

Evaluation of Sources and Options for Possible Clean up of Anthropogenic Mercury Contamination in the Ankobra River Basin in South Western Ghana

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ABSTRACT

The study assesses the spatial distribution and sources of mercury contamination in the Ankobra River Basin in south-western Ghana and discusses possible remediation options and challenges. Eighty-two (82) samples of water and streambed sediments from areas of active and historic artisanal mining and historic mine spoil from large-scale mining were analysed for their total mercury content using cold vapour Atomic Fluorescence Spectrometry (CV-AAS). The highest Hg concentrations were recorded from historic mine tailings, legacy of large scale mines in the area, which averaged 795 ppb but ranged from 80 ppb to 2500 ppb. Concentrations in streambed sediments averaged 139 ppb, but ranged from 63 ppb to 270 ppb. Water, expectedly, gave the lowest Hg concentrations with a mean value of 1.5 ppb, but ranged from below detection to 8 ppb. Areas worked by artisanal miners and historic tailings dumps at Bondaye and Prestea recorded the highest mercury values. These high mercury concentration sites constitute potential sources of major mercury pollution in the area and therefore require major and urgent clean up to mitigate any major health risks. However, any remediation strategy would require further and detailed study of the contaminated sites and an evaluation of known remediation techniques to achieve maximum results.

Keywords: Ankobra Basin, Mercury Contamination, Clean-Up, Old Tailings, Sediments, Water

1. Introduction

Mercury pollution is a very serious environmental problem because elevated concentrations are toxic to living organisms with the degree of toxicity varying with its chemical form. Organic mercury, particularly methyl mercury is said to be more than 1000 times as toxic as elemental mercury. The effects of mercury on humans are well documented. It causes damages to the central nervous system and is especially toxic to the foetus [1,2].

Mercury in the environment comes from both natural and anthropogenic sources. Naturally, cinnabar (HgS) is practically the only source of the metal, while the most important anthropogenic sources of mercury pollution are from the mining industry [3].

Commercial deposits of cinnabar have not been reported in Ghana, although stream channel sampling have revealed a promising mercury dispersion zone in the valley of Tromia in Brong Ahafo region of the country [4]. On

the whole, no significant natural sources of the metal are known in Ghana as efforts at other areas in the country have so far not indicated mercury concentrations significantly above its crustal abundance of 30 ppb. However, studies in traditional mining centres in Ghana such as Obuasi and Tarkwa have reported elevated mercury levels in stream water, sediments, fish, and plants [5,6]. Most of these studies assigned the activities of artisanal miners, who use mercury for gold recovery, as the primary source of mercury dispersion in Ghana. The present study area has over 500 years of artisanal activities. Apart from these artisanal miners, mercury was pervasively used in large-scale mining in Ghana until the early 1990s when it was officially prohibited in large-scale mining. During that period, over 15 large-scale gold mines in the Tarkwa mining district, many of them abandoned today, used mercury for gold recovery. The area has seen over 100 years of large-scale gold mining [7]. These mines left on their

trail scattered mercury-laced tailing dumps. For instance, over hundred years of gold extraction using mercury in the three underground mines at Prestea, Tuapim and Bon-daye, about 65 km from Tarkwa, has generated three vast expanse of tailings dumps, covering a total area of about 30 km², while similar operations at the Tarkwa underground mine has also generated tailings covering over 16 km² of land space.

Studies have shown that the Ankobra River Basin, which takes drainage from these mining anthropogenic activities, and is indeed itself being mined by both legal and illegal artisanal miners, has poor abundance of fish and invertebrates because of heavy metal pollution. Other studies have reported widespread augmented mercury levels in food crops such as cassava, cocoyam and in fish in the area [6].

There has not been any systematic study to assess the extent of Hg contamination in the area. In fact, the impacts and extent of mercury pollution in Ghana are not yet understood. This exploratory data clearly shows that the need to clean up mercury in the area is a delayed priority. This paper, which explores the problem of mercury pollution in the Ankobra River Basin and its mosaic of tributaries, has provided data that justifies the urgent call for the clean up of the contaminated sites. Various clean up options have been discussed.

2. The Study Area

The study area is in the Wassa West District of the Western Region of Ghana (Figure 1), and is a major mining

hub in Ghana, defined by several major mining towns such as Nsuta, Tarkwa, Damang, Abosso, Bogoso, and Prestea. The area is one of the few remaining corridors of Ghana's tropical rain forest that is fast depleting by human activity, including mining. Annual rainfall data for the area indicate minimum and maximum values of 1449 mm and 2608 mm respectively, while annual temperatures range from 25°C to 29°C [8].

The Ankobra River and its mosaic of tributaries (Figure 2) receive various mine-impacted water from large-scale gold mines at Prestea, Bogoso, Tarkwa and Damang, as well as small-scale, often illegal mining operations, within the area.

The gold occurs in lenses of sulphide-bearing quartz veins, mainly in carbonaceous phyllite, as disseminated sulphides in the metavolcanics, or as oxidised derivatives of the two types in the Birimian rocks and in conglomeritic horizons as free milling gold in the Tarkwaian. It is the oxidised ores and the free milling varieties that are most amenable to dressing with mercury.

3. Materials and Methods

A total of 70 water samples from streams, boreholes, and hand dug wells; 6 samples each of stream sediment from channel-bed alluvium and material from old tailings dumps, respectively, were collected and their locations noted with a Global Positioning System (GPS) and recorded on a sample location map (Figure 2). Sample collection, preservation, storage, preparation and quality control/quality assurance (QC/QA) protocols followed those outlined by

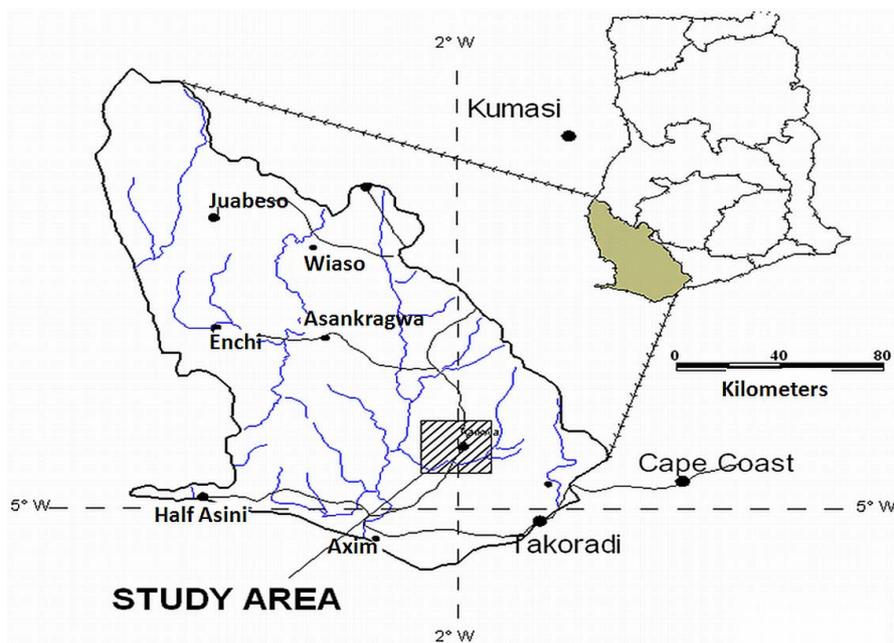


Figure 1. A map of Ghana showing the study area.

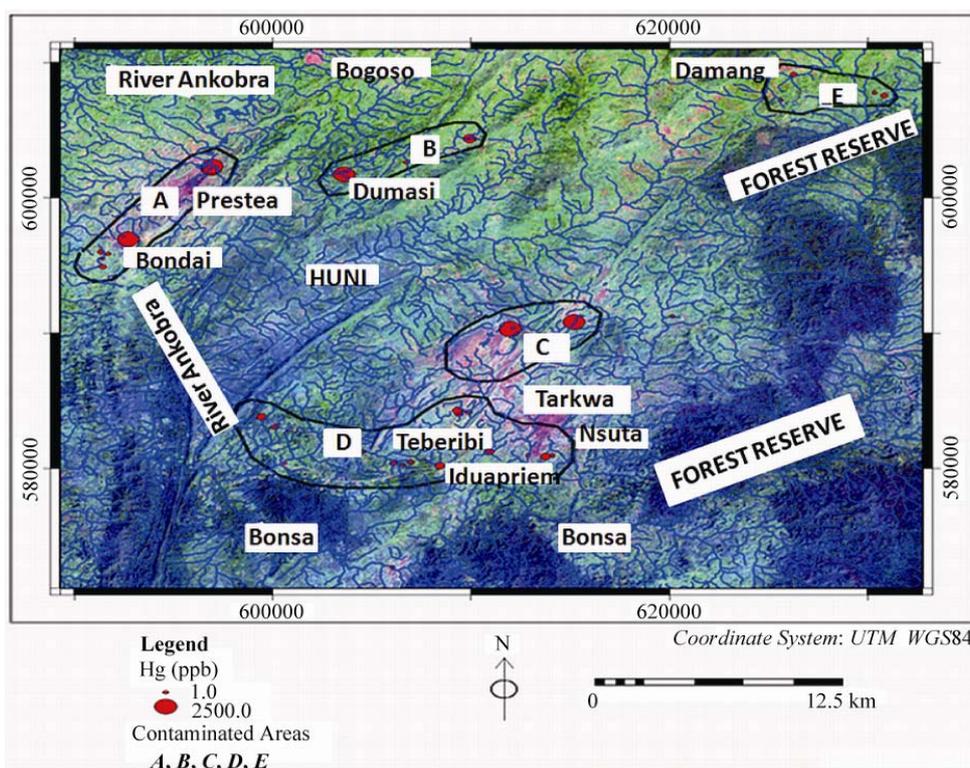


Figure 2. Mercury contaminated sites identified for possible clean-up planning.

Eppinger *et al.* [9], APHA [10], Bloom and Fitzgerald [11] and Barcelona *et al.* [12]. Water samples were acidified with pure nitric acid (HNO₃) to pH less than 2 to prevent possible reaction of the dissolved species [13] and total mercury determined by cold vapour Atomic Fluorescence Spectrometry (CV-AAS) and expressed in parts per billion (ppb) with detection limit of 1 ppb.

Plastic scoop was used to sample stream sediments and tailings material into polyethylene sampling bags and tightly secured. The samples were oven-dried at 40°C and sieved to 80 meshes. Total nitric acid extraction was then applied to this fraction to obtain a leachate, which was then analysed for Hg using the same cold vapour Atomic Fluorescence Spectrometry.

Analyses were performed at the Water Research Institute (WRI) of the Council for Scientific Research (CSIR), with duplicates of select samples analysed at the SGS Commercial laboratory and the Ecological Laboratory (Ecolab) of the University of Ghana for quality assurance and control purposes.

control purposes.

4. Results

The results of mercury concentrations in the various media are presented as summarised descriptive statistics in **Table 1**. The concentration of total mercury in stream sediments and mine tailings are presented in **Tables 2** and **3**, respectively. The samples exhibit variable total Hg mercury concentrations ranging from 33 ppb - 25,000 ppb in old mine tailing dumps, 63 ppb to 270 ppb in streambed sediments and from <1 ppb to 8 ppb for water samples (**Table 1**).

4.1. Hg in Mine Tailings and Streambed Sediments

Mine tailings and stream sediments have mercury concentrations of over 10 - 100 fold the levels in water. The highest Hg concentrations were recorded from historic mine tailings with average concentration of 795 ppb.

Table 1. Summary descriptive statistics of Hg concentrations in various media in ppb.

Sampling Media	Mean	Median	Standard Deviation	Minimum	Maximum	Count
Water	1.5	1	1.25	<1	8	70
Streambed sediments	139	100	87.65	63	270	6
Old Mine Tailing Dumps	795	72	1154.67	33	2500	6

Table 2. Concentration of mercury in various mine spoil and stream sediments.

Sample	Description	Hg (ppb)
Old mine tailing dumps		
PGRTD01	Old Tailings at Prestea, now being mined by PSGL	2500
SSPGRB01	Sediments from stream taking seepage from tailings at Bondaye	97
SSGFL01	Soil from rehabilitated waste rock site	43
TSGFL01	Tailings from abandoned underground mine	80
PGRTD02	Old tailings being re-mined by Bondaye	2050
TSGFL04	Ancient tailings from Tarkwa underground mine	33
Streambed Sediments		
SSA01	Sediments from the Ankobra river at point where drainage from PSGL Operations enter it	230
TSPGRB01	Sediments from stream draining old tailings at Bondaye	270
GMCTS01	Stream sediments from the Kawere stream near Nsuta	103
SSPGRB03	Stream draining ancient tailings dump near Bondaye	63
SS1	Stream sediments from Bonsa Stream	63
SSTGL-6	Stream sediments from Bedibewuo stream near Tarkwa	70

Material taken from tailings dumps in Bondaye and Prestea underground mines gave the highest mercury values of 2025 ppb and 2500 ppb respectively (**Table 2**) and area A in **Figure 2**.

Mercury levels in stream sediments are generally lower than those from the tailings dumps. The highest Hg values of 270 ppb and 230 ppb were obtained from stream sediments samples taken from a tributary of the Ankobra draining the old tailing dump at Bondaye and the Ankobra River itself respectively. Augmented mercury concentrations ranging from 63 ppb to 103 ppb were obtained from sediment samples at the Bonsa River, Bedibewuo stream, and the Kawere, where active artisanal mining activities are brisk (**Table 2**).

4.2. Water Samples

Water samples showed the lowest mercury concentrations among the three media sampled, and ranged generally from below detection to 8 ppb, with high concentrations coincident with areas of small-scale mining activity, such as streams in the Bogoso area, including the Ankobra River. All samples from streams with artisanal mining activities gave Hg concentrations of at least 1 ppb. High mercury values were also observed from water from streams that drain the old tailings dumps at Prestea and Tarkwa, with the highest value of 8 ppb recorded in a stream that takes drainage from the Bondaye old tailings dump which gave the very high Hg concentration of 2050 ppb.

4.3. Discussion

The data presented can be considered as one of the first steps to understanding the sources and problem of mer-

cury contamination in the Ankobra River Basin. Water exhibited much lower Hg concentrations than tailings and sediments. Hg concentration in water from many streams far exceeded the World Health Organization (WHO) maximum guide limit of 1.0 ppb [14]. These elevated mercury concentrations occur in streams in areas with intense small-scale mining activity and from streams carrying drainage from the old tailings dumps with high Hg levels. The most pervasive contamination of Hg in stream waters generally come from the Ankobra River and a mosaic of tributaries around the Bogoso area where artisanal mining activities are most profound, particularly around the village of Dumasi and its satellite communities (**Figure 2**). However, the single highest mercury concentration in water came from a stream draining old tailings dumps at Bondaye with elevated mercury levels.

These observations are not surprising as mercury is the chemical used in gold extraction by these traditional small miners. All samples taken from streams where these small miners operate gave high mercury values. Some of these miners amalgamate their concentrate right in the streams leading to the spilling of the Hg into the streams (**Figure 3**). In fact the low level of mercury in even stream waters with active artisanal mining activities is not surprising. Hem [15] has pointed out that mercury in water opened to the atmosphere is likely to be much lower owing to its tendency to escape via vaporization. It may also form chloride and hydroxide complexes depending on pH and total chloride concentration.

Sediments from streams and old tailings dumps have Hg concentrations far in excess of the maximum allowable concentration of 10 ppb of Hg in these media that

Table 3. Summary of remediation methods.

METHOD	DESCRIPTION	ADVANTAGES	DISADVANTAGES	SPECIAL REQUIREMENTS
Removal	Dredging and pumping out contaminated materials	Well-tested and effective	Expensive, lengthy process; disposal sites can leak and re-release contaminant; significant disturbance of the environment	Expensive equipment; must be monitored periodically and followed by either treatment and/or burial and containment in other location
	Physical treatment (<i>i.e.</i> sorting)	Good for large quantities of sediment (20 - 40 tons/hour)	Does not work with high silt, clay content soils/sediments	
Treatment	Thermal treatment resulting in volatilization	Mercury compounds are highly volatile at low temperature	Causes more atmospheric mercury pollution	These methods often are best applied of site in contaminated medium that has been removed
	Chemical treatment on site or off site	Mercury reacts with other compounds and can be made biologically unavailable	Adding foreign chemicals into an ecosystem can be dangerous when you aren't sure of the outcome	
Immobilization	Physical barriers placed on site to contain the contaminant so it can no longer spread through the ecosystem	Well-tested and effective	High cost, barriers are of questionable permanence, unknown unintended ecological effects from the destruction of the benthic ecosystem	Barriers can be top, bottom or lateral side barriers; sometimes barriers can be natural and not man made
Microbial Action	Using microbes that can demethylate mercury to clean contaminated mediums	Effective in sludges, wastewater and controlled environments like the laboratory	Not proven for on site remediation	Forms the basis of phytoremediation
Phytoremediation	Various techniques using plants to remove mercury from the environment or immobilizing it within the environment; methods include degradation, extraction, containment or a combo of all three	Cost effective, less intrusive than other methods, pollution captured can be recycled and reused instead of mining more	Plants grow slow and results take a while, mercury captured in the plant may be available to wildlife feeding on the plant, not well tested, environment must be suitable to the accumulating plant	Best for sites with low to medium levels of contamination
Water Quality Management	Manipulating the water quality such as oxygen content or pH to ensure methyl mercury production will not occur	Cost effective, less intrusive, not highly technical	Manipulations need to be monitored, and may likely need manipulation often; may disrupt some ecosystem functioning	Most easily implemented by current water managing agencies

Source: (Adopted from Fuller [3]).

would require immediate remedial action [16]. Mercury concentrations in these media are about 5 to more than 500 times the maximum allowable limits. The results demonstrate that Hg use by artisanal miners and Hg in old

tailings dumps of large scale mining activities constitute the two major anthropogenic sources of mercury contamination in the area.

The two extremely high anomalous Hg values in the



Figure 3. Artisanal miners wining gold from the bed of the Bonsa River using mercury.

Bondaye and Preseta mine ancient tailings (Area A in **Figure 2**) are related to historic Hg use in gold processing. From the inception of large-scale mining in the area from 1897 to the early 1990s, Hg was the chemical of choice for gold extraction by all commercial gold miners in the area. Small-scale miners are presently reworking the tailings dumps illegally, sending uncontrolled sediments and leachate containing Hg into the Ankobra and its tributaries.

4.4. Containing Widespread Contamination in the Basin

The relatively low level of Hg concentration in water—compared to concentration in sediments and mine tailings—is not surprising. The results are indeed consistent with observation from studies elsewhere, where it has long been recognised that Hg is more efficiently transferred from water to bottom sediments [17-19]. Such rapid transfer is possibly through mechanisms such as sorption on suspended or bed load material, clay and organic material [20]. This is supported by the study of Hg speciation in bottom sediments of water reservoirs, which has shown that physically sorbed admixture is the predominant form of Hg occurrence in bottom sediments [17]. Such forms of Hg exhibit weak bonds and can easily be extracted from the sediments under conditions of rainstorms resulting in seasonal flushing of doses of Hg into water [20]. The high Hg concentrations in streambed alluvium and old mine tailings in the area constitute major sources of Hg contamination in surface waters. Varekam *et al.* [18] have pointed out that such high Hg contaminant sources present serious environmental problems as erosion of soils with high mercury loading brings these mercury bearing particles into the aquatic system.

Earlier studies have indicated augmented mercury concentrations in fish and plant species from the study area

[6]. One possible pathway for fish and plant uptake of Hg would be transfer from sediments through methylation, which ensures a more bioavailable form of Hg [21]. It is also known that invertebrates that ingest large quantities of sediments may accumulate higher concentrations of Hg toxin than species that ingest leaf material [21]. The dangers posed by high mercury concentrations in sediments have equally been echoed by Hem [15] who pointed out that mercury ingested from sediments gets concentrated in the successive biological species along aquatic food chains so that fish that live in mildly contaminated environment may contain too much mercury to be used safely for food.

These mercury-laced dumps and sediments pose real threat to the general environment in the area, as these sources are capable of re-supplying mobile mercury to streams in the area during rainstorms. Currently the old tailings dumps have been evaluated to contain considerable gold resources, and ever since this disclosure, thousands of illegal small-scale miners have besieged these dumps. Their activities are sending considerable tailings into the drainage system.

There is the urgent need to put intervention measures in place to clean up the area to prevent widespread mercury contamination in the wider Ankobra basin that serves numerous communities. Any efforts to contain the contamination and possibly carry out remediation of mercury endemic sites would require careful planning. In the first place, it would require either curtailing the work of small-scale miners using mercury or providing the miners with technical support and education to use mercury retorts. However these efforts at ensuring that these miners use retorts in the past has been quite fruitless.

4.5. Options for Remediation and Challenges

Mercury pollution is an acclaimed human health hazard and the degree of its toxicity is dependant on its speciation. When converted to methyl mercury by bacteria in stream water and sediments, its toxicity could be augmented up to a thousand fold that of elemental mercury due to its facilitated ability to cross cell membranes and interact in biological systems [1]. Consequently, remediation of mercury contaminated sites, where they are located close or have the potential to impact watersheds, is gaining urgent priority in water quality management globally.

The impacts and extent of mercury pollution in Ghana are not fully understood. Remediation strategy for these contaminated sites would be challenging, as remediation can only be effective if there is a thorough understanding of the spatial scale of the pollution and the chemical forms of the mercury. This exploratory work has pro-

vided useful information on the sources and scale of mercury contamination in the study area. The contaminated sites are shown in **Figure 3** as A, B, C, D, and E. Sites A and C are ancient tailings dumps at Prestea and Tarkwa, respectively. Site B is the Ankobra River near Dumasi while sites D and E are streams being worked by small scale miners.

However, the information cannot be said to be adequate for full-scale remediation of the problem as this would require thorough understanding of the scale of pollution, the chemical forms of the mercury in the contaminated media, the range of mercury-relevant sites parameters, that usually vary from location to location due to changes in temperature, pH, flow rate, solvent types, etc. [3].

The current levels of data is therefore limited for any full scale clean up measure, but provide the basis for further work to provide the needed information for cleaning the contaminated sites. According to the USEPA [19] six main categories of remediation techniques have been widely used-removal of the contaminated media; treatment of the medium, immobilisation of the contaminant, microbial remediation, phytoremediation and water quality management. The merits and demerits of each of these techniques have been summarised by Fuller [3] (**Table 3**).

Any strategy to decontaminate the identified sites would require an evaluation of these techniques on the basis of their potential to succeed. Since the Ankobra Basin is extensive, it will probably require multiple remediation methods at the different sites. This will probably require detailed individualised response plans that require more detailed information for the different sites in the basin. Such a remediation strategy is necessary and urgently needed to clean the Ankobra River and its tributaries and the scattered mercury-laced old tailings dumps identified in this study to prevent a pluming ecological disaster in the area.

4.6. Securing Processing Alternatives to Mercury in the Artisanal Mining Sector

The remediation must address mercury sinks and production pathways as the most critical targets for cleaning. In this particular study area, the challenges presented by contaminated old tailings site could be overcome once barriers are erected to prevent dispersal of material from the contaminated tailings while remediation takes place. However, it might be more challenging to address this problem with respect to areas of small scale miners, particularly, illegal miners. These migratory miners serve as constant supply of fresh mercury to streams in the area and unless their activities are curtailed, any remediation measure would be a wasteful exercise.

It is clear that efforts to stop the operations of these artisanal miners will be a fruitless venture, under current constrained opportunities for alternative sources of livelihood in the country. The other option is to examine and possibly implement alternative processing technologies other than mercury. Alternatives to mercury amalgamation such as, gravity concentration, cyanidation and froth flotation have successfully replaced mercury in the large-scale mining sector. However the adoption of such technologies to the artisanal mining sector would equally be as problematic as mercury for several reasons including cost considerations and capacity constraints. Gravity concentration presents a better opportunity for success. However the nature of occurrence of the gold in typical artisanal work sites in Ghana makes the application of gravity concentration unattractive. Most of the gold is too fine and gravity concentration would not be an effective technology.

These problems notwithstanding, it is an important challenge for efforts to be geared towards the development of alternative processing technology for the artisanal mining sector. Until an alternative to mercury is found, any efforts any to clean up contaminated sites might only constitute a temporary solution.

5. Conclusions and Recommendations

The application of mercury in gold ore dressing in small-scale mining and historic application of mercury in gold extraction by large-scale miners have resulted in contamination of portions of the Ankobra Basin, including scattered mercury-laced old tailings dumps at Bondaye, Prestea and Tarkwa. These mercury contaminated tailings dumps and streambed alluvium present serious environmental challenges as these serve as reservoirs for the supply of Hg into water bodies through erosion. The regulatory authorities would have to discourage the direct discharge of untreated mine drainage into streams, particularly the Bansa and Ankobra Rivers, which serve as sources of domestic water supplies for the area. Urgent measures are needed to clean up delineated mercury contamination in the area. However, this would require a more detailed study of the sites and a thorough evaluation of available remediation options and their effectiveness.

Since small-scale mining is an unavoidable livelihood activity, efforts should be made to explore the use of mercury free extraction technology in the sector.

Efforts must be made to develop alternative processing technologies to replace mercury in the artisanal mining sector.

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