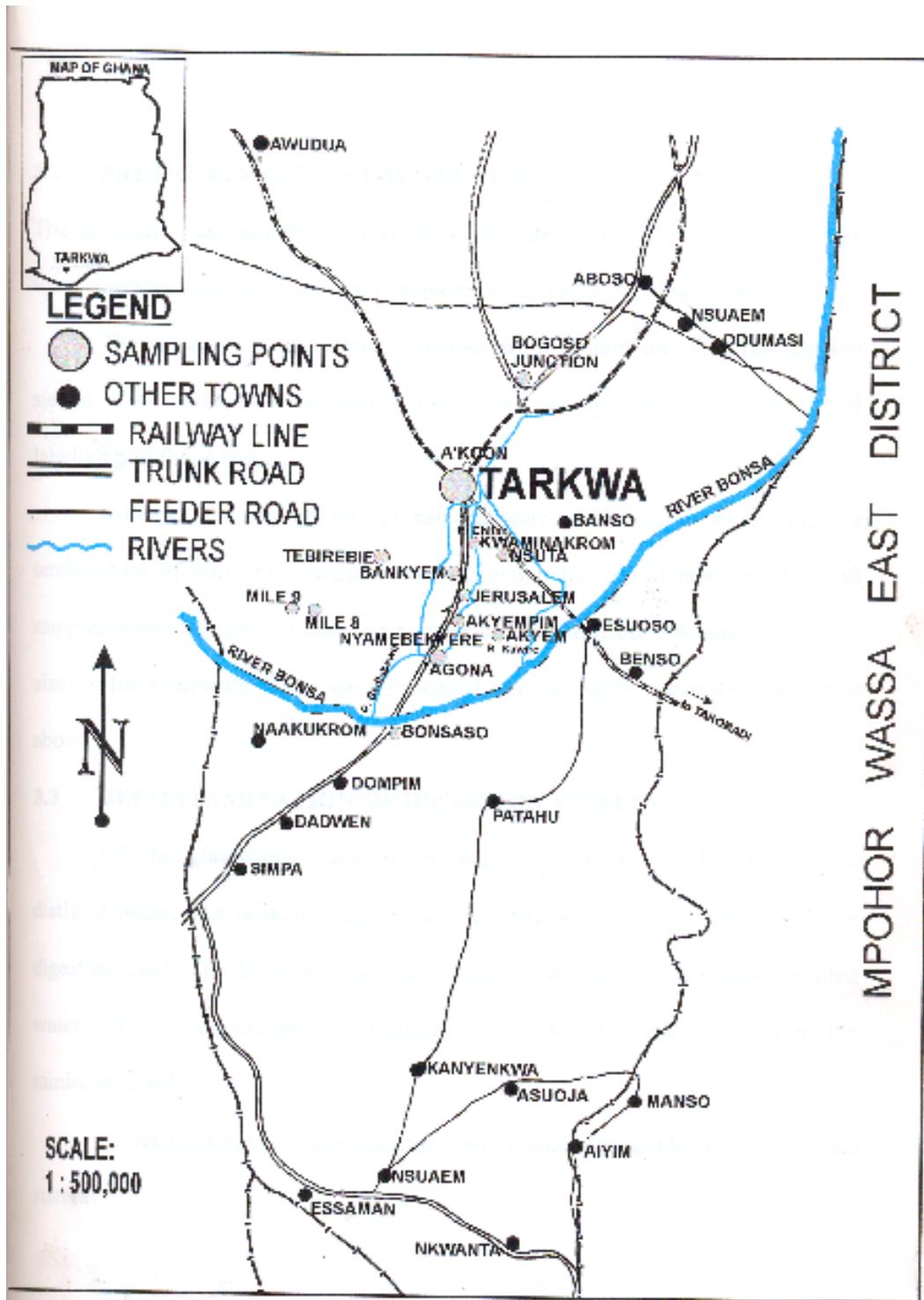


Figure 1

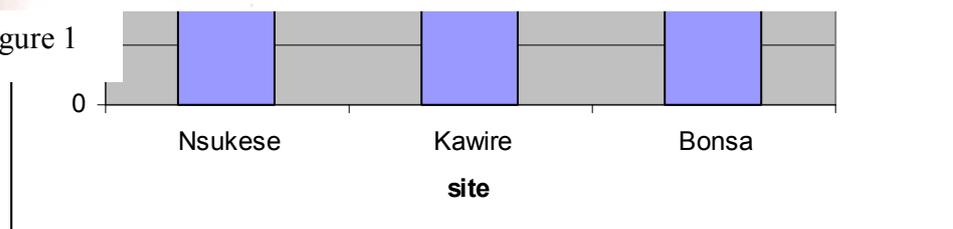


Figure2

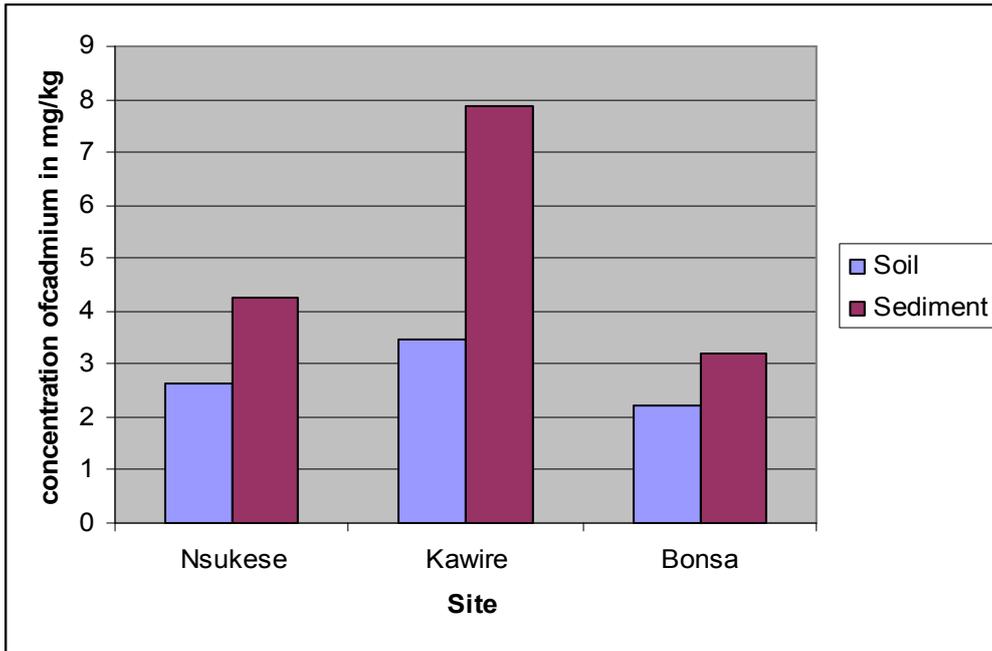


Figure3

Figure 1 Map of Tarkwa and its Environs showing sampling points.

Figure2 Mean cadmium concentration in water samples in  $\mu\text{gL}^{-1}$

Figure3 Mean cadmium concentration in soil and sediment samples in  $\text{mgKg}^{-1}$