Assessment of Dissolved Mercury in Surface Water along the Lower Basin of the River Pra in Ghana

William O. Oduro
Council for Scientific and Industrial Research
Institute of Industrial Research
P. O. Box LG 576 Legon
Accra, Ghana.

Richard Bayitse
Council for Scientific and Industrial Research
Institute of Industrial Research
P. O. Box LG 576 Legon
Accra, Ghana.

Derick Carboo
Department of Chemistry
University of Ghana
P. O. Box LG 56, Legon
Accra, Ghana.

Benony Kortatsi
Council for Scientific and Industrial Research
Water Research Institute, P. O. Box 38
Achimota, Accra, Ghana.

Isaac Hodgson
Council for Scientific and Industrial Research
Water Research Institute, P. O. Box 38
Achimota, Accra, Ghana.

Abstract

The region along the Lower Pra River Basin has been studied for dissolved Hg concentration in the surface water of the river and its tributaries which serve as source of drinking water for communities along the basin. The study area encompassed 6 communities in the Mpohor Wassa East district of the Western Region of Ghana with a population of 122,595. Samples of surface water were collected from locations in the period September 2006 to March 2007 spanning the wet (rainy) seasons and dry seasons chronologically. The seasonal variation in dissolved mercury concentration during the wet and dry seasons in the study area was also investigated. The dissolved Hg concentration in surface water was assessed using cold vapor AAS. The average dissolved Hg concentration in the main river (48.40 ± 26.08 ng/mL) and in the tributaries (27.59 ± 18.23 ng/mL) were above the WHO guideline value of 1.0 ng/mL. The trend in contamination levels along the river Pra suggested incidence of both remote pollution and localized pollution occasioned by artisanal alluvial gold mining activities within this enclave using mobile rigs which constitute rafts with mechanized dredging equipment mounted on them.

Keywords: Mercury Pollution, Surface Water, Artisanal Gold Mining.

1. INTRODUCTION

Mercury (Hg) as a naturally occurring element is predominately found in the earth crust as cinnabar ore (HgS) in trace amounts in minerals and rocks, and also in fossil fuels such as coal (AMAP/UNEP, 2008; García-Sánchez *et al*., 2009). The release of Hg into the environment can be through natural means such as volcano eruption and weathering as well as a variety of anthropogenic sources such as mining, burning of fossil fuel, and combustion of municipal and medical waste (Jackson and Jackson, 1995; Li, *et a*l., 2009).

Mercury in any form is toxic but the acuteness in toxicity mainly lies in how it is absorbed (lipid solubility and permeability to the blood-brain barrier) and the rate of excretion (Diner and Brenner, 2009). Short alkyl organic mercury is most toxic, however, when elemental and inorganic mercury is released into the environment, bacterial action causes them to undergo methylation. The products of methylation, like monomethyl mercury (CH_3Hg^+), are soluble in water, readily absorbed by fish and the adipose cells but slow to be eliminated, hence are bio-accumulated and becomes neurotoxic.

The primary mechanisms for transporting atmospheric Hg to the terrestrial and aquatic systems according to the Selin model is through wet and dry depositions with the dry deposition more than two fold greater than wet deposition (AMAP/UNEP, 2008). Elemental Hg can circulate in the air for long period of time before depositing. This is because of its high dispersion leading to long residence times of between 0.5-2 years in the atmosphere. It is therefore, normally transported from likely sources of emission to locations remote from the pollution centers (Schroeder and Munthe, 1998). The effect of Hg pollution may therefore not just be limited to the geographical location of the discharge point (local pollutant) but several kilometers radius (global pollutant) of the point of original discharge (Harada *et al*., 2001; Johansson *et al*., 2001). Reactive gaseous mercury (RGM) and particulate mercury tend to fall out of the atmosphere more quickly than elemental Hg and are more likely to deposit closer to the source from which they are emitted (Schroeder and Munthe, 1998).

Public concern over mercury pollution reached its peak in the 1970s following a number of incidents where the discharge of elemental mercury into watercourses was linked to fatalities and severe health problems in local residents (Jackson and Jackson, 1995). The use and discharge of Hg into the environment has since received stricter control and monitoring. Artisanal small-scale gold mining is the single largest contributor to intentional discharge of Hg to the environment with a global estimate of 650-1000 tonnes of mercury released per annum (AMAP/UNEP, 2008). It is also the primary anthropogenic source of environmental Hg in Ghana (Hilson and Pardie, 2006). Poor amalgamation practices in rudimentary gold mining are responsible for the emission and abusive discharge of mercury into the ecosystem (Swain *et al*., 2007; Meech *et al.,* 1998; Pfeiffer and Larceda, 1988).

The Pra river system, the longest in south western Ghana, takes its source from the Kwahu plateau and flows 240 km into the Gulf of Guinea through its estuary at Shama (Ayibotele and Nerquaye-Tetteh 1989). The north part of the Pra River basin (especially its main tributaries) is still worked extensively for artisan gold with amalgamation the main technique in the isolation of the gold from the gangue (Spiegel, 2009, Hilson and Pardie, 2006). However, the lower watershed is widely acclaimed to have no direct mercury input source since these areas are not known for artisanal gold mining (Donkor *et al*., 2006b). The communities along this watershed depend on the river Pra as source of their drinking water either directly or through a water works situated in the area (Ghana Population and Housing Census, 2000). The acute health risk associated with the exposure to Hg pollution through drinking water supply thus necessitates the continuous monitoring of the lower Pra River basin around areas perceived as non gold mining areas. The literature available on Hg pollution in Ghana considered survey data in some of the rivers draining the south-western gold belt with known direct mercury input sources (Bannerman *et al.,* 2003; Bonzongo *et al.,* 2003; Golow and Adzei, 2002; Golow and Mingle, 2003; Donkor *et al*., 2006a; Babut *et al.,* 2003; Adimado and Baah, 2002). However, Donkor *et al*., (2006b) assessed the mercury contamination levels along the entire Pra River basin with consideration also given to locations at the lower basin perceived as non gold mining areas with no known direct mercury input sources.

Periodic assessment of the dissolved mercury levels in surface water at the lower reaches of the Pra River and its tributaries will provide adequate information on the surface water quality in communities located in areas with no known source of Hg input and hence the health implications on these communities. It will also provide information to enable the mapping out of communities remotely or locally affected by the activities of artisanal gold mining in order to regulate their activities and also effectively protect environment that has not already been contaminated with Hg.

2. Materials and Methods

2.1 Study area

The study area, as shown in Figure 1, is in six communities namely; Enyinabrim, Abetemasu, Sekyere Nsuta, Krobo, Daboase and Beposo (arranged in the order of north most to south most) on the lower Pra Basin at Mpohor Wassa East District in the Western Region of Ghana with a population of 122,595.

These communities are reported to have no known direct Hg input sources (Donkor, *et al*., 2006b). Only Daboase which constitute about 11.3% of the population in the district have access to pipe-borne water, 30.4% depend on borehole water whilst the remaining 58.3% depend on the river Pra and its tributaries for their source of water (Ghana Population and Housing Census, 2000).

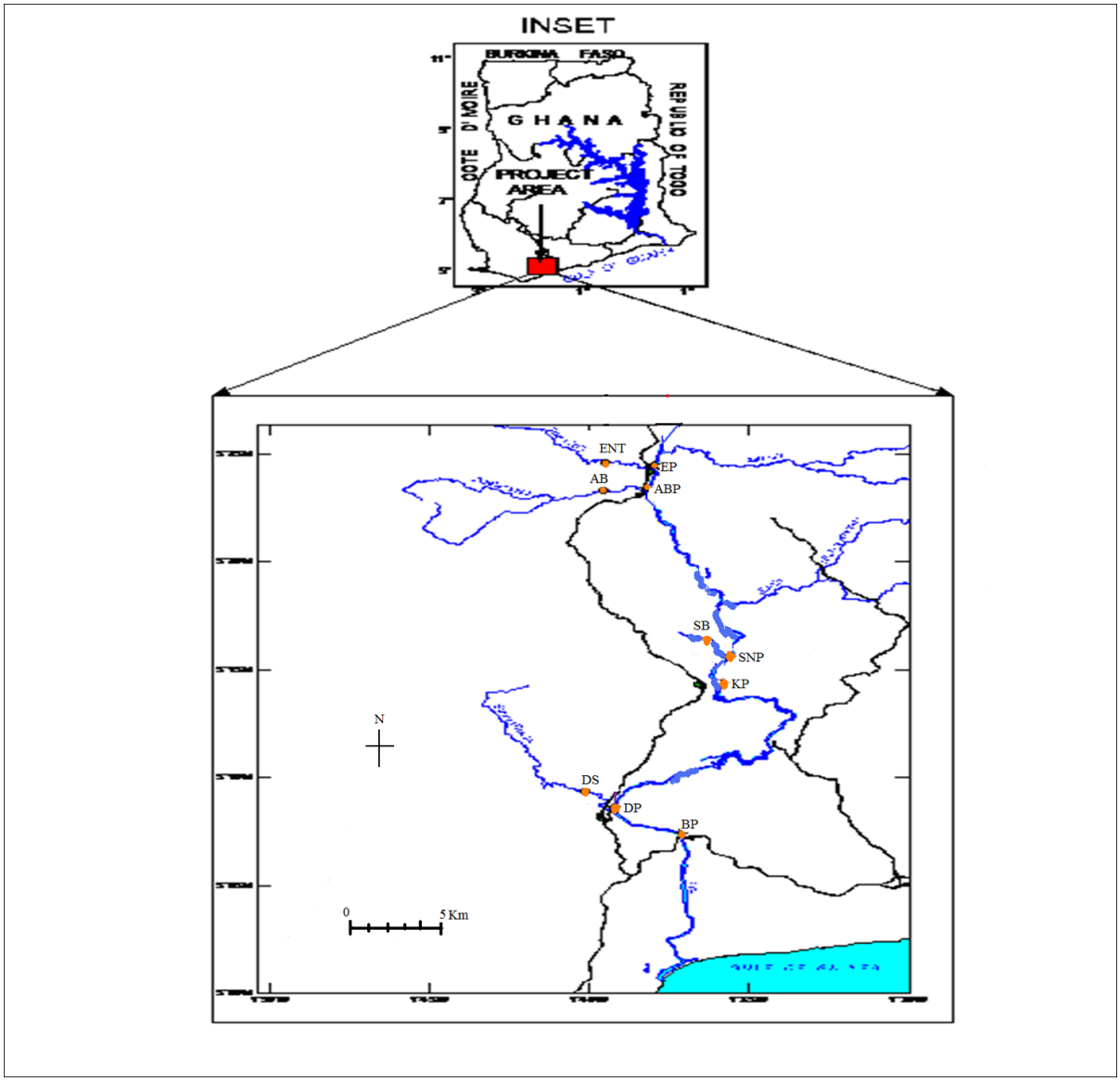

Figure 1 Map of the Pra River Basin showing the study area, with the letter codes showing the specific sample location. Inset is a map of Ghana with the study area indicated by arrow.

2.2 Sampling and Method of Analysis

3. Sampling

Surface water samples were taken from the river Pra and its adjoining tributaries (where available) in all the six (6) communities. The sampling locations were selected to reflect the wider geographical sampling area. At Beposo and Krobo, samples were taken from the Pra River only, because there are no tributaries located within the sampling area in these two communities. Samples from tributaries were taken close to the point where the stream flows into the river Pra at Enyinabrim, Abetemasu, Sekyere-Nsuta and Daboase.

The upstream sampling was taken from Enyinabrim-Pra River (EP), Enyinabrim-Nana Toi stream (ENT), Abetemasu-Pra River (ABP) and Abetemasu-Abetemasu stream (AB). At the midstream, samples were taken from Sekyere Nsuta-Pra River (SNP), Sekyere Nsuta Buabasa stream (SNB) and Krobo-Pra River (KP).

The downstream sampling sites were at Daboase-Pra River (DP), Daboase Subri (DS) and Beposo-Pra River. The stretch of the Pra River from EP to BP is about 88 km.

Duplicate 1.5 L surface water samples were taken from each sampling location per month from September 2006 to March 2007 giving a total of 140 samples to reflect the seasonal variations with its associated hydrodynamics and sediment dynamics. Generally, in the tropical climate, the wet season is characterized with considerably higher river outflow velocities and sediment transport is dominated by advection process (van Maren and Hoekstra, 2004). The wet season therefore, will more likely reflect pollution of areas with no known direct Hg input sources as a result of the transport of particulate Hg associated with sediments from artisanal gold mining activities remote from the sampling areas. On the other hand, in the dry season, tidal currents dominate flow patterns of rivers in the tropical climate and sediment is mainly resuspended locally (van Maren and Hoekstra, 2004). Thus, the dry season studies can depict accurately cases of local pollution as the dissolved Hg concentration can be more associated with leaching from sediments in the local environment.

4. Sample Preparation

Surface water samples for mercury analysis were sampled into acid pre-washed 1.5 L polyethylene terephthalate (PET) plastic bottles, and acidified with concentrated HNO_3 acid to the pH of 2 (measured with a HANNA portable digital pH meter) and clearly labeled. The acidified labeled samples were stored in an ice chest with melting ice cubes to maintain a temperature of 4 ^oC or below before transporting to the laboratory for analysis during each of the monthly sampling periods (Bonzongo *et al*., 2003).

4.1 Method of Analysis

The pH of the acidified surface water sample was further reduced to a pH of below 2 with HNO_3 acid to keep the Hg ions in solution and filtered through 0.45µm membrane filter to remove particulate matter. The dissolved mercury concentration (DHg) was analyzed using Pye Unicam 969 Atomic Absorption Spectrophotometer, equipped with a cold mercury vaporization unit, at a wavelength of 253.7 nm and the concentrations estimated from a calibration curve (APHA, AWWA, WPCF, 1985).

5. Results and Discussions

5.1 Mean Concentration of Mercury in the aqueous phase

Results from the continuous monitoring of the concentration of total Hg (DHg) in water bodies within the sampling location over the 7 months period as shown in Figure 2a clearly shows that Hg contamination in the main Pra River (48.40±26.08 ng/mL) far exceeds that in the tributaries (27.59±18.23 ng/mL). However, the levels of Hg in the tributaries are still higher than the WHO 1996 recommended guideline value of Hg in water bodies (1.0 ng/mL). Studies conducted by Donkor et al., (2006b) in the 2002 wet season and 2003 dry season along the Pra River at the lower river basin at similar sampling locations, where no known direct Hg input sources is believed to occur, reported an average DHg of 0.26 ng/mL. However, 4 years after that study the DHg contamination levels have increased several folds to an average value of 48.40 ng/mL. The DHg is highest downstream (60.69±27.72 ng/mL) at Daboase and Beposo and lowest midstream at Sekyere Nsuta and Krobo (38.77±16.42 ng/mL). The highest average (67.78±26.59 ng/mL) was recorded on the Pra River around the Daboase Community.

The distribution in DHg in the surface water samples along the Pra River of the study area (Figure 2b) clearly shows remote pollution and contamination along sampling locations downstream from EP to KP (a distance of about 42 km) as a result of the river current carrying species of Hg originally used in the amalgamation process by artisanal gold mining activities in the more prevalent communities on the upper part of the Pra River Basin downstream. However, the trend in the DHg contamination levels between KP and BP suggests incidence of typical cases of illegal gold mining (between KP and DP, a distance of about 38 km) leading to localized discharge of Hg which adversely affects communities downstream. This contributed to high DHg levels at DP (67.78±28.72 ng/mL) and BP (53.60±29.07 ng/mL). The high DHg at EP (60.35±24.44 ng/mL) may also be occasioned by the presence of cataracts on the river Pra at this community causing high turbulence that promotes the leaching of Hg species in sediments in the riverbed into the surface water.

The concentrations of Hg in sediments have been shown from previous studies in Hg contaminated water bodies to be relatively high compared to that in the surface water (Li *et al.*, 2009).

The lowest Hg concentration along the main Pra River is at Krobo (30.87±21.42 ng/mL). The Hg pollution in the tributaries, ENT (23.61±13.4 ng/mL), AB (30.40±10.99 ng/mL), SNB (32.18±25.09 ng/mL) and DS (24.17±18.53 ng/mL) could be akin to pollution as a result of reactive gaseous mercury (RGM) from combustion of the gold amalgam by artisanal miners depositing on soils leading to the formation of Hg-organic complexes which are eventually leached into water bodies through flood waters in the wet season.

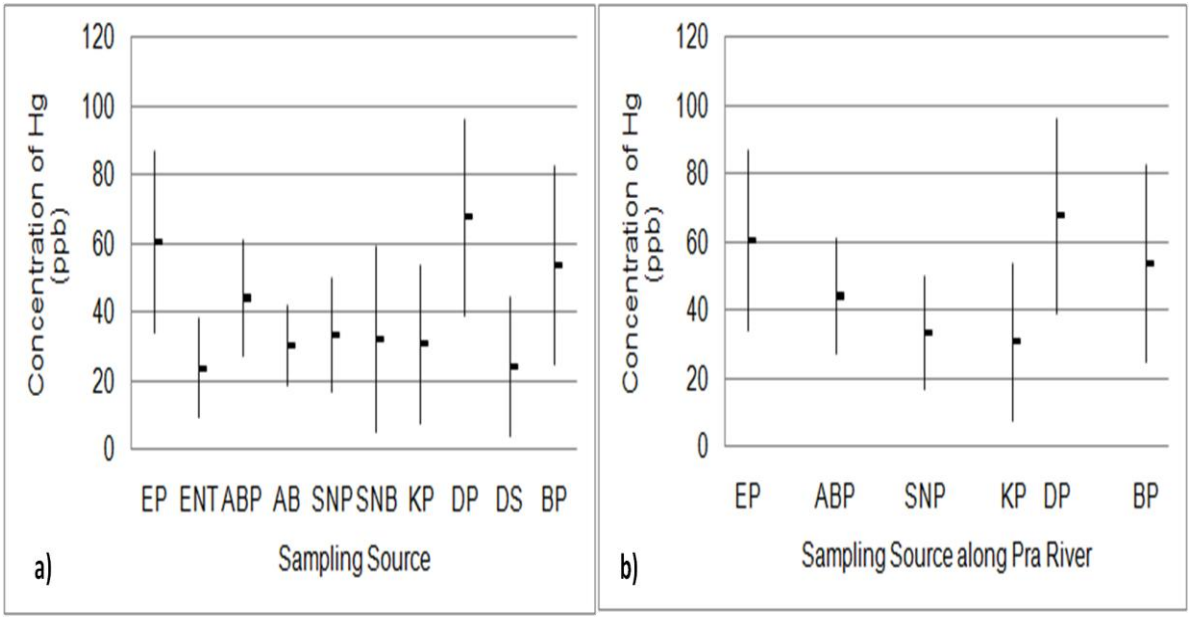

Figure 2 Mean concentrations ± Standard deviation of THg (ppb) over the study period of September to March spanning both the wet and dry seasons with a) sampling sites of both the river Pra and tributaries arranged in the order of upstream to downstream and b) showing Concentration of THg at sampling sites along the river Pra alone.

The importance of soil erosion as a mode of transport of Hg from anthropogenic sources associated with particulate matter into the aquatic systems has been highlighted by Roulet *et al* (1998) in his study in the Amazon. Similar results were found by Couture and Lambert (2003) studying areas in Guyana affected by artisanal and small scale mining. They concluded that erosion of land sediments caused by storms or hydraulic monitors (used by gold miners on land) transports high amounts of Hg-bearing organic matter associated with fine particulates into river bodies.

5.2 Seasonal variation in the concentration of Hg in surface water

Averagely, the wet season (September to November) generally had a lower DHg (29.49±16.66 ng/mL) compared to the dry season (47.97±9.76 ng/mL) which span the period December to March (Figure 3). It is only in BP the south most sampling site that the DHg in the wet season was higher than the dry season (Figure 3b).

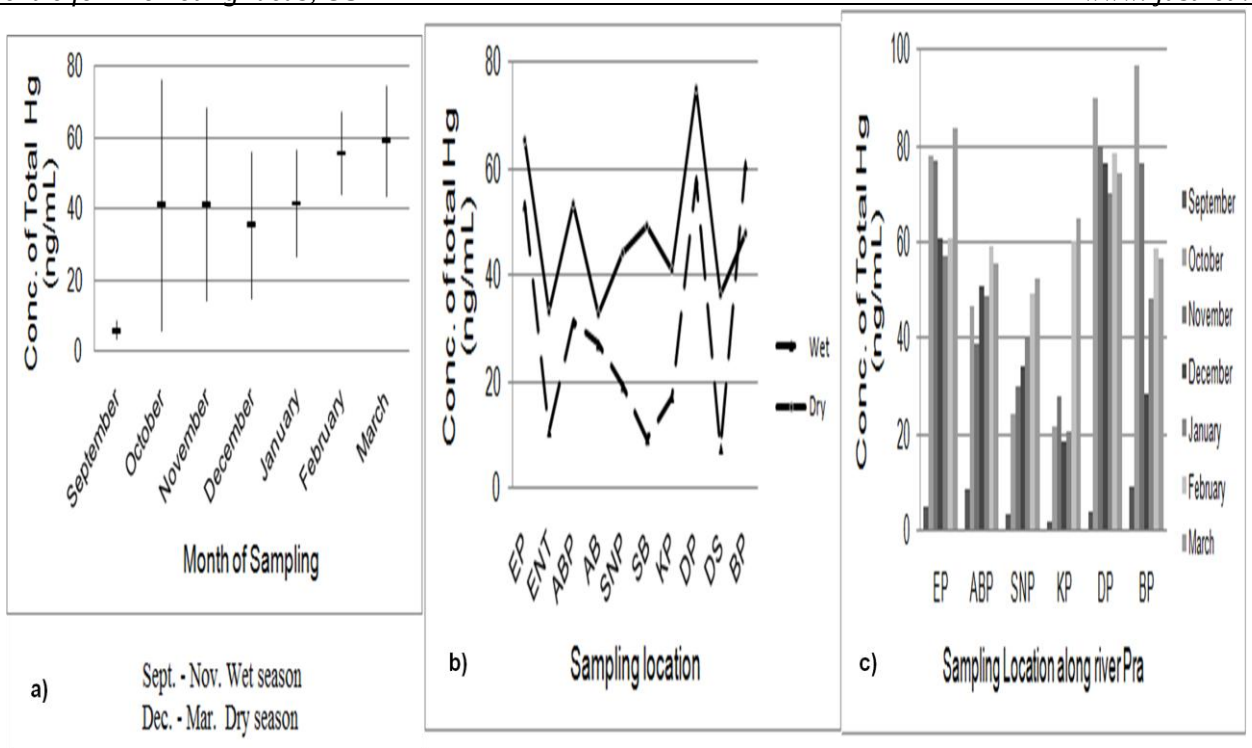

Figure 3 The seasonal distribution of mercury in wet and dry seasons a) shows the mean THg ± Standard deviation (ppb) over the different months b) shows mean THg during the wet (dash line) and dry (solid line) seasons at the study area and c) shows the monthly variation of Hg concentration along the Pra River.

There are a number of reasons that could be adduced to the seasonal variation in mercury contamination in the lower basin of the river and its tributaries. Firstly, the swifter current in the water bodies in the wet season could lead to reduced equilibration time for the partitioning of the different species of Hg between the sediments and the surface water, hence the lower DHg in the aqueous phase. Secondly, the dilution effect of the increased volume of water in the water bodies during the sampling period could account for the smaller concentrations during the wet season. Also AGM activities commonly take place during the dry seasons because the process involves the extraction of gold from alluvial concentrations in streambeds or riverbeds. Therefore, a slower current aids their operations better than a swifter current in the wet season by enabling a more efficient dredging of the riverbeds and streambeds. However, AGM is not exclusively done in the dry season especially with the advent of more sophistication in the equipment for the trade. The DHg in the entire lower reaches of the Pra River increases from a low of 5.92±2.46 ng/mL in September to a high of 59.15±15.39 ng/mL in March at the peak of the dry season when the volume of water in the water bodies is at its lowest (Figure 3a). The high Hg contamination at BP during the wet season (Figure 3b) indicates the possible effect of the transport of contaminated sediments and flood waters from remote sources of Hg input to the furthermost downstream sampling location.

Studying the trend in DHg contamination levels along the river Pra for the months of October and November (which are months which reflect the average DHg over the 7 month period) as shown in Figure 3c gives some indication of the type of pollution which is predominant in the study area. The mean DHg along the river Pra in EP is 78.16 ng/mL for October and 76.8 ng/mL for November. The DHg level drops significantly to 46.57 ng/mL in October and 38.68 ng/mL in November at ABP a nearby location still upstream the river Pra, a distance of about 8 km south of EP. Moving a further 35 km of south of ABP, the sampling locations midstream generally had relatively lower contamination levels, SNP (24.27 ng/mL and 30.15 ng/mL) and KP (21.74 ng/mL and 28.06 ng/mL), for the months of October and November respectively. Then the DHg rises sharply at DP (89.84 ng/mL and 80.24 ng/mL) and BP (96.95 ng/mL and 76.62 ng/mL) sampling locations further downstream about 38 km south of KP. The sharp variation gives strong indication that mercury contamination is predominantly from localized activity compared to transportation of the pollutant from a source further upstream. The trend in distribution of Hg along the study area suggests isolated cases of illegal small scale mining (Galamsey) activities at places between Krobo and Daboase, the evidence of which is pictorially captured in Plate 1b.

The Hg concentration in the surface water at KP was low in spite of the mobile alluvial gold mining rig that was sighted in the area (Plate 1a). This is because the mobile rig was located a few kilometers downstream of the sampling location suggesting that the pollution activity could more adversely affect sampling locations south of KP like DP (38 km south of KP) and BP (a further 9 km south of DP) hence the high DHg levels in these sampling locations. This source of direct Hg discharge as complemented by the deposition and transportation from the more notorious mining areas north of the study area is proposed as the mechanism for pollution/contamination of downstream sample locations along the river Pra. The incidence of illegal miners straying into communities traditionally not noted for artisanal alluvial mining could lead to significant localized Hg pollution. However, their activities could escape notice due to their mobile nature as shown in Plate 1. The wide variation in results during the wet season especially in October and November could be due to a more recent history of artisanal mining activity prior to sampling.

Plate 1 Illegal alluvial gold mining using mobile rigs in the lower Pra Basin a) Krobo during the dry season and b) Daboase during the wet season.

Elemental Hg is now known to spread very effectively from diverse sources to both terrestrial and aquatic systems. Sediments function as sinks and potential sources of Hg which once contaminated, pose a risk to aquatic life for many years. Depending on the environmental conditions present Hg compounds in aquatic systems could be transformed and liberated from sediments to water phase, ingested by aquatic biota, or be conveyed with sediment particulate matter to new previously uncontaminated locations (Ullrich *et al.*, 2001).

6. CONCLUSION

The investigation of incidence of mercury contamination in surface water describes its presence, variation and location of sources of Hg input in the lower Pra River system within the study area that covers a stretch 88 km from the upper most sampling location to the south most sampling location along the river course in an area previously assessed as not having a known direct Hg input source. The average Hg contamination level along the main river is 48.40 ng/mL whilst the tributaries have a concentration of 27.59 ng/mL of Hg. The source of mercury in the system could clearly be traced to incidence of remote pollution up to the midstream locations with the source of Hg from upper part of the river system. Pollution at the lower watershed of the study area is occasioned predominantly by direct Hg input source through activities of artisanal gold miners operating from mobile rigs and to a lesser extent to remote pollution sources through transportation by the river current from active artisanal gold mining enclaves as a result of weathering of contaminated soil from flood waters as well as wet and dry depositions. Environmental contamination by mercury is clearly a growing problem even today in the communities a bit remote from the active artisanal alluvial gold mining areas in the Pra Basin hence countermeasures need to be adopted before it is too late. In order to prevent damage in the earliest possible stages, the state of contamination must be constantly monitored and prevention measures like policing the water bodies, educating artisanal miners of the dangers in mercury use and the deployment of a more efficient and environmentally friendly gold separation process must be taken.

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