Sources of Arsenic Distribution at Obuasi in Ghana

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Abstract - There have been various studies to establish the potential sources of arsenic responsible for pollution of surface water and groundwater in the Obuasi Municipality of Ghana. This study seeks to provide better understanding of the identified sources and their characteristics in the study area. In the study rock and soil samples were taken from identified active and inactive arsenic storage structures for analyses of their photomicrographs and selected metal content. Results of photomicrographic study indicate geologic features of arsenic source minerals such as pyrite, arsenopyrite in different states of oxidation. Other minerals present were pyrrhotite, chalcopyrite, sphalerite, stibnite and galena. It suggests significant potential for acid-mine drainage in the study area. Majority of gangue minerals contain acid-buffering or carbonate-bearing rocks/alterations relevant to control the AMD effect they generate whilst others do not and will therefore rely on the acidbuffering effect of the surface water or groundwater constituents. Arsenic and trace element analysis of tailings dams and tailings footprints around surface water and groundwater suggests that the oxidation of arsenic rich minerals reduces as you move away from the water sources and underscores the importance of water to the oxidation and mobility of arsenic in the study area. Acid base accounting of tailings material from Anglogold Ashanti Obuasi Mine Oxide Treatment Plant (OTP) and Sulphide Treatment Plant (STP) confirms the likelihood of acid mine drainage from the tails of the OTP and STP.

Keywords - Arsenic Photomicrograph Sources Obuasi

I. INTRODUCTION

egal and illegal exploitation for gold combined with the anatural geochemical dispersion from exposed arsenic mineralization has resulted in arsenic contaminated water, animals, plants and soils in the Obuasi Municipality ([1], [2], [3], [4], [5], [6], [7] and [8]). Rock and soil are the main sources of arsenic which are eventually recycle into plants, animals, humans, surface water and groundwater ([2], [9] and [10]). The study area has many government regulated active and inactive arsenic storage sites composed of rock waste dumps, tailings dams, arsenic trioxide storage sites, heap leach sites, some visible dumped rock sheathing for roads and other constructional activities ([3] and [11]). There are also many illegal mining sites scattered across the Obuasi community ([12], [13], [14], [15] and [16]). Studies have identified relationship between arsenic and other tracers in clarified surface water and groundwater [4]. However, its filtration residue and its host mineralogy in areas of close proximity to mining related arsenic storage infrastructure in Obuasi Municipality has not been well studied. This study seeks to provide understanding of the sources and distribution of arsenic and its relationship

with surface water and groundwater of the Obuasi Municipality.

II. MATERIALS AND METHODS

Soil, rock, surface water and groundwater samples were taken from various sites in the Obuasi Municipality of Ghana (Figure 1). Photographs of potential arsenic-generating sites and close-up photographs of rocks were taken of material from active and inactive rock waste dumps, rehabilitated sites, galamsey sites, old rock sheathed roads, and heap material from river beds. Photomicrographs of the rock samples were subsequently taken. Surface water samples were collected from 20 river sampling points, 25 ponds and 120 streams. Groundwater samples were also collected from 113 community boreholes (CBH), 18 AngloGold Ashanti Obuasi Mine monitoring boreholes (MBH) and 11 hand-dug wells in the study area and analysed for total arsenic. Filtration residues from filtered surface water and groundwater samples in the study area was analyzed after oxalate extraction for As, Na, Ca, Mg, K, Fe, Cu, Zn, Al, Ba, Sr, Li and Mn by AAS analysis. The filtration residues were selected based on the proximity of the water to active and inactive/decommissioned rock waste dumps, tailings dams, heap leach, arsenic trioxide powder storage, galamsey sites, river sand and rock sheathing on roads.. Soil samples were also taken from the surface water sampling site for oxalate selective dissolution and AAS analysis. Acid base accounting and the tailings characteristics of tailings material from the Oxide Treatment Plant (OTP) and Sulphide Treatment Plant (STP) of Anglo Gold Ashanti Obuasi Mine at Sansu was performed to determine the acid generating potential and assess the readily mobile trace elements and arsenic available for release into the surrounding surface water or groundwater.



Figure 1: Sampling Locations with Satellite Image at Background (Source: Modified after [17])

III. RESULTS AND DISCUSSIONS

A. Photomicrography of Rocks

Partially oxidised rocks were taken from an acidic stream in an artisanal mining site (Figure 2). Photomicrograph of the rocks indicates variety of sulphide minerals together with carbonates (calcite and dolomite), oxides and silicates. Figure 3 shows sphalerite is in granular texture with inclusions of gold, bordered by bladed stibnite grains, sphalerite with isolated grains of gold, euhedral grain of pyrite with sphalerite, isolated grains of pyrite and chalcopyrite in sphalerite. Pyrhotite occurs as anhedral mass, disseminated grains, isolated grains in polished sections. Figure 3a shows scattered grains of dolomite (Dol) with pyrrhotite (Pho), galena (Ga), and pyrite (Pyr), Figure 3b shows equant grain of pyrite with arsenopyrite (Asp) surrounded by quartz (Qz), Figure 3c shows isolated grains of pyrite and chalcopyrite (Cha) in sphalerite (Sph). Figure 3d shows large grain of chalcopyrite surrounded by sphalerite and stibnite included with pyrite in a partially weathered state.





Figure 2: (a) Photographic Image of Partially Oxidised Rock taken from Acidic Stream in an Artisanal Mining Site with High Total Arsenic and (b) Closeup-view of Partially Oxidised Rock



Figure 3: Photomicrograph of Rock from Partially Oxidised Rock taken from Acidic Stream in an Artisanal Mining Site with High Total Arsenic Content

Rock samples were taken from a waste dump suspected to generate ARD (Figure 4). Figure 5 shows photomicrographs of the rocks taken from a waste dump suspected to generate ARD in the study area. From the photomicrograph, gold occurs as grains in polished sections. In association with other minerals gold occurs in pyrite associated with dolomite, sphalerite, stibnite, arsenopyrite and quartz. Figure 5a shows grains of gold (Au) in pyrite in ppl associated with dolomite. Figure 5b shows bladed stibnite grain bordered on the sides by sphalerite with gold and quartz inclusions. Figure 5c shows grains of sphalerite with an inclusion of gold and disseminated quartz and stibnite. Figure 5d shows sphalerite bordered by bladed stibnite grains with arsenopyrite inclusions and surrounded by quartz.



Figure 4: Photographic Image of (a) Waste Dump showing Rain-washed Water Collecting from Acid Rock Drainage (ARD) where Rock Sample was taken and (b) Closeup view of Rock Sample



Figure 5: Photomicroghaph of Rock taken from Waste Dump showing Rainwashed Water Collecting from Acid Rock Drainage (ARD)

Rock samples were taken a road leading to a rehabilitated site with pools of water gathered around the rock dump (Figure 6). Figure 7 shows photomicrographs of the rocks indicating pyrite occurs as shears with granular texture, isolated grains, equant grains, euhedral or sub-hedral grains or pebble. In association with other minerals, pyrite was observed as euhedral and sub-hedral grains with chalcopyrite, as equant grain with disseminated grains of chalcopyrite, massive or granular texture with isolated inclusions of anhedral chalcopyrite as pebble surrounded by silicates, as large euhedral grain with sphalerite, as euhedral grain surrounded by quartz. Figure 7a shows euhedral and subhedral grains of pyrite with chalcopyrite in plane polarized light (ppl). Figure 7b shows euhedral grain of pyrite surrounded by quartz. Figure 7c shows grains of arsenopyrite in ppl with disseminated grains of chalcopyrite. Figure 7d shows pebble of pyrite surrounded by silicates in ppl.



Figure 6: (a) Photographic Image of Rocks dumped on Road around Rehabilitated Site with Pool of Water, and (b) Closeup view of Partially Weathered Rock



Figure 7: Photomicrograph of Rocks Dumped on Roads around Rehabilitated Sites

Rock samples were taken from a road sheathed with suspected sulphide material in weathered state (Figure 8). Figure 9 shows photomicrographs of the rocks indicating that gold occurs as grains in polished sections. In association with other minerals, gold is observed as an inclusion with grains of sphalerite, gold has a granular texture in association with dolomite and pyrite. Figure 9a shows gold with framboidal (granular) texture in ppl. Figure 9b shows large euhedral grain of pyrite in ppl with sphalerite showing orange internal reflection at the middle top. Figure 9c shows granular texture of pyrite with isolated inclusions of chalcopyrite in ppl. Figure 9d shows granular mass of pyrite with inclusions of chalcopyrite in ppl.



Figure 8: (a) Photographic Image of Road Sheathed with Suspected Sulphide Material in Weathered State, (b) Close-up view of Fully Weathered Suspected Sulphide Mineral, (c) Close-up view of Fresh Sulphide Minerals



Figure 9: Photomicrograph of Rocks from Road Sheathed with Suspected Sulphide Material in Weathered State

Rock samples were taken from a heap of rough sand around River Nyam (Figure 10). Figure 11 shows photomicrographs of the rocks and indicates chalcopyrite occurs as anhedral mass, disseminated grains, isolated grains in polished sections. Arsenopyrite also occurs as sub-hedral to euhedral grains in polished sections. In association with other minerals, arsenopyrite was observed in occurrence with gold and chalcopyrite as an intergrowth with pyrite with inclusions of pyrrhotite, in some quartz masses. In association with other minerals, chalcopyrite was observed as disseminated with equant grains of pyrite, as isolated inclusions with granular pyrite and included in granular mass of pyrite. Figure 11a shows abundant occurrence of pyrite with granular texture being replaced by chalcopyrite and gold inclusion. Figure 11b shows sheared pyrite with granular texture. Figure 11c shows isolated grains of gold with sphalerite in ppl, Figure 11d shows stibnite with lamellae twinning bordered by sphalerite and disseminated quartz.





Figure 10: (a) Photographic Image of Heaped Rough Sand around River Nyam, and (b) Close-up view of Rock taken from Nyam River



Figure 11: Photomicrograph of Rocks taken from a Heap of Rough Sand around River Nyam

Sulphide minerals in different states of oxidation identified in the study area are pyrite and arsenopyrite. Other sulphide minerals present were pyrrhotite, chalcopyrite, sphalerite, stibnite and galena. Galena and pyrrhotite were in relatively smaller quantities while pyrite, chalcopyrite, stibnite, sphalerite and arsenopyrite were in relative abundance. The major gangue minerals identified was quartz. Pyrite was identified in almost all the samples whereas arsenopyrite with the characteristic rhombic or lath-shaped features with fractures was often found associated with pyrite. Pyrite was identified in most samples as anhedral crystal which is sometimes also dissseminated in the rock. The pyrite mineral is often with inclusions of minerals such as pyrrhotite and galena.

Results of the photographic and photo-micrographic study indicate geologic features of arsenic source minerals such as pyrite, arsenopyrite in different states of oxidation. Other minerals present were pyrrhotite, chalcopyrite, sphalerite, stibnite and galena. Graphitic intergrowth of feldspar and quartz with others show a matrix of fine grained quartz. Sericite is observed as randomly or minutely aligned with the clay minerals. Calcite is observed as solitary euhedral crystals or as interstitial masses associated with different minerals. Rutile was observed in the polished sections as a primary secondary mineral. Gangue minerals which are most common are dark carbonaceous materials, rutile and quartz and dolomite.

The above suggests significant potential for acid-mine drainage from rocks and soils collected in the study area. Majority of gangue minerals contained acid-buffering or carbonate-bearing rocks/alterations. This is relevant for effective development of strategies for acid mine drainage remediation. Some rocks/soils have adequate acid-buffering component to control the AMD effect they generate whilst others do not and will therefore rely on the acid-buffering effect of the surface water or groundwater constituents. Gold is observed to be associated with pyrite, arsenopyrite and other sulphide minerals in different states of oxidation. This suggest the activity of illegal gold miners during exploitation may initiate the AMD process and mobilise asenic at old arsenic storage structures.

B. Distribution of Arsenic and Tracer Metals in Filtrate, Filtration Residue and Soils

Arsenic content of selected filtration residue (water sediments) from areas of high arsenic concentration in both surface and groundwater varied from 1.8 to 6.7 g/kg, with a mean value of 5.2 g/kg. In surface soils collected from the same area, arsenic content ranged from 5.2 to 74 g/kg with a mean value of 8.5 g/kg. The highest arsenic value of 74 mg/kg in soils around the Arsenic Storage Area at the STP which is over ten-fold higher than the world arsenic soil average of 5-6 mg/kg [18] suggests possible spillage of arsenic-trioxide powder during transportation to the burial site. High arsenic content of the upper soils could also be as a result of historic atmospheric input from the arsenic roaster and current smelting activities from the STP. Figure 12 presents relationship between arsenic in soil and arsenic in residue for surface and groundwater sites, whilst Figure 13 presents relationships between arsenic in filtrate and arsenic in soil. Figure 14 also present relationships between arsenic in filtrate and arsenic in residue.





Figure 12: Relationships between Arsenic in Soil and Arsenic in Residue for (a) Surface Water and (b) Groundwater Sites



Figure 13: Relationships between Arsenic in Filtrate and Arsenic in Soil for (a) Surface Water and (b) Groundwater Sites





Figure 14: Relationships between Arsenic in Filtrate and Arsenic in Residue for (a) Surface Water and (b) Groundwater Sites

Figure 15 presents relationship between extracted Fe in soil and Fe in filtrate for surface and groundwater sites, whilst Figure 16 presents relationships between arsenic in soil and Fe in soil. Figure 17 also present relationships between arsenic in residue and Fe in residue.



Figure 15: Relationships between Extracted Fe in Soil and Fe in Filtrate for (a) Surface Water and (b) Groundwater Sites



Figure 16: Relationships between Arsenic in Soil and Fe in Soil for (a) Surface Water and (b) Groundwater Sites





Figure 17: Relationships between Arsenic in Residue and Fe in Residue for (a) Surface Water and (b) Groundwater Sites

Figure 18 presents relationship between extracted Fe in residue and Fe in filtrate for surface and groundwater sites, whilst Figure 19 presents relationships between arsenic in residue and Fe+Mn+Al in residue. The strong correlation between the concentration of iron and arsenic in the filtrates and those in the filtration residue and soils suggests that the dissolved iron and arsenic in the water is linked to the sediments and soils of the immediate environment and can aid demobilization of arsenic. Figure 19 also suggest that other elements such as Al and Mn can aid the demobilization of arsenic in the study area.



Figure 18: Relationships between Extracted Fe in Residue and Fe in Filtrate for (a) Surface Water and (b) Groundwater Sites





Figure 19: Relationships between (Fe+Al+Mn) in Residue and As in Residue for (a) Surface Water and (b) Groundwater

The soils of the area are well drained, porous and loamy [19]. This suggests unimpeded infiltration into the groundwater and surrounding surface water. The positive correlation between arsenic in soils and filtration residue and Fe in soils and filtration residue could be as a result of weathering of arsenopyrite and adsorption of As onto the Fe hydroxides. Usually the solubility of Fe and As decreases or increases simultaneously [20]. In aerobic environments, 90% of dissolved arsenic is in the form of arsenate which binds to hydroxides of Fe and Al and may become soluble when subjected to reducing conditions ([21 and [22]). This is confirmed with significant concentrations of arsenic in filtration residue and its positive trend with Fe, Al and Mn. Such a phenomenon is likely to aid demobilization of arsenic and suggests the need for efficient filtration of all surface water and groundwater before drinking or for cooking. Figure 20 is a map of the study area showing the concentration of iron in soils and filtration residue of surface water obtained from sites with high arsenic concentration (>0.010 mg/l). Figure 21 is a map of the study area showing arsenic in soils and filtration residue obtained from the surface water sites with high arsenic concentration (>0.010 mg/l). Figure 21 indicates significant concentrations of arsenic in filtration residue of water from the study area. This confirms the need for efficient filtration of all water before drinking or for cooking.



Figure 20: Map of Spatial Distribution of Filtered Total Arsenic in Obuasi Municipality Surface Water showing Fe in Soils and Filtration Residue



Figure 21: Map of Spatial Distribution of Filtered Total Arsenic in Obuasi Municipality Surface Water showing Arsenic in Soil and Filtration Residue

C. Arsenic Source Indicators of Active and Inactive Tailings Deposition Sites

Table 1 shows As, Cu, Pb and Zn content of active tailings dams and old tailings foot prints of the study area. Comparing the concentration of selected metals in water and filtration residue and soils collected from the same site, there is correlation between As. Cu. Pb and Zn in soils around active and inactive arsenic storage structures and that of the surface and groundwater as well as the filtration residue. The order of abundance of selected metals in the filtration residue from the study area is As>Cu>Pb>Zn. It was observed that areas with footprint of tailings deposition contain more oxalate extractable trace elements in filtration residue than areas with active tailings dumping. This confirms that gold mine tailings dams were implicated as source of trace elements and arsenic contamination in adjoining soils, surface and groundwater ([22] and [23]). These trace metals and arsenic could be transported through flooding and normal rain events as well as wind erosion of the uncapped tails during storms events. Overall, the trend of elements concentration in the soils as you move away from streams and rivers in this study was Cu>Pb>As>Zn. This suggests that the oxidation of arsenic rich minerals reduces as you move away from the water sources and underscores the importance of water to the oxidation and mobility of arsenic in the study area.

Table I: Trace Metal Content of Old Tailings Footprint and Active Tailings Dams Sites

Trace Element	Sites	Mean	Median	Standard Deviation
As (mg/kg)	Active Tails	459	501	134
	Tails Footprint	1421	2091	623
Cu (mg/kg)	Active Tails	65.9	72.4	23.6
	Tails Footprint	187.4	156.8	87.3

Pb (mg/kg)	Active Tails	28.6	32.1	11.2
	Tails Footprint	71.3	68.9	17.2
Zn (mg/kg)	Active Tails	21.4	25.2	9.1
	Tails Footprint	36.4	43.5	17.4

D. Characterization of AGA Obuasi Mine Tailings Material

Tailings of the study area consist of liquid and solid phases. The particle size distribution and its corresponding concentrations of sulphur, arsenic and gold in the tailings randomly sampled from three old Oxide Treatment Plant (OTP) and Sulphide Treatment Plant (STP) tailings material at Sansu as shown in Table 2 indicates arsenic in very fine is likely to be mobilized without further comminution of the tails. The estimated date of deposition of the tailings material is between 1995 and 2005. Figures 22 and Figure 23 shows particle size distribution of the tails samples from OTP and STP respectively. The high grade of the tails explains the frequent disturbance of the tails by illegal miners.

Table II: Gold, Sulphur and Arsenic Concentration of OTP and STP Tailings Material

Sample Code	Au (ppm)	S (%)	As(%)
OTP 01	1.21	0.11	0.12
OTP 02	0.41	0.08	0.09
OTP 03	0.53	0.17	0.07
STP 01	1.24	0.35	0.36
STP 02	1.99	0.52	1.42
STP 03	1.33	0.41	0.87



Figure 22: Particle Size Distribution and Corresponding Au, S and As of OTP Tailings



Figure 23: Particle Size Distribution and Corresponding Au, S and As of STP Tails

Arsenic Content and Acid Base Accounting of STP and OTP Tails: Acid generating potential of the OTP and STP tailings deposit will generally be influenced by the concentration of sulphides and calcerous minerals present. The sulphides generate the acid whiles the calcerous minerals neutralize its effect, with the balance between the neutralizing potential (NP) and the acid generating potential (AP) predicting the potential for Acid Mine Drainage (AMD). Table 4 shows the acid mine drainage potential of the tailings material. AMD will occur when reactivity of the material is below 3 [23]. This suggests likelihood of tails of the OTP to oxidise and mobilize arsenic. However, given the closeness of the reactivity of the STP to 3 it is also very likely to generate acid and mobilize arsenic.

Parameter	STP Tailings	OTP Tailings
As (ppm)	11000	1352
Percentage Sulphur	0.42	0.15
Acid Production (AP)	15.12	3.51
Neutralization Potential (NP)	48.13	0.23
Reactivity (R) = NP/AP	3.18	0.07

Table III: AMD Potential of Old OTP and STP Tailings

IV.CONCLUSION

Photo-micrographic study indicates geologic features of arsenic source minerals such as pyrite, arsenopyrite in different states of oxidation. Other minerals present were pyrrhotite, chalcopyrite, sphalerite, stibnite and galena. It suggests significant potential for acid-mine drainage in the study area. Majority of gangue minerals contain acidbuffering or carbonate-bearing rocks/alterations relevant to control the AMD effect they generate whilst others do not and will therefore rely on the acid-buffering effect of the surface water or groundwater constituents. Surface water and groundwater in close proximity to the identified arsenic storage structures were also sampled and the liquid and solid phases analysed for total arsenic, readily mobile (oxalate extractable) arsenic and tracer element by AAS analysis. An area with the highest arsenic value of 74 mg/kg in soil was an old Arsenic Trioxide Storage Area which is over ten-fold higher than the world arsenic soil average of 5-6 mg/kg, suggesting possible spillage of arsenic-trioxide powder during transportation to the burial site. Significant concentration of arsenic in filtration residue of water from the study area confirms the need for efficient filtration of all water before drinking or for cooking. Strong positive correlation between concentrations of iron and arsenic in surface water and some groundwater filtrates and those in the filtration residue and soils suggests that the dissolved iron and arsenic in the water is linked to the surface water sediments and soils of the immediate environment and can aid demobilization of arsenic There is further indication that other elements such as Al and Mn can aid the demobilization of arsenic in the study area. Arsenic and trace element analysis of tailings dams and tailings footprints around surface water and groundwater suggests that the oxidation of arsenic rich minerals reduces as you move away from the water sources and underscores the importance of water to the oxidation and mobility of arsenic in the study area. There is indication that trace metals and arsenic could be transported through flooding and normal rain events as well as wind erosion of the uncapped tails and exposed arsenic storage structures during storms events. Acid base accounting of tailings material from Anglogold Ashanti Obuasi Mine Oxide Treatment Plant (OTP) and Sulphide Treatment Plant (STP) confirms the likelihood of acid mine drainage from the tails of the OTP. However, given the closeness of the reactivity of STP to 3, it is very likely to generate acid and mobilize arsenic. The study did not address in detail the micro-dynamics of the host rock/soil, deposited tails, old tailings footprints, old heap leach, old arsenictrioxide storage, waste rocks and processing plant spills/leakages and its possible downstream impacts on naturally weathering mineral deposits and galamsey activity in surface water and groundwater of the study area. With a better understanding of the dynamics in the geology of tailings dams, tails from artisanal mining, and other waste mineral deposits and their interactions with already mixed surface water, mixed groundwater, relatively unpolluted water, storm water etc. it is possible to assess the influence of biological factors for development of constraints for mobility of arsenic and its species in the study area.

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