Patterns for Arsenate and Trace Element Relationships in Surface Water and Groundwater of Obuasi Municipality of Ghana

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Abstract: Obuasi Municipality is a historic gold mining tropical community that has a massive cocktail of old and active anthropogenic arsenic and trace metal storage structures and activities. Given the potential health impact of elevated arsenic and trace metals in surface and ground water of Obuasi Municipality, it is necessary to assess the distribution and possible link between arsenic and trace metals found in surface water and ground water of the study area. Arsenic is predominant as arsenate in the Obuasi Municipality. In response to this need, the study used statistical and geochemical analytical tools to identify patterns of relationships between arsenate distributions and trace metals in surface water and groundwater of the study area.

Keywords: Arsenic, Arsenate, Trace Metals, Obuasi, Ghana, Surface Water, Groundwater

1. Introduction

Obuasi Municipality is located in the western part of the main Ashanti-Prestea gold belt mineralization and lies in the southern part of Ashanti Region of Ghana. The study area has a long history of artisanal mining predating large scale mining. Artisanal mining was recorded in the area as early as 1471[1, 2, 3, 9]. Currently, active artisanal mining is intense, but conducted by illegal miners, since almost the entire area is covered by the concession of Anglogold Ashanti Limited, Obuasi Mine [1, 9]. Arsenic which is often associated with gold in the study area occurs predominantly as arsenopyrite and as a trace element in the pyrite, pyrrhotite, bournonite, tetrahedrite, sphalerite and aurostibnite [4, 9]. The gold particles are generally fine-grained but some are visible to the naked eye [4]. Gold sulfide ores occur as disseminated assemblage of arsenopyrite, pyrite, pyrrhotite with minor chalcopyrite, stibnite, sphalerite and galena in metasediments and metavolcanics in which carbonate and sericite are the prominent alteration minerals [4,5]. Important gangue minerals in the study area are quartz, carbonate, chlorite, and sericite, along with carbonaceous matter [4,5]. Generally, the finer arsenopyrite grains are found to contain high gold concentrations occurring as sub-microscopic gold particles, and supergene concentration of gold from the sulfides extends from depth of between 30 m to 80 m [2]. Ore deposits of the study area occur in a major shear zone with a proven lateral extent of 8km and depth of 1600m (Amanor and Gyapong, 1988). Figure 1 shows a geological map of the study area.

Previous mining operations in the Obuasi Municipality has left behind open mined out pits which are filled with water serving as habitat for fishes and other aquatic organisms. Liquid discharges at AGA from the past to present which are likely to contribute to release of arsenic and other trace metals into surface and ground water are effluent from the processing plants, seepages and discharges from tailings dams, run-off pits and exploration activities. AGA has operated the Sulphide Treatment Plant (STP), Tailings Treatment Plant (TTP) commissioned in 1988, Oxide Treatment Plant (OTP), Pompora Treatment Plant (PTP) commissioned in 1947, and the Heap Leach Plant (HLP) commissioned in 1990. Liquid effluent from STP which includes precipitated arsenic as ferric arsenate, sulphur as calcium sulphate, metals as insoluble hydroxides and flotation tails CIL residue from the BIOX leach process is pumped to the Sansu Tailings Dam (STD). The TTP tailings network of AGA, include the Pompora Tailings Dam, Kokoteasua East Dam and the Sansu Tailings Dam. Seepages from finger drains and run-offs from the Pompora Dam area flow into coffer dams, whereas decant water from the Kokoteasua East Dam flows into the Pompora valley. Decant

from STD reports to a holding pond and is subsequently discharged into the Nyam River. Liquid effluent from the OTP is mainly from CIL residue circuit which is discharged into the STD. Process plant water at the OTP is recycled through the STD. Liquid effluent from the PTP area which include rainfall runoffs, decant water from Kokoteasua East Tailings Dam, Pompora Dam, underground water from North Ramp Mine, excess water from the Pompora sump is discharged into the Kwabrafo stream. The HLP has been decommisioned. There are various pits and waste dumps scattered with most of them concentrated at the central portion of the study area. Most of these pits were backfilled with material that potentially contain gold and arsenic and are likely to release arsenic when rehabilitation delays or the rehabilitated area is further disturbed. Arsenic occurs as a major constituent in more than 200 minerals, including elemental arsenic, arsenides, sulphides, oxides, arsenates and arsenites [17]. Most are ore minerals or their alteration products. However, these minerals are relatively rare in the natural environment [11, 17]. The greatest concentrations of these minerals occur in mineralised areas and are found in close association with the transition metals as well as Cd, Pb, Ag, Au, Sb, P, W and Mo [6, 13, 17]. Arsenic is found primarily in the earth's crust with natural concentrations ranging between 0.1 to 40.0 mg/kg and average concentrations from 1.5 to 5.0 mg/kg and is released naturally through volcanic, forest fires and geothermal, activities [14, 20]. It is also found naturally in rocks, soils, sediments, water and biota around the surface of the earth [12]. Arsenic is often associated with iron and manganese in some sedimentary and igneous rocks [12, 18,19]. Relevant and common arsenic containing minerals are arsenopyrite (FeAsS), realgar (AsS), and orpiment (As_2S_3). In the Obuasi Municipality, arsenic has been found to be associated with Ferrisymplesite ($Fe_3(AsO_4)_2.6H_2O$), Symplesite ($Fe_3(AsO_4)_2.8H_2O$), Liskerdite ($AlFe)_3AsO_4(OH)_6.5H_2O$ and Arseniosiderite ($Ca_3Fe_4(AsO4)_3(OH)_8$ [4]. Arsenic and trace metals may be released naturally to ground water or surface water through weathering, erosion and dissolution. Release of arsenic into the environment often results in significant environmental consequences [7, 9, 10, 11] as it is released along with other toxic metals. Table 1 shows a list of common minerals that contain arsenic. Arsenic has been observed to be prevalent in the Obuasi Municipality [1, 4, 15, 17]. Currently no pattern has been established as a relationship between arsenate and trace metals in surface or groundwater of the Obuasi Municipality. This study seeks to identify any available pattern for management decisions.
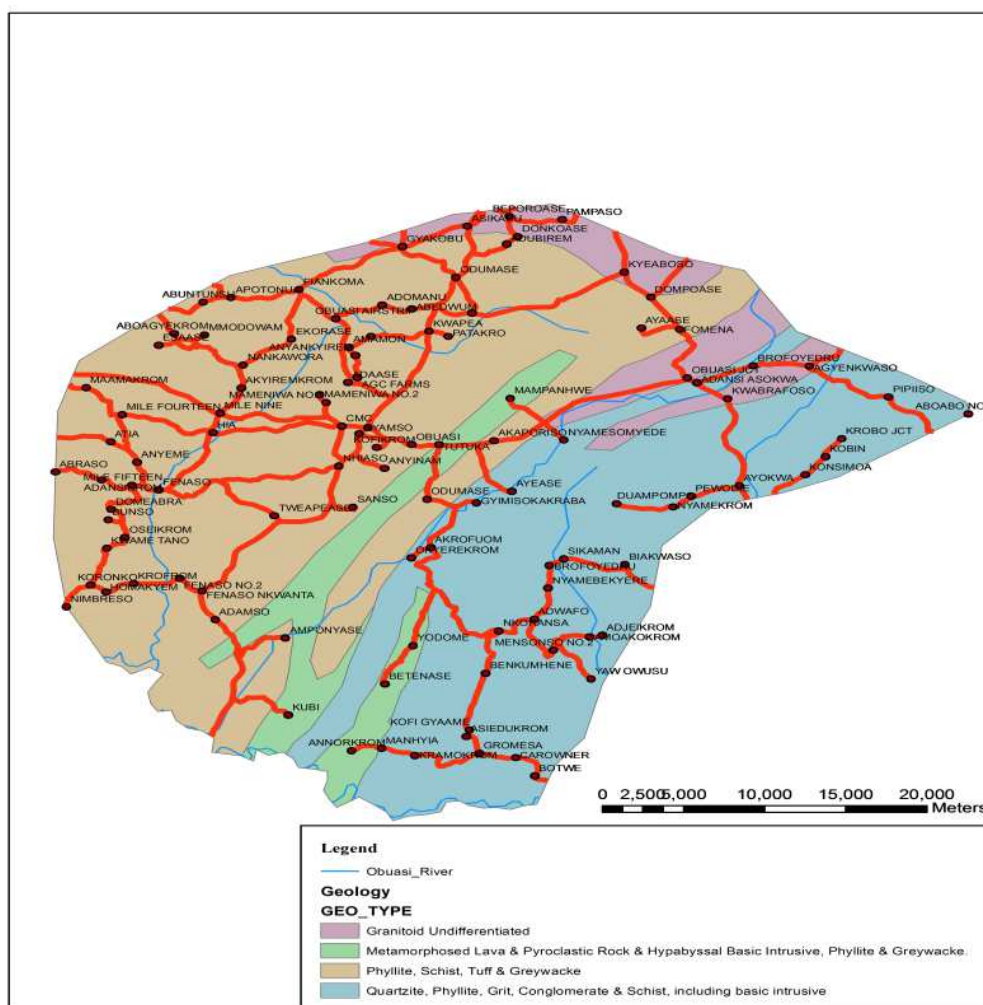

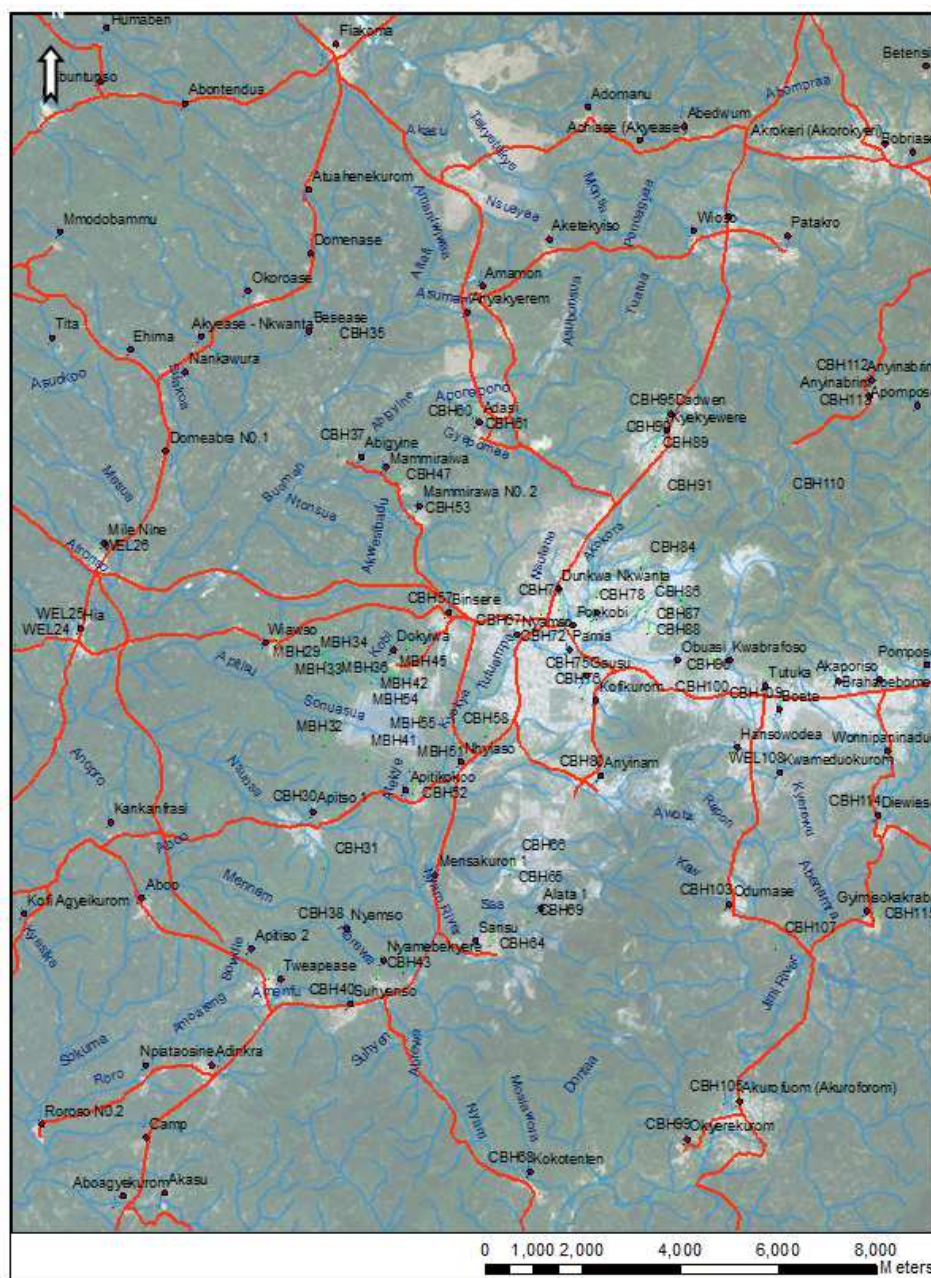*Figure 1. Geological Map of Obuasi Municipality (Source: Extracted from Geological Map of Ghana).*

Table 1. *Common Minerals of Arsenic.*

Name	Chemical Formula
Arsenopyrite	$FeAsS$
Smalite	$CoAs_2$
Lollingite,	$FeAs_2$
Cobaltite	$CoAsS$
Orpiment	As_2S_3
Gersdorffite	$NiAsS$
Realgar	As_4S_4
Tennantite	$4Cu_2SAs_2SiS_3$
Chloanthite	$NiAs_2$
Proustite	$3Ag_2SAs_2S_3$
Niciolite	$NiAs$
Enargite	$3Cu_2SAs_2S_5$

[Source: Ferguson, 1990]

2. Materials and Methods

Water Sampling: In total, 230 surface water samples were collected from 25 river sampling points, 160 stream sampling points and 45 ponds. As well, 142 ground water samples were collected from 108 community boreholes, 18 monitoring boreholes, 11 hand-dug wells and 5 mechanised borehole systems in 96 settlements in the study area (Figure 2).

Figure 2. *Surface and Groudwater Sampling Points on Surface Water Map Superimposed on Rapid Eye Satellite Image of Obuasi Municipality.*

The groundwater and surface water samples were transported in ice chests with ice packs stored at approximately 4°C and analyzed at the Societe General Surveillance (SGS) MASLAB Environmental Laboratory in Ghana. Samples which were analysed for heavy and base metals were preserved with 5ml of ultrapure grade concentrated HCl acid in the laboratory. All samples collected for arsenic analysis were preserved using ultrapure grade HCl acid. Approximately 90 µl of acid was added per 60 ml sample that resulted in a pH slightly below 2.0. A Varian SpectrAA 55 atomic absorption spectrometer with a Varian Vapor Generating Accessory (VGA) 77 was used for analyzing the samples for dissolved arsenic. The instrument was calibrated using freshly prepared arsenic standards (2, 5, 10, 20, 30 µg/L) with a 0.1% HCl acid concentration. Agilent Spectra AA55 Atomic Absorption Spectrophotometer (AAS) was used to analyse metals whiles the Agilent VGA 77 Vapour Generating Accessories along with the Agilent Spectra AA 55 was used for analysis of total As. The Agilent VGA 77 unit was operated with 99.99% Argon in a dust-free environment at the required pressure range of 300 to 400 kPa (43 to 57 psi) and normal flow rate of 100 mL/minute. For quality assessment/quality control standards including NIST Standard Reference materials and a dionised water (as a reference sample blank) were analyzed together with the water samples. Data quality was assessed using charge balance calculations, replicate samples and sample blanks. Charge balance errors are typically <5%. Replicate arsenic analysis samples and standards showed a precision within 5%. Blank assays were found to be negligible. The limit of detection for As(III) and total arsenic with the VGA/AAS technique is 0.001 mg/l with an error of ± 70% at the 95% confidence interval. Concentrations between 0.001 and 0.010 mg/l have an error of ± 25% at the 95% confidence interval. Concentrations between 0.010 and 0.050 mg/l have an error of ± 7% at the 95% confidence interval, and concentrations greater than 0.050 mg/l have an error of ± 3% at the 95% confidence interval. Inorganic As(V) was determined by calculating the difference between total inorganic As and As(III). This assumes there is no organic arsenic present in the water.

Table 2. *Arsenic Guiding Standard for Ghana Groundwater and Surface Water.*

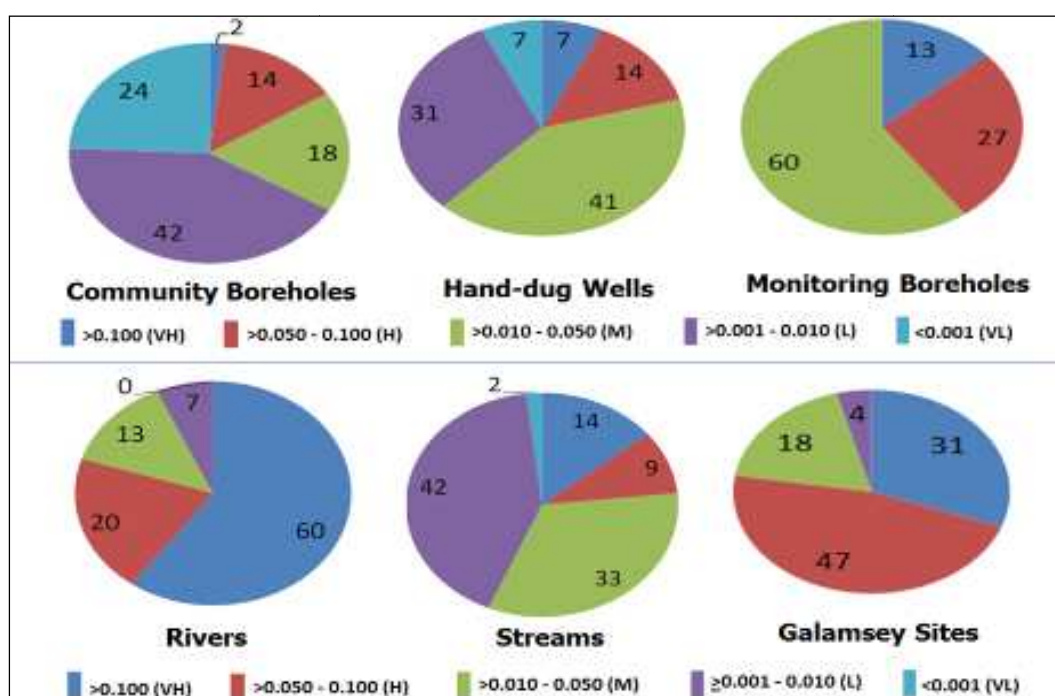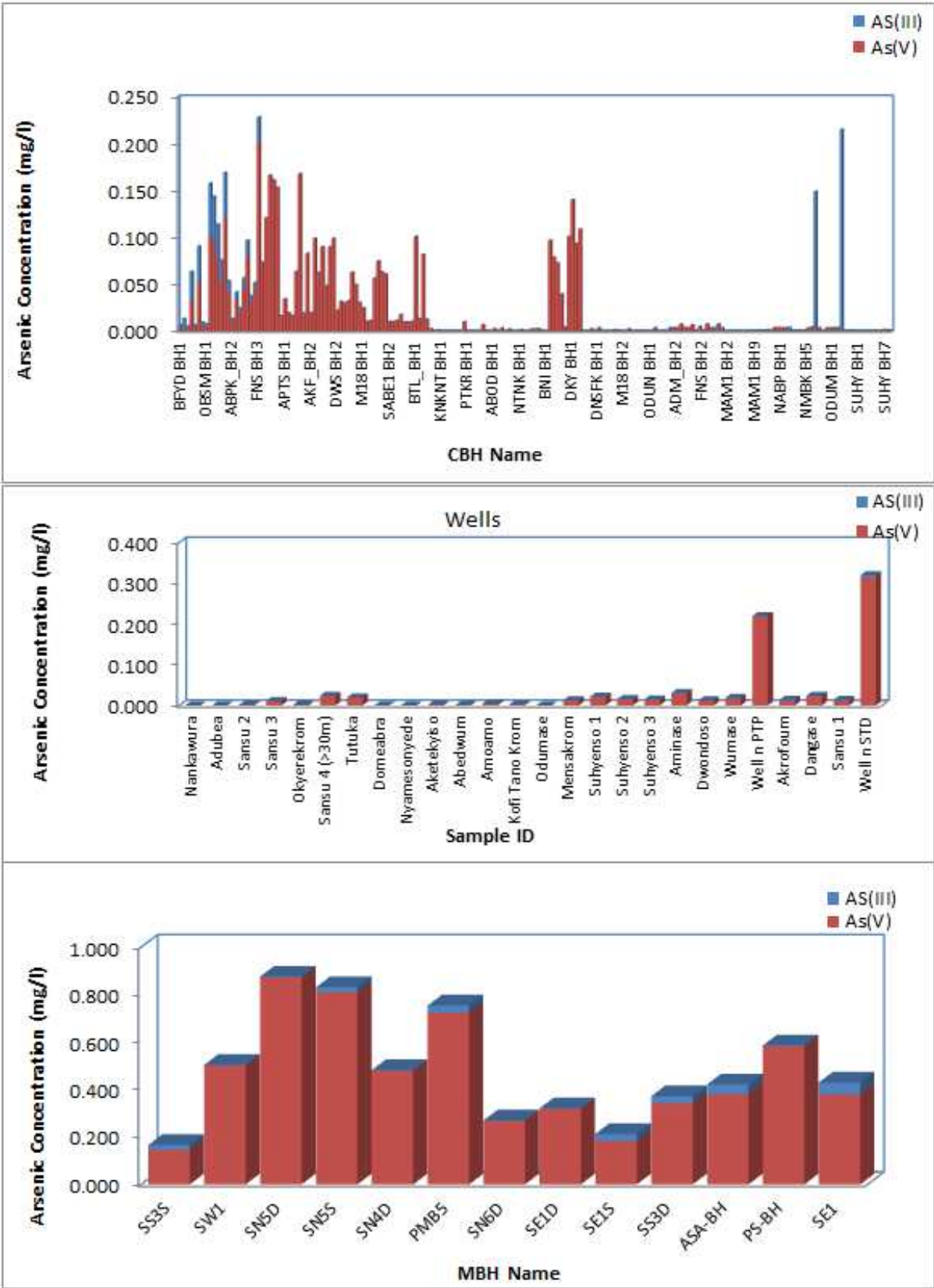| ARSENIC GUIDING STANDARDS		
Guiding Standards	Risk Class	Arsenic Conc. (mg/l)
Greater than EPA Akoben Effluent Limit	Very High	>0.100
Greater than EC Limit to EPA Akoben Limit	High	>0.050 – 0.100
Greater than WHO/GWC Limit to EC Limit	Medium	>0.010 – 0.050
Greater than Detection Limit to WHO Limit	Low	>0.001 – 0.010
Less than or Equal to Detection Limit	Very Low	≤0.001
EPA – Ghana Environmental Protection Agency		
EC – European Commission		
WHO – World Health Organisation		
GWC – Ghana Water Company		

Figure 3. *Percentage Arsenate in Surface Water and Groundwater of Obuasi Municipality (As concentrations in mg/l).*
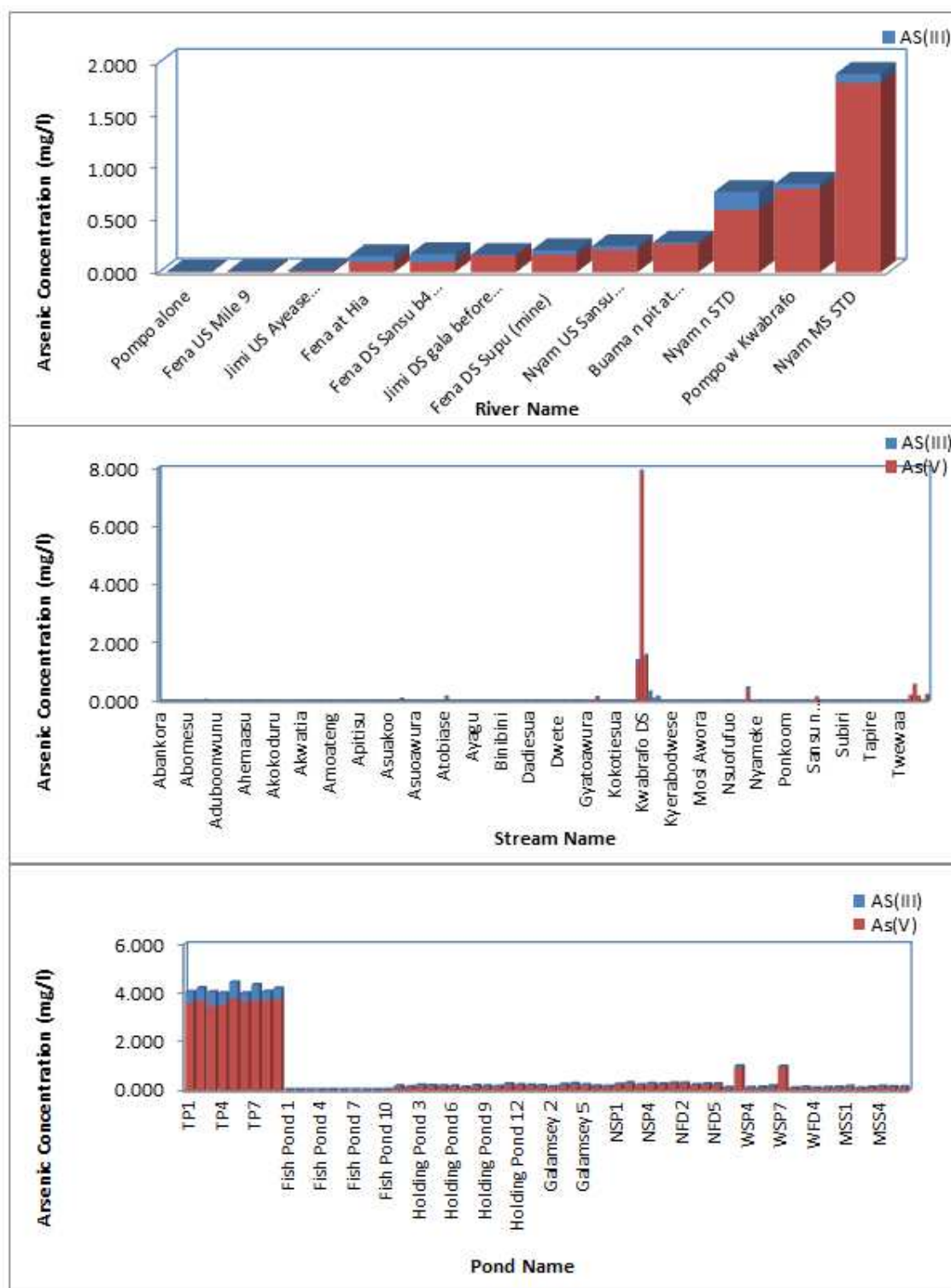
Figure 4. Arsenate Distributions in Surface Water and Groundwater of Obuasi Municipality.

3. Results and Discussion

3.1. Statistical Summary of Arsenic in Surface and Groundwater of Obuasi Municipality

Percentage distribution of arsenate in the study area is shown in Figure 3 whiles arsenate content of surface and groundwater sites is shown in Figure 4. Generally, except for monitoring boreholes which are not used for domestic activity, groundwater (CBH, 66%; Wells, 40%; MBH, 0%) has relatively higher percentage of sampling sites than surface water (streams, 44%; rivers, 7%; and ponds 4%) with arsenate concentration below the WHO standard of 0.010 mg/l) in the study area. It is also observed that except for monitoring

boreholes, groundwater (CBH, 98%; Wells, 93%; MBH, 87%) has relatively higher percentage of sampling sites than surface water (streams, 86%; rivers, 40%; and ponds, 69%) with arsenate concentration below the EU standard of 0.050 mg/l in the study area. Generally, except for monitoring boreholes, groundwater (CBH, 84%; Wells, 81%; and MBH, 60%) has relatively higher percentage of sampling sites than surface water (streams, 77%; rivers, 20%; and ponds, 22%) with arsenate concentration below the EU standard of 0.050 mg/l in the study area.

3.2. Influence of Trace Elements on Arsenate Concentration

To evaluate the distribution of arsenic in the studied water, concentrations of various trace elements including Al, Ag, B, Ba, Be, Ca, Ce, Co, Cr, Cs, Cu, Eu, Dy, Fe, Ga, Gd, Ge, Ho, K, Li, Lu, Mg, Mn, Mo, Na, Nd, Ni, Pb, Pr, Rb, Sb, Sm, Sr, Tb, Tl, Tm, U, Y, Tb, Zn and Zr were determined in selected water samples and statistical analysis performed on the dataset to identify trend in the analytical results. Generally, trace elements such as B, Be, Ce, Co, Cr, Cs, Eu, Dy, Ga, Gd, Ge, Ho, Lu, Mo, Nd, Ni, Pr, Pb, Rb, Sb, Sm, Sr, Tb, Tl, Tm, U, Y, Tb and Zr were not detected in statistically significant quantities for analysis. However, trace elements such as Al, Ba, Cu, Fe, Li, Mn, Sr, and Zn showed varying trends and were used in the analysis to determine their relationship with total arsenic or any of its species. Arsenic appears to show some relationship with Sr and to a lesser extent Ba in both surface and groundwater. The associations between As and Sr in groundwaters of the study area supports the fact that arsenic has been derived from arsenic bearing ore minerals.

3.3. Influence of Trace Elements on Arsenate Concentration in CBH

Three classes of CBH were identified per their trace element relationship with As(V) in the study area as follows (Figure 5):
1. CBH with very low to medium arsenate (0.001 mg/l to 0.010 mg/l) showed positive linear correlation with Fe, Sr, Li, Mn, Zn whilst, Ba, Cu showed negative linear correlation; and
2. CBH with medium to high arsenate (0.010 mg/l to 0.100 mg/l) showed positive linear correlation with Sr and Al whilst, Fe, Ba, Cu, Zn, Li showed negative linear correlation.
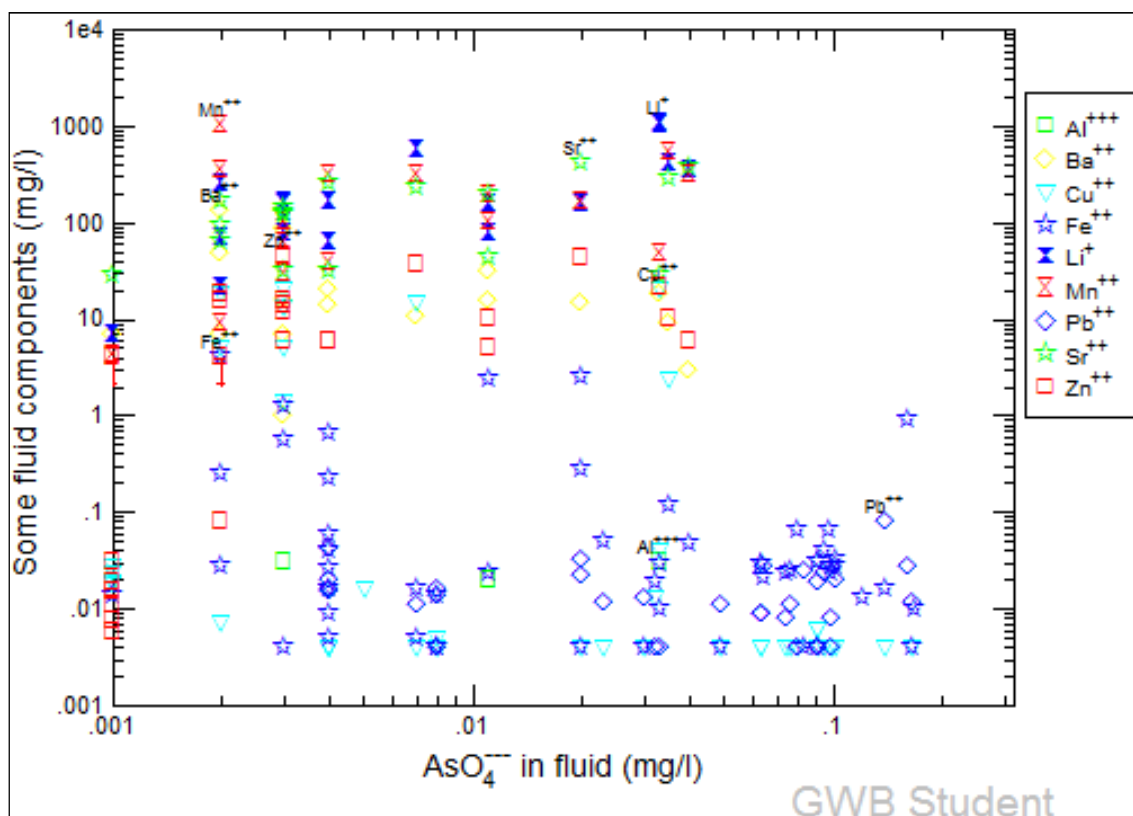

Figure 5. *Log-Log Relationship between As(V) and Trace Elements in CBH.*

3.4. Influence of Trace Elements on Arsenate Concentration in Wells

Two classes of wells were identified per their trace element relationship with As(V) in the study area as follows (Figure 6):
1. Wells with very low to medium arsenate (<0.010 mg/l) showing negative correlation between As(V) and Fe, Zn, Al and positive correlation for Sr, Li, Ba, and Mn; and
2. Wells with medium to very high arsenate (>0.010 mg/l) showing negative correlation between As(V) and Cu, Ni, Sr, Zn, Mn and positive correlation for Fe, Ba, Al.
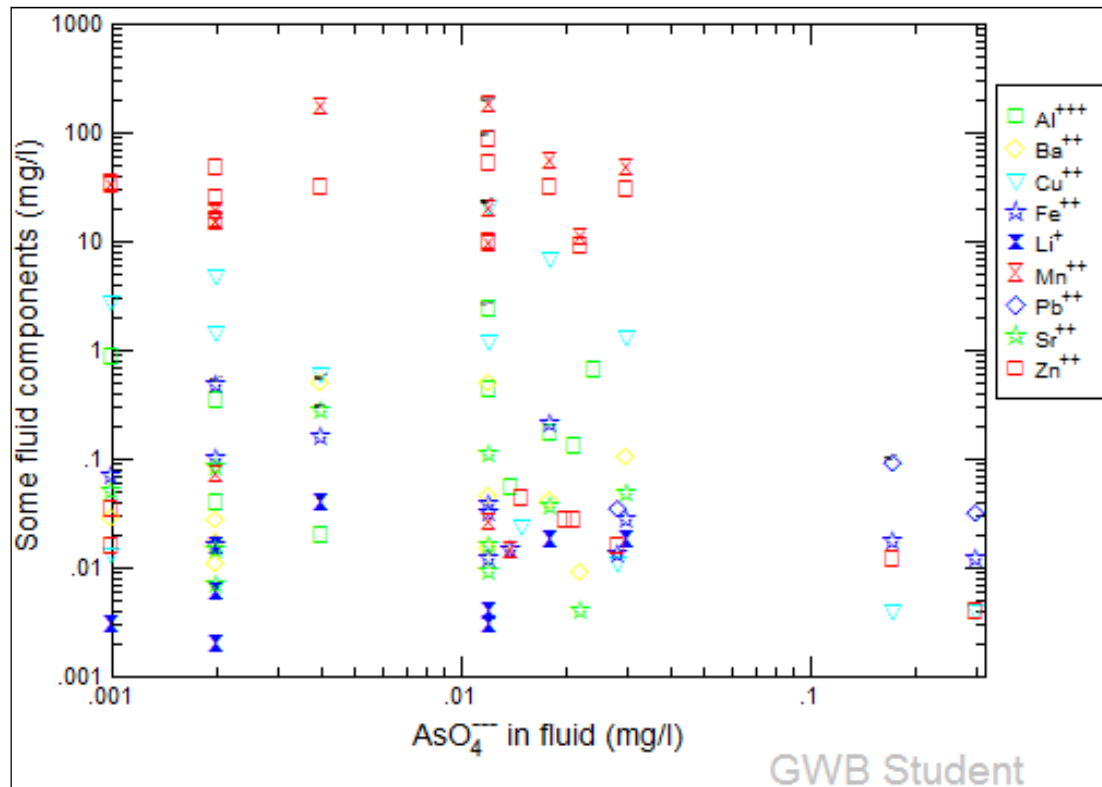
Figure 6. Log-Log Relationship between As(V) and Trace Elements in Wells.

3.5. Influence of Trace Elements on Arsenate Concentration in MBH

Arsenate concentration in MBH showed positive correlation with Cu and negative correlation with Fe, Zn and Mn (Figure 7).
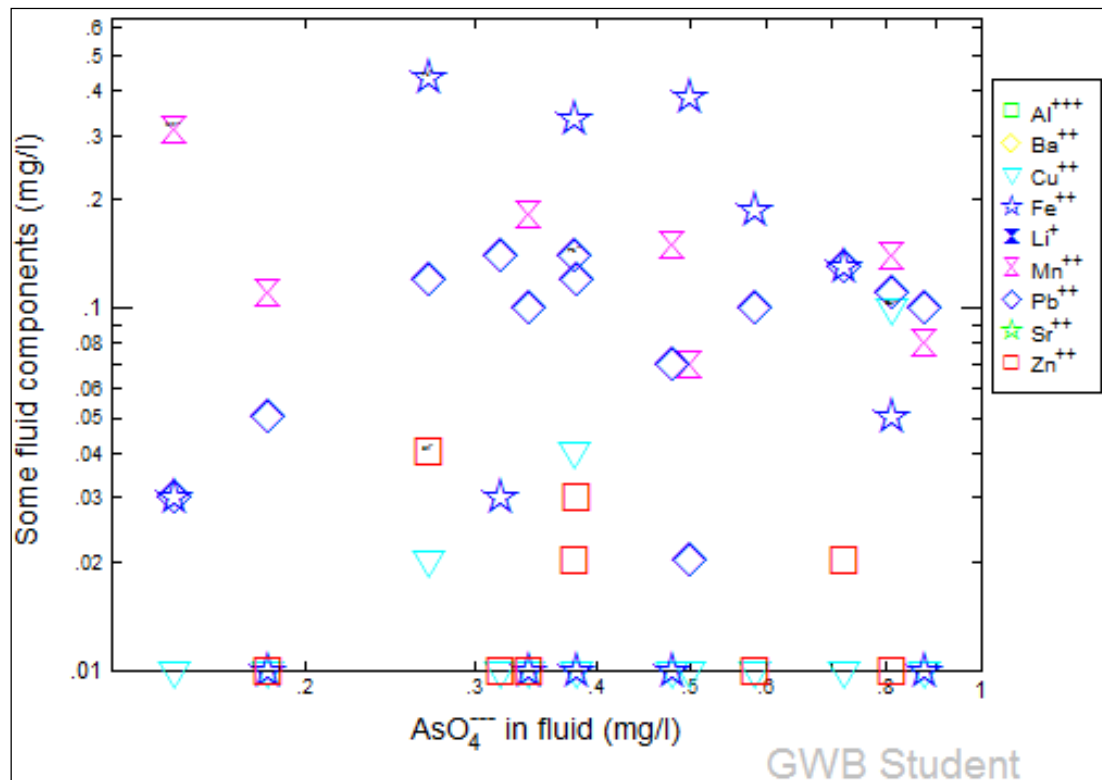

Figure 7. Log-Log Relationship between As(V) and Trace Elements in MBH.

3.6. Influence of Trace Elements on Arsenate Concentration in Streams

Three classes of streams were identified per their trace element relationship with As(V) in the study area as follows (Figure 8):
1. Very Low to low arsenate (0.001 mg/l to 0.010 mg/l): Negative linear correlation between Mn, Cu and positive linear correlation for Fe, Al, Ba, Sr, Li and Zn; and
2. Medium arsenate (0.010 mg/l to >0.050 mg/l): Negative linear correlation between Mn, Cu and positive linear correlation for Sr, Li, Fe, Zn, Ba, and Al.
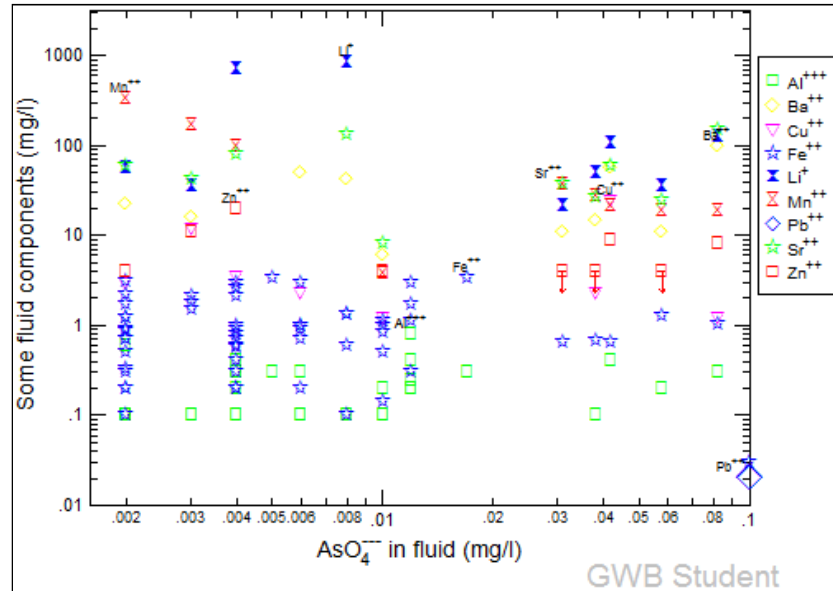

Figure 8. *Log-Log Relationship between As(V) and Trace Elements in Streams.*

3.7. Influence of Trace Elements on Arsenate Concentration in Rivers

Rivers were identified per their trace element relationship with As(V) in the study area as follows (Figure 9):
1. Very low to high arsenate (<0.100 mg/l): negative linear correlation with Sr and Cu; and positive linear correlation with Sr, Mn, Li, Al, Fe, Zn and Ba.
2. Very high arsenate (>0.100 mg/l) negative linear correlation with Zn, Fe and Mn; and positive linear correlation with Al, Cu, Li, Sr and Ba
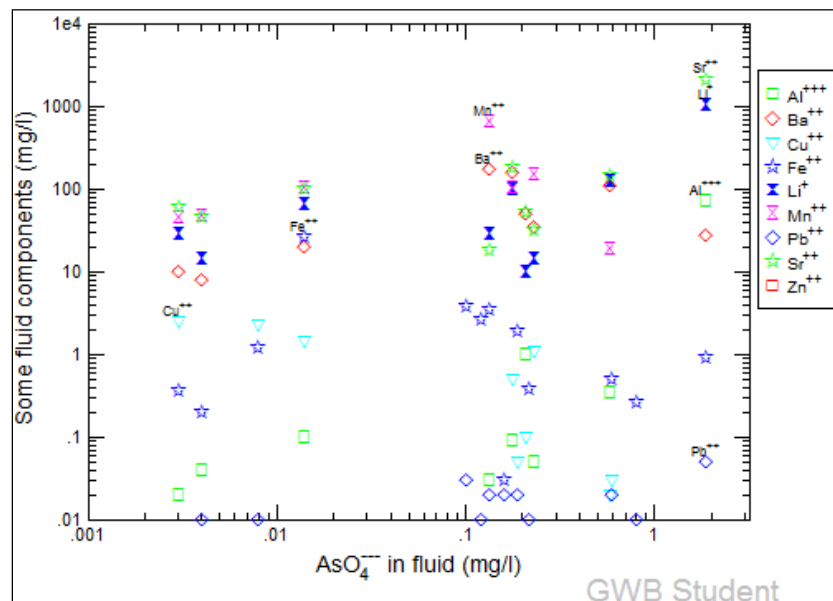

Figure 9. *Log-Log Relationship between As(V) and Trace Elements in Rivers.*

3.8. Influence of Trace Elements on Arsenate Concentration in Ponds

1. No clear trend between As(V) and the trace elements was identified. However, three main clusters were observed on the Semi-log plot of As(V) *vs*. log of selected trace elements (Figure 10).
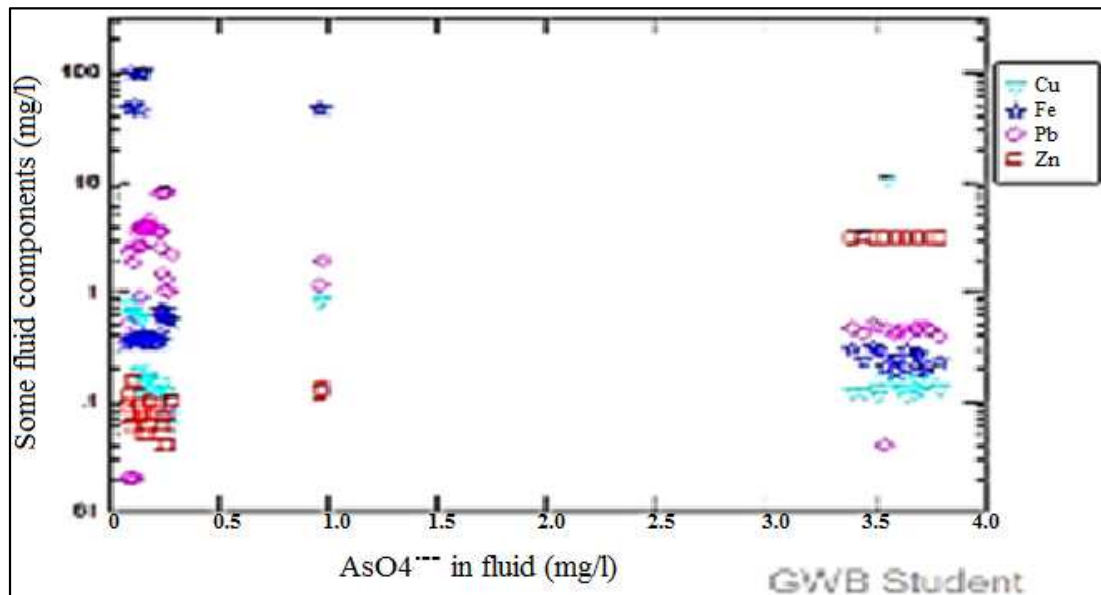

Figure 10. *Semi-Log Relationship between As(V) and Trace Elements in Ponds.*

3.9. Summary of Trace Elements and Arsenate Concentration in Surface and Groundwater

The relationship between arsenate and trace elements in groundwater of the study area can be summarized as follows:

CBH: It was observed that generally for CBH at low to medium As(V) concentration, as As(V) increase Fe, Sr, Li, Mn, Al and Zn increase. The positive trend changes at medium to high As(V) concentration when Fe, Mn and Zn begin to decrease whilst Sr, Li, and Al continue to increase with arsenate increase. Ba and Cu however consistently decrease with arsenate increase.

Wells: Interestingly for wells at low to medium As(V), Sr, Li, Mn, Ba begin to increase whilst Fe, Al and Zn, begin to decrease. As arsenate concentration increases from medium to very high, Fe and Al begin to increase and Cu, Li, Sr, Zn, Mn begin to decrease. Ba however is consistently increasing. The following is a breakdown of the relationship between the individual trace elements and As(V) concentration in groundwater:

1. Cu is constantly reducing in groundwater with increasing As(V);
2. Li and Sr are constantly increasing in wells and constantly decreasing in CBH whilst Ba and Li are constantly increasing in CBH and constantly decreasing in wells;
3. At low arsenate: Fe increase in CBH and decrease in wells, but at high As(V) Fe decrease in CBH and increase in wells;
4. At low As(V): Al decrease in CBH and wells, but at high As(V), Al increase in CBH and wells; and
5. At low As(V): Mn, Zn, Li increase in CBH and wells, but

at high As(V), Mn, Zn, Li decrease in CBH and wells.

Figure 11 presents patterns for As(V) and trace elements relationship in wells and CBHs for the study area.
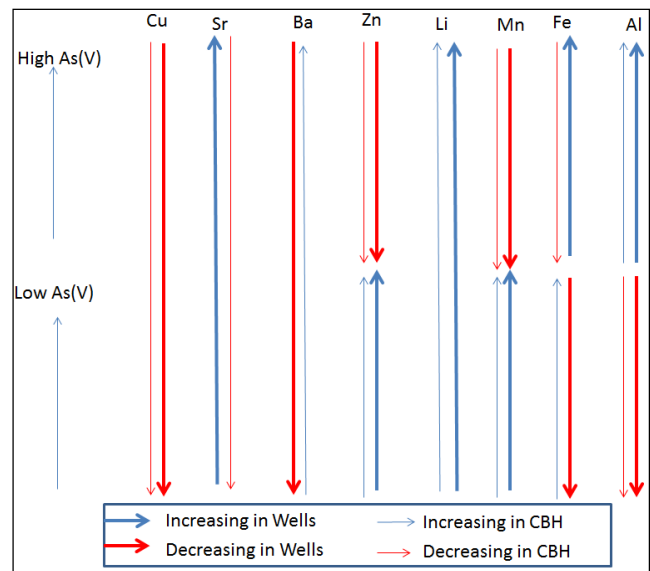

Figure 11. *Patterns of Arsenate and Trace Elements Relationships in Wells and CBHs.*

The generally high concentration of Mn, Cu, Li, Sr, Ba, Zn, Fe and Al in wells and boreholes suggests they are products of dissolution of host minerals occurring together. The relatively low pH of the water and concentration of these trace elements reflect the elements' abundance in the geological units being drained. It can also be observed that as Sr and Li are being leached from the host rock in wells at all concentrations, the

process is reversed with the removal of Ba, and Cu from solution. Likewise, Zn and Mn are leached into solution at low arsenate concentration with the removal of Fe and Al. The process is reversed at high arsenate where Zn and Mn are removed, whilst Fe and Al are leached back into solution. Iron (Fe) and Mn may be released microbiologically and sometimes concurrently by the reductive dissolution of their metal oxides. At the circum-neutral pH of the study area (low arsenate), Mn is much more slowly oxidized than Fe and explains the low Fe and high Mn content of the groundwater. As the redox potential of the groundwater is lowered oxygen and nitrate will be reduced followed by Mn, Fe and SO_4^{2-} at high arsenate concentrations. Repeated redox cycles can increase the concentration of secondary oxides of Fe, Mn and Al in the sediments of the groundwater which can be demobilized later upon agitation, microbial action or temperature changes. This suggest two arsenic mobilization processes are taking place in wells where in one instance there is infiltration from an external source (probably close arsenic storage structures) whilst the second process is leaching of the mineralized host rock. The processes taking place in CBH are similar to that in wells, except that in CBH, Zn, Mn and Fe are leached into solution at low arsenate concentration with a concurrent removal of only Al. The process is also reversed at high arsenate where Zn, Mn and Fe are removed, whilst Al is leached back into solution. It would therefore be misleading to attempt to predict the concentration of arsenic in groundwater on the basis of their Fe contents alone. However, it can be noted that wells (not CBH) with low Fe will tend to have low arsenate concentration. All others cannot be clearly predicted. Even though it is not sufficient to predict the actual concentration of arsenic from the Fe concentration of the groundwater, the presence of high Fe in any well or borehole is a definite indication of high arsenic in groundwater. The relationship between arsenate and trace elements in surface water of the study area can be summarized as follows:

Streams: At very low to low increasing arsenate, Fe, Ba, Sr, Li, Al, Zn increase and Mn, Cu decrease. As arsenate increase to medium Fe, Ba, Sr, Li, Al, Zn continue to increase whilst Cu and Mn consistently decrease.

Rivers: At very low to high increasing As(V), Fe, Al, Zn, Mn, Ba, Sr, and Li begin to increase and Cu begin to decrease till very high arsenate when Al, Cu, Li, Sr increases and Ba, Fe, Mn, Zn begin to decrease. The following is a summary of the relationship between the individual trace elements and As(V) concentration in surface water:

1. Sr, Ba, Li and Al consistently increase in Streams and rivers;
2. Fe and Zn consistently increase in streams, but increase in rivers at low As(V) and decreases at very high As(V);
3. Mn consistently decrease in streams, but increase in rivers at low As(V) and decrease at very high As(V); and
4. Cu consistently decrease in rivers, but decrease in rivers at low As(V) and increase at very high As(V).

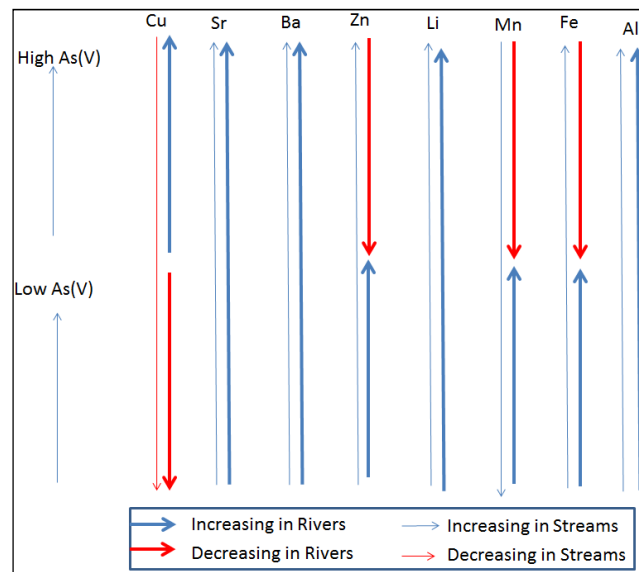Figure 12 presents patterns for As(V) and trace elements relationship in surface water for the study area.

Figure 12. Patterns of Arsenate and Trace Elements Relationships in Streams and Rivers.

The positive correlation between arsenate and Sr, Ba, Li, Al at all concentrations of arsenate suggest that arsenic and these trace elements are likely derived from leaching of the localized mineral [16]. Low pH and high concentrations of Mn, Zn and Fe suggests oxidation of the host minerals is taking place in streams to oxidise pyrite and release SO_4^{2-} and Fe into solution. The oxidation process is likely to mobilise arsenic into streams. The reverse process of reduction is taking place at high arsenate concentrations in rivers where pyrite is being formed with the cementation of zinc and formation of minerals of manganese. The relatively low pH and highly reduced rivers is likely to initiate reduction of As(V) and mobilise As(III) into rivers. Figure 13 shows the relationship between As(III) content and Eh with pH of rivers.
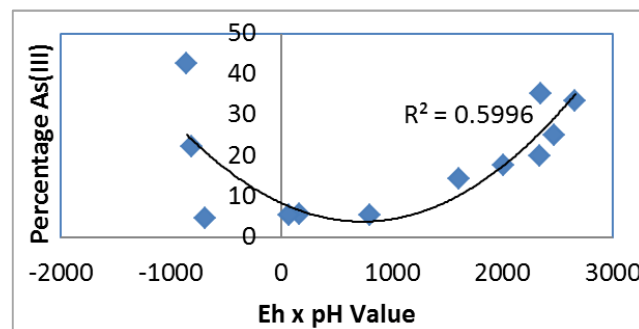

Figure 13. Relationships between Percentage As(III) and Eh x pH of Rivers.

4. Conclusion

The study has confirmed the distribution of arsenate and other trace metals in the Obuasi Municipality and identified patterns between some of the trace metals and arsenate concentration of surface water and groundwater in the study area. In particular metals such as Cu, Sr, Ba, Zn Li, Mn, Fe and Al have been found to have definite patterns with low or high levels of arsenate in the surface and groundwater of the study

area. It is not advisable to attempt to predict the concentration of arsenic in groundwater on the basis of their Fe contents alone. However, it can be noted that wells (not community boreholes) with low Fe will tend to have low arsenate concentration. All others cannot be clearly predicted. Even though it is not sufficient to predict the actual concentration of arsenic from the Fe concentration of the groundwater, the presence of high Fe in any well or borehole is a definite indication of high arsenic in groundwater of Obuasi Municipality.

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