

## Mercury in River Water and Sediments in Some Rivers near Dunkwa-On-Offin, an Alluvial Goldmine, Ghana

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Received: 11 April 2002/Accepted: 27 November 2002

Gold mining in Ghana contributes about 20% of foreign exchange earnings of the country. Since gold mining is associated with the release of other metals it puts immense stress on the environment. In Ghana large industrial operations like Ashanti Goldfields Corporation do not use mercury amalgamation method for extraction of gold. Small scale gem winners and Continental Goldfields Limited use mercury for extracting Gold. The Continental Goldfields Limited was a large-scale dredge mining company. It used dredges to extract gold from the alluvial gravels of the Offin River and its tributaries at Dunkwa-On-Offin.

The mercury used by both small scale and Continental Goldfields Limited might have vaporized into the atmosphere and be brought onto the surface of the earth in precipitation as rainfall or any other process. Such fallouts may contaminate rivers, crops, soils, livestock and humans in the neighbourhood, parts of the country and parts of the African Continent in general. The presence of mercury in the environment may harm living organisms (WHO 1991, Irukyama 1966, Lindquist et al 1984).

The report presented here is part of the studies aimed at finding out how mercury is distributed in Ghana. This reports only levels of mercury in river water and river sediments at Dunkwa-On-Offin and its environs.

### MATERIALS AND METHODS

Water samples were taken from rivers Fum, Offin, Oda and Pra for four months in July to February 2000 (Figure 1). An improvised water sampler made from PVC tube with a length of 30 cm and about 12 cm in diameter at lower end and about 9 cm diameter at the upper end. The water samples were taken from depths of 0.8 and 2m from various bridges on the rivers and tributaries. On each bridge 9 water samples were collected. Three points were samples in triplicate. The sampler was lowered into the river and flushed out three times to ensure representative sampling. The first six samples were put in glass bottles containing 5 ml of preserving agent which was 1:1 concentrated  $H_2SO_4$ : 5%  $K_2CrO_4$ . They

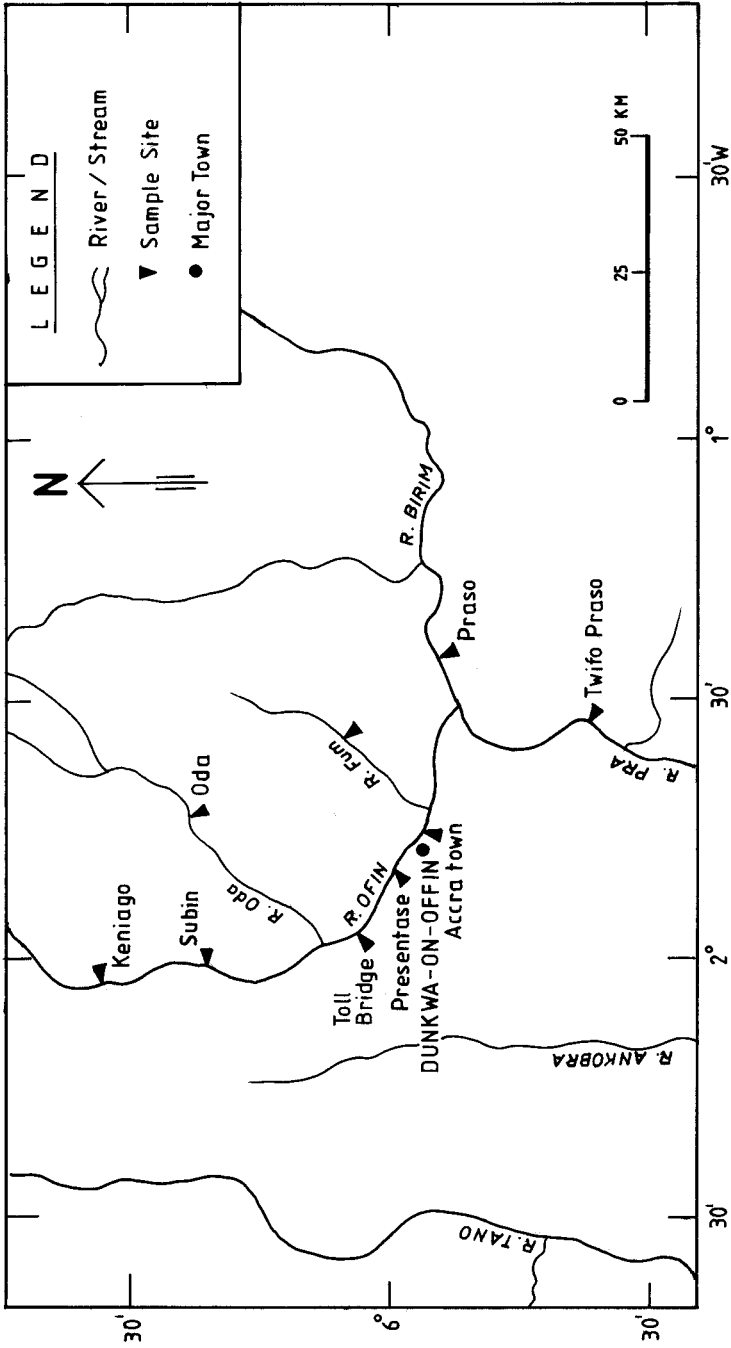


Figure 1 : Sites Sampled on rivers near Dunkwa-on-Offin

were capped tightly with their stoppers. The preservative oxidized any mercury in the water to the +2 state and brought the pH of the water to less than 2. The last three samples were not preserved but used to measure the pH and the temperature which was read with mercury thermometer in the field. The water samples were conveyed to the laboratory for treatment and analysis.

River sediments were collected from the edges with 2 - 3 feet PVC tubing with 4 cm internal diameter because grab and core samplers were not available in the Department. The tubing was immersed into the river down to the bottom sediment. The palm was placed firmly onto the open end and by virtue of suction the grabbed sediment was then held in the tubing. The sediment was then placed in glass beakers and covered with petri dishes held in position with rubber bands. Six sediment samples were taken at the accessible river banks. They were conveyed to the laboratory stored in the fridge to await treatment and analysis.

In the laboratory 100 ml of each water sample were transferred into BOD bottle, 5 ml of concentrated  $H_2SO_4$  and 25 ml of concentrated  $HNO_3$  were added. 50 ml of double distilled water was added to the sample and 15 ml of 5%  $KMnO_4$  were added to oxidize all mercury to the +2 state and allowed to stand for 15 minutes for the purple colour to persist. 8 ml of 5%  $K_2S_2O_3$  solution were also added to oxidize any organic mercury in the solution to +2 state. The bottles were stoppered tightly and covered with aluminium foil and then placed in water bath maintained at a temperature of  $95^\circ C$  for 2 hours. The samples were then cooled at room temperature and then 50 ml of distilled water added. To the digest in the bottle about 6 ml of 12% 1:1  $NaCl : (NH_2OH)Cl$  was added in bits to reduce the excess permanganate purple colour to colourless. Such treated samples were then stored in the refrigerator to await analysis.

Using the FIAS - MHS, the digest, a carrier solution of 3%  $HCl$  and a reducing agent 1.1%  $SnCl_2$  in 3%  $HCl$  were automatically sucked into a mixing chamber. In the chamber after mixing all the mercury in the +2 state were reduced to the elemental state. Argon gas was used to aerate the mixture and the elemental mercury was carried into the cold vapour cell mounted on the Perkin Elmer 5000 C Atomic Absorption Spectrophotometer (AAS) and concentration measurement made and recorded automatically. The mercury hollow cathode lamp was operated at 6mA and monitored at the 253.7 nm resonance line with a band width of 0.7 nm. Analyses were done in triplicate by sucking 5  $\mu l$  volume of the digest.

River sediments were spread over glass plates in the laboratory and allowed to dry to constant weight at room temperature between  $24$  and  $33^\circ C$ . They were not exposed to draught of wind. They were ground to fine powder in a mortar with pestle. 5 ml of double distilled water and 5 ml of aqua regia were added to accurately weighed 0.2g of sediment sample in BOD bottles and immediately the bottles were stoppered. Each bottle was thoroughly mixed and

then placed in a water bath maintained at 95°C for 2 minutes. The bottles were removed and allowed to cool. 50 ml of double distilled water and 15 ml of 5% potassium permanganate solution were added to each sample mixture in the bottles. The bottles were stoppered and then covered with aluminium foil. The solution was mixed thoroughly by shaking and then placed in a water bath at 95°C for 30 minutes for complete oxidation of all mercury in the sediment sample. The sample was allowed to cool to room temperature and 6 ml of 12% 1:1 NaCl-NH<sub>2</sub>OHCl solution were added to reduce the excess permanganate colour in the sample mixture. The total mercury levels in the digest were determined by the cold vapour technique described above and converted to µg/kg dry weight of sediment.

The reproducibility tests carried out in replicates gave a mean of 1.246 µg/L, standard deviation of 0.073 and standard error of 0.023. The coefficient of variation was 5.83% for 1.25 µg mercury per litre of water. The recovery tests for spiked samples ranged between 91.81 to 107.6% for amounts between 1.8 and 18.98 µg/L. For spiked river sediments the recovery was between 94.03 to 97.77%.

## RESULTS AND DISCUSSION

With a few exceptions Accra-Town, Centre of Dunkwa-On-Offin had the highest amount of mercury in the water, Table 1. The levels of mercury in the Offin may be due to dredge mining and indigenous mining activities of amalgamation along the river. The levels of mercury in River Offin ranged from a mean of less than 0.100 µg/L in August at Subin to 3.092 µg/L at Accra-Town. In addition activities such as burning of fossil fuel (coal) and the presence of a train station where coal is used by the locomotives might account for the levels of mercury at Accra-Town.

The Rivers Oda and Fum might have contributed appreciably to levels of mercury in the Offin River, Table 1 but the contributions might be dependent on the volume of water in them. It is not unlikely that extraction of gold with mercury amalgamation by small scale winners might be taking place in their hinterland areas.

The River Offin and its tributaries Oda and Fum did make a contribution to mercury in the Pra. In all the rainfall pattern seems to influence the amount of mercury in the river water. This might be due to increase in-washed surface soil which might contain mercury from amalgamation sources in the rivers were much lower than the WHO 1976 recommended levels of 5 µg/L.

The mercury content in sediment in the River Offin was highest at Presentase instead of Accra-Town, Table 2. The amounts of mercury in River Fum sediment was similar to what was found in River Offin, Table 2.

The amount of mercury in River Pra might have been contributed by Rivers Offin, Fum and Oda. It appeared the amount of rainfall influence the amount of mercury in the sediments also. The sedi-

Table 1. Mercury in  $\mu\text{g/L}$  in Rivers Offin, Pra, Oda and Fum

	July	Aug.	Sept.	Feb.	Mean	SD
River Offin						
Site Kaniago	0.240	0.130	1.881	0.884	0.784	0.8
Site Subin	0.408	0.095	1.824	0.855	0.796	0.75
Site Toll Bridge	0.293	0.104	2.362	1.002	0.983	0.89
Site Presentase	0.272	0.105	2.066	9.927	0.897	0.78
Site Accra Town	0.364	0.109	3.092	0.911	1.258	1.21
River Pra						
Site Twifo Praso	0.326	0.104	1.974	1.043	0.862	0.84
Site Praso	0.433	0.115	1.494	1.966	1.002	0.87
River Oda	0.611	0.105	2.112	0.441	0.817	0.89
River Fum, Fumso	0.751	0.019	1.818	0.542	0.783	0.76

Table 2. Mean mercury in  $\mu\text{g/g}$  dry river sediment from July through February, 2000.

	July	Aug.	Sept.	Feb.	Mean
River Offin					
Subin	0.231	0.030	1.070	0.345	0.419
Presentase	0.204	0.039	1.631	0.989	0.716
Accra Town	0.281	0.053	1.055	0.619	0.502
River Pra					
Twifo Praso	0.261	0.041	1.797	0.344	0.727
Praso	0.210	0.144	1.573	0.606	0.633
River Fum					
Fumso	0.210	0.047	1.127	0.469	0.475

ment might be serving as a reservoir for mercury. However the absence of amounts of mercury which was higher than recommended WHO (1976) levels might be due to high vapour pressure of the metal and the constant high ambient temperature 23 - 36°C of the environment.

#### REFERENCES

- Irukayama K. (1966) 3rd International Conference on Wat Pollut Res 3 153-160.
- Lindquist O., Jernels A., Johnson K., Rodhe R. (1984) Mercury in Swedish Environment; global and local sources. Solna National Environmental Protection Board (Report No. 1816) 105 pp.
- WHO (1976) Environmental Health Criteria 1, Mercury 131 pp.
- WHO (1991) Environmental Health Criteria 118, Inorganic Mercury 147 pp.