

Seasonal and Temporal Distribution of Arsenic

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Abstract:- In this study seasonal and temporal distribution of arsenic was assessed over a period of one year. During the study water and soil samples were taken from streams, rivers, old and active process ponds, tailings dams, tailings footprints, heap leach sites, arsenic trioxide storage sites, waste rock dumps as well as gold processing plants which treat arsenic ores. The study concluded the temporal distribution of arsenic in surface water follows a linear seasonal trend whereas all year round it generally follows a polynomial trend. It is not advisable to attempt to predict the concentration of arsenic in groundwater on the basis of the Fe contents alone. However, the presence of high Fe is a possible indication of high arsenic in groundwater. It is noted however that wells with low Fe will tend to have low arsenate concentration. There is a temporal nonlinear relationship between As and Fe concentrations which proposes a natural remediation of the polluted water source and indicates how long it may take for the water to revert to a compliant concentration when measures are taken to stop activities that mobilize arsenic. This suggests that if the current anthropogenic activities releasing arsenic is halted and with the appropriate concentration of iron in solution, the surface water may demobilize arsenic back into the host mineralogy. There are seasonal changes in arsenic content of the monitoring boreholes in Arsenic-trioxide Storage Area (ASA) suggesting the mobility of arsenic with infiltrating water as an important transport pathway to groundwater.

I. INTRODUCTION

Obuasi Municipality is a historic gold mining tropical community that has a massive cocktail of old and active liquid and solid arsenic storage facilities (Banson *et al.*, 2016). Small scale and illegal mining has become a significant gold producing activity in almost every community in the Obuasi Municipality (Banson *et al.*, 2018a). Large scale gold mining in the historic Obuasi community begun since 1890 and it has left behind geochemical dispersion from arsenic mineralization which has resulted in arsenic contaminated water, plants and soils at Obuasi (Ahmad and Carboo, 2000). There are massive old and active liquid and solid arsenic storage facilities such as process ponds, tailings dams and tailings footprints, heap leach sites, arsenic trioxide storage sites, waste rock dumps as well as gold processing plants which treat arsenic ores (Banson *et al.*, 2018b). Likewise, in the past there was airborne gaseous dispersion of arsenic through the arsenic dust/fumes that exited from the exhaust stack of the Ashanti Goldfields Ashanti (AGA) Obuasi Mine's sulphide roaster plant (Golowet *et al.*, 2010). The dust and fumes containing arsenic was transported by wind to settle on the soil, humans, and rivers (Golowet *et al.*, 2010). During precipitation or rainfall, the dust "may be oxidized to arsenic

trioxide by oxygen in the air and sulphide oxidized to sulphate in dew and rainwater" (Golowet *et al.*, 2010). The soil is the main target of contamination and so whatever vegetation grows and decays goes right back in the soil which results in the contamination of the groundwater (Banson *et al.*, 2018c). Another source of arsenic pollution at Obuasi is the extensive amount of run-off water that was disposed of through dams (Banson *et al.*, 2016). According to Gish *et al.* (2010), the groundwater is not as polluted as the streams or rivers mainly due to the high dissolving process of the arsenic and due to the basement rocks that lie between the groundwater and the soil (Banson *et al.*, 2018a). Obuasi receives a high annual rainfall due to the tropical rainforest that surrounds it (Smedley, 1996). Therefore, the only disadvantage is that whatever arsenic is deposited on the surface soil may be carried to greater depths with time by rainwater (Gish *et al.*, 2010).

The climate of Obuasi Municipality is semi-equatorial with a double rainfall regime and a mean annual rainfall of 125 mm to 175 mm. In the wet season the study area has mean annual temperature of 25.5 °C and relative humidity between 75% and 80% (Anon., 2010). The study area has undulating topography with hills rising up to about 250 m above sea level (Kesse, 1985). Streams in the study area are seasonal with some drying up in the dry season leaving stream channels with probable seepage or effluent from anthropogenic sources. In the dry season streams with flow rates between 0 and 2,000 m³/hr drain the study area, whereas in the wet season the streams drain the study area faster between 374 and 10,454 m³/h (Foliet *et al.*, 2012). The study area is underlain by Paleo-proterozoic Birimian rocks characterized by rich gold-bearing sulphide and arsenic rich ore deposits (Kesse, 1985). This has attracted mining operations which has been going on in the area since the 1890s (Anon., 2006) and has the potential to release arsenic into surface and groundwater. Both company and illegal mining activities are the potential source of arsenic release in the study area. There are approximately 57 communities in the study area with an estimated total population of 170,000 (Anon., 2010 and Anon., 2012a). There are approximately equal percentages of males and females (Anon., 2010; and Anon 2012a). At the study area, there are surface water (streams, rivers and ponds), AGA monitoring boreholes (MBH) and community boreholes (CBH). The streams drain through series of tailings dam sites that posed site-specific local water quality problem sources in the area. The MBH sites are located about 5-200 m from the tailings dams with depths ranging between 30 and 40 m, while the CBH sites are

located about 400–800 m away from tailings dams with depths ranging between 60 and 80m. The Obuasi Municipality is therefore placed in a suitable setting for studying the relation between seasonal and temporal conditions and arsenic distribution in surface and ground water.

II. MATERIALS AND METHODS

The main methods used were field assessment to identify the main arsenic release indicators in the study area. Statistical analysis was conducted on identified arsenic release indicators in the study area. Maples 2018 software was used to determine the root of sixth degree polynomial equations generated from this study.

A. Water and Soil Sampling

Initial sampling was carried out from February 2012 to September 2013. More samples were taken subsequently (October 2013 to November 2014) for specific analyses. Sample locations are shown in Figure 1. Water depth sampler was used for sampling surface water. Groundwater samples from existing monitoring boreholes were taken with bailers after purging where possible. In total, 244 surface water samples were collected from 14 dams, 25 streams, 160 rivers and 45 ponds. As well, 267 groundwater samples were collected from 108 community boreholes, 18 AGA monitoring boreholes, 11 hand-dug wells and 5 mechanized borehole systems in 96 settlements in the study area. A total of 120 grab soil samples were taken at a distance of three metres from the banks of streams and rivers or three metres from the location of a borehole or well.

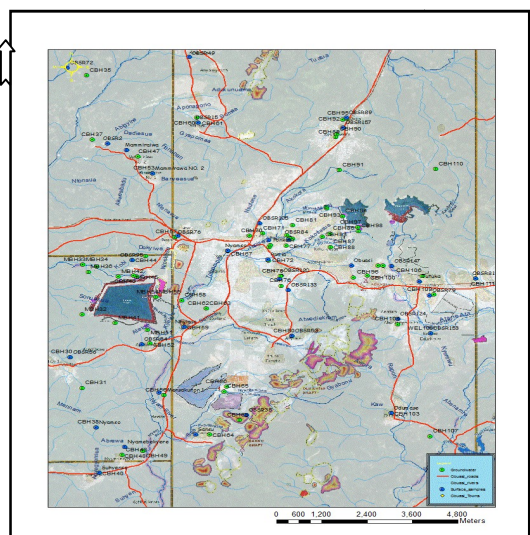


Figure 1: Sampling Locations with Satellite Image at Background

(Source: Modified after Anon., 2010 and Anon., 2012b)

Samples were not taken if they were difficult to access. The soil samples were packaged and sent to the lab for air drying and sieving with a 2 mm mesh to eliminate gravels and other unwanted matter. The soil was further sieved with a 0.5 mm sieve and 0.4 g weighed for ammonium oxalate extraction and

subsequent AAS analysis. Figure 2 shows a summary inventory of surface water sources or discharges in the study area.

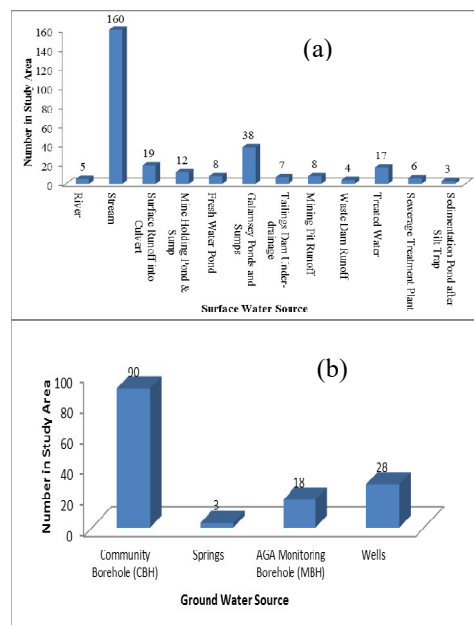


Figure 2: Summary of (a) Surface Water and (b) Groundwater in Study Area

Physico-chemical parameters of some water samples were measured in-situ using a multipurpose (pH, total dissolved solids, electrical conductivity, dissolved oxygen and redox potential meter) Horiba Multi-parameter Water Quality Meter model U-52G. The Horiba meter was calibrated and stored according to the manufacturer’s instructions and cleaned between uses with di-ionized water. Occasionally the probes were physically cleaned with tissue paper. The pH mode has a range of 0 to 14 with a resolution/accuracy/repeatability of 0.01 / ±0.1/ 0.05 pH units. An embedded automated temperature probe with a range of -10° to 55 °C with resolution/accuracy of 0.1 / ±0.2 °C was used to measure the temperature of all water samples. The meter was used to measure Total Dissolved Solids (TDS) with a range of 0 to 100 g/L with resolution of 0.1% F.S, accuracy of ±5 g/L and repeatability of ±2 g/L. Fresh National Institute of Standards and Testing (NIST) pre-mixed buffer solutions of 4.00, 7.01, and 10.01 pH units at 25 °C, accurate to ±0.02 pH units, and TDS solutions of 10 ppm, 100 ppm and 1000 ppm, accurate to ±1% of readings were used for daily pH and conductivity calibrations. It was calibrated daily according to the manufacturer’s instructions.

Some samples were analyzed directly on the field for pH, TDS, Electrical Conductivity and Dissolved Oxygen and Eh, whilst others were sent to the laboratory for analysis. Water samples sent to the laboratory were collected into 250 ml, 500 ml and 1000 ml sample bottle holding rod attached to 250 ml, 500 ml and 1000 ml bottles. Four samples were collected at each site. Water samples were then stored in an ice chest

packed with iced block before transporting to the laboratory. During sampling, water in excess was drained and if necessary a second sample was taken to fill up the container. An Oakton PC 700 Portable pH/mV/ °C Meter MP 125 with a 3-in-1 IP 67 electrode was used to measure pH, Eh and temperature of water samples sent to the laboratory. The pH mode has a range of -2 to 16 with a resolution/accuracy of 0.01/±0.01 pH. The mV mode has a range of ±2000 mV and resolution/accuracy of 1/±2 mV. An embedded automated temperature probe with a range of -5° to 105 °C with resolution/accuracy of 0.1/±0.2 °C was used to measure the temperature of all water samples. The meter was used to measure Total Dissolved Solids (TDS) with a range of 0 to 200 ppt with resolution of 0.01, 0.1 ppm, 0.001, 0.01, 0.1 ppt and accuracy of ±1% reading. Fresh National Institute of Standards and Testing (NIST) pre-mixed buffer solutions of 4.01, 7.00, and 10.01 pH units at 25 °C, accurate to ± 0.02 pH units, were used for daily pH calibrations. It was calibrated daily according to the manufacturer's instructions. Turbidity of the samples was analyzed using a Hach Turbidimeter 2100AN that utilizes a tungsten light source and silicon photodiode operating at a measurement range of 0 to 10,000 NTU and accuracy of ±2% of reading plus 0.01 NTU from 0 to 1000 NTU, ±5% of reading from 1,000 to 4,000 NTU and ±10% of reading from 4,000 to 10,000 NTU. Dissolved oxygen in water samples was measured using an Oakton DO 2700 Portable Meter. The Oakton DO meter has a range 0.0 to 50.00 mg/L. The resolution is 0.01 mg/L with accuracy of ±0.5% of full scale. The meter is temperature compensated with an operating temperature range of 0.0 to 50 °C. It was calibrated according to the manufacturer's instructions daily.

B. Sample Preparation

The laboratory samples were transported in an ice chest with ice packs stored at approximately 4°C and analyzed at the Perseus Mining Environmental Laboratory. Samples collected into 1000ml polypropylene bottles without preservation were used for measurements of pH, turbidity, conductivity, dissolved oxygen and apparent colour without filtration immediately they arrived in the laboratory. Samples collected for cation, anions, arsenic and cyanide analyses were filtered through 0.45 µm, 47 mm diameter filter paper placed in a Cole Parmeralgene vacuum filtration setup within 24 hours of sampling in the Perseus Environmental Laboratory. Samples which were analysed for heavy and base metals were preserved with 5 ml of Analar grade of concentrated HCl after filtration 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 55B atomic absorption spectrometer with a Varian Vapor Generating Accessory (VGA) 77 was used for analysing 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. An external Certified Quality Control Standard from Australian Chemical Reagents (ACR) prepared to an arsenic concentration of 10

ppb in accordance with ISO 17025 recommended procedures used to verify the accuracy of the prepared arsenic standards. In addition, a continuing calibration verification (CCV) standard with an arsenic concentration of 10 ppb, was run after every 10 samples. The mean percent recovery of all CCV standards was less than 5%. The method detection limit, calculated as the standard deviation multiplied by the Students' T value for a 99% confidence level (n=10) with a 1 µg/L standard, was determined to be approximately 0.986 µg/L.

III. RESULTS AND DISCUSSION

A. Temporal Distribution of Arsenic and Iron

Based on preliminary data analysis, follow-up sampling was done at specific locations of high arsenic concentrations in the surface water sites and monitoring boreholes of the Sansu Tailings Dam (STD) in the study area to analyze the time effect on concentration of arsenic and iron as an arsenic indicator. Areas sampled are shown in Table 1. Unfortunately, it was not possible to obtain samples from the western part of the Sansu Tailings Dam. Figure 3 presents a temporal plot of arsenic in the monitoring boreholes after heavy downpour in February 2013 with a possible over flow of some of the finger drains, channels and ponds.

Table 1: Selected Surface Water and Groundwater Monitoring Points in the Obuasi Municipality

Sample ID	Sample Description	Sample Type
NMC	Nyam in the Middle Course	SW – River
NNY	Nyam Near NyameBekyere	SW – River
KUPS	Kwabrafo Upstream	SW – Stream
KAM	Kwabrafo at Amansan Clinic	SW – Stream
SW1	Sansu West 1 at Sansu Tailings Dam	MBH
SW2	Sansu West 2 at Sansu Tailing Dam	MBH
SE1S	Sansu East 1 Shallow at Sansu Tailings Dam	MBH
SE1D	Sansu East 1 Deep at Sansu Tailings Dam	MBH
SS3S	Sansu South 3 Shallow at Sansu Tailings Dam	MBH
SS3D	Sansu South 3 Deep at Sansu Tailings Dam	MBH
SN5S	Sansu North 5 Shallow at Sansu Tailings Dam	MBH
SN5D	Sansu North 5 Deep at Sansu Tailings Dam	MBH

It was observed in Figure 3 that monitoring boreholes in the western part of the STD have relatively higher arsenic concentrations followed by those in the southern, eastern and northern. This proposes leakages or overflow of the STD with subsequent transportation of arsenic by the groundwater current from east to west (Figure 4). Shallow MBH's are also observed to contain more arsenic than deep MBH's.

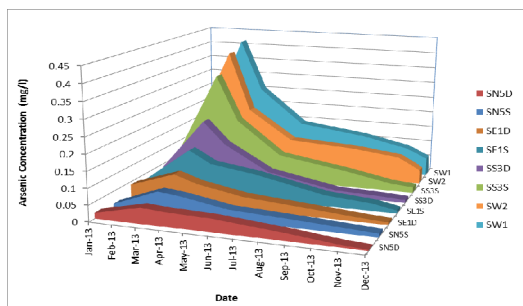


Figure 3: Time Plot of Total Arsenic in Monitoring Boreholes around STD



Figure 4: Satellite Image of STD

(Source: Modified after Anon., 2010 and Anon., 2012b)

Figure 5 to Figure 8 shows a temporal distribution of total arsenic and iron in four surface water sampling points over a period of 12 months in the study area. This period covered both the wet and dry seasons. It was observed that all sampling points have a strong polynomial correlation with R^2 of As distribution ranging from 0.82 to 0.86 and that of Fe distribution ranging from 0.94 to 0.98. The relationship between arsenic and iron distributions was observed to be generally identical with some exhibiting a near-mirror pattern.

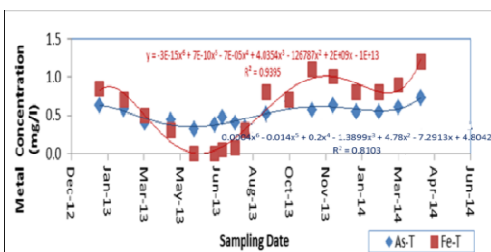


Figure 5: Concentrations of Arsenic and Iron with Time in River Point KAM

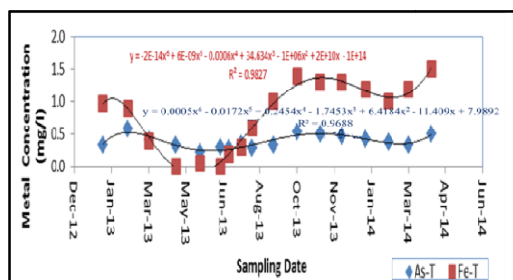


Figure 6: Concentrations of Arsenic and Iron with Time in River Point KUP

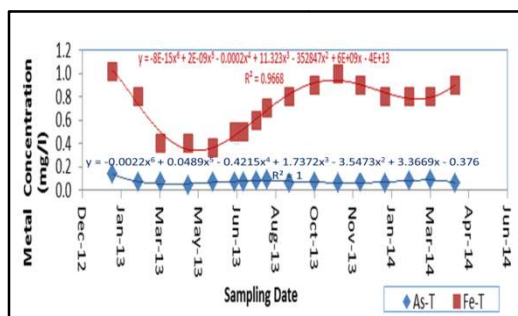


Figure 7: Concentrations of Arsenic and Iron with Time in River Point NMC

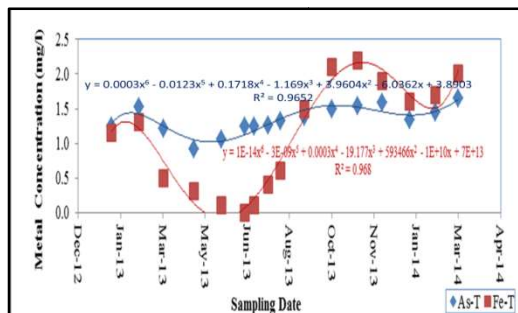


Figure 8: Concentrations of Arsenic and Iron with Time in River Point NNY

The relationship between arsenic concentration and time at specific sample points indicated a polynomial pattern with equations 1 to 4. Where y represents concentration (mg/l) and x represents time (month), the R^2 of each equation and the time frame (months) over which the individual points may have their arsenic concentrations compliant to the WHO arsenic standard of 0.010 mg/l (Anon., 2011) is shown in equations 1 to 4.

Kwabrafo Stream at Amasan Clinic (KAM):

$$y = 0.0004x^6 - 0.014x^5 + 0.2x^4 - 1.3899x^3 + 4.78x^2 - 7.2913x + 4.8042 \quad [1]$$

$R^2 = 0.8103$, [Time (0.010 mg/l): No real time]

Kwabrafo Upstream (KUP):

$$y = 0.0005x^6 - 0.0172x^5 + 0.2454x^4 - 1.7453x^3 + 6.4184x^2 - 11.409x + 7.9892 \quad [2]$$

$R^2 = 0.9688$, [Time (0.010 mg/l): 0.9 months]

Nyam River at the Middle Course (NMC):

$$y = -0.0022x^6 + 0.0489x^5 - 0.4215x^4 + 1.7372x^3 - 3.5473x^2 + 3.3669x - 0.376 \quad [3]$$

$R^2 = 1$, [Time (0.010 mg/l): 4.9 months]

River Nyam near Nyamebekyere (NNY):

$$y = 0.0003x^6 - 0.0123x^5 + 0.1718x^4 - 1.169x^3 + 3.9604x^2 - 6.0362x + 3.8903 \quad [4]$$

$R^2 = 0.9652$, [Time (0.010 mg/l): 21.7 months]

Regression analysis of equation 1 to 4 indicated the R^2 ranged between 0.81 and 1.00 for As and 0.94 to 0.98 for Fe. The

above proposes a temporal nonlinear relationship between As and Fe concentrations. It also proposes the natural remediation of the polluted water source and indicates how long it may take for the water to revert to a compliant concentration when measures are taken to stop activities that mobilize arsenic. It suggests that if the current anthropogenic activities releasing arsenic is halted and with the appropriate concentration of iron in solution, the surface water may demobilize arsenic back into the host mineralogy.

The temporal mirror-like trend in arsenic and iron distribution in the study area suggests natural remediation of the polluted water source and indicates how long it may take for the water to revert to a compliant concentration. It underscores the importance of iron in prediction of arsenic in surface water and suggest that if the current anthropogenic activities releasing arsenic is halted and with the appropriate concentration of iron in solution, the surface water may demobilize arsenic back into the host mineralogy. The decrease in arsenic concentration upstream of mining and galamsey activities could be due to microbial mediation and phytoremediation during the dry season. During the dry season there is considerable decrease in volume of some streams and rivers. Some galamsey operators also divert some of the streams and decrease the volume. This action tends to increase the microbial load on some streams or rivers which might increase microbial reduction, thereby demobilizing arsenic. It also allows some phyto-planktons such as water lilies and hyacinth to remove mobilized arsenic from the water.

B. Seasonal Distribution of Arsenic

It was observed that rivers in close proximity with active mining or galamsey (illegal mining) structures or activities in the study area had relatively high arsenic concentrations in the wet season than in the dry season. Rivers closer to inactive mining structures also had moderate levels of arsenic concentrations. However the arsenic concentration increases as they flow through these structures. River Pompo downstream had total arsenic of 0.786 mg/l in the dry season but increased to 1.212 mg/l in the wet season. The high increase can be due to overflowing and flooding from the Pompora TSF to release effluent and leachate through the Kwabrafo stream which itself passes through old tailings dam footprints and galamsey sites. River Fena upstream of Mile 9 had total arsenic concentration of 0.015 mg/l in the dry season but decreased to 0.012 mg/l in the wet season. River Buaman, upstream of Amamom had arsenic concentration of 0.005 mg/l in the dry season but decreased to 0.003 mg/l in the wet season. Apart from a shallow monitoring borehole (SE1S)at the Sansu East section of the Sansu Tailings Dam (Figure 9)there is lack of seasonal relationship between As and Fe in the MBHs which suggest some chemical reaction is taking place between arsenic and Fe in the water. Figure 10 shows the seasonal variations of selected water quality parameters in MBHs of the study area.

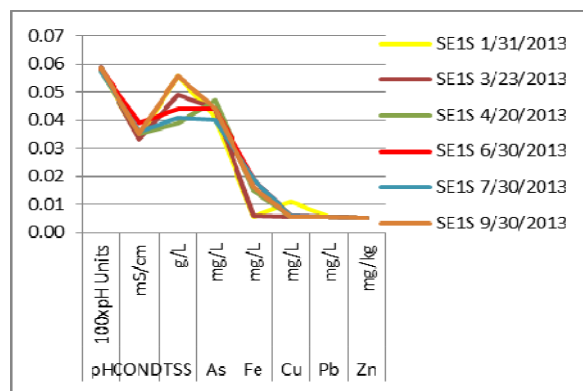


Figure 9: Seasonal Variations of Selected Parameters in MBHs of SE1S around the Sansu Tailings Dam

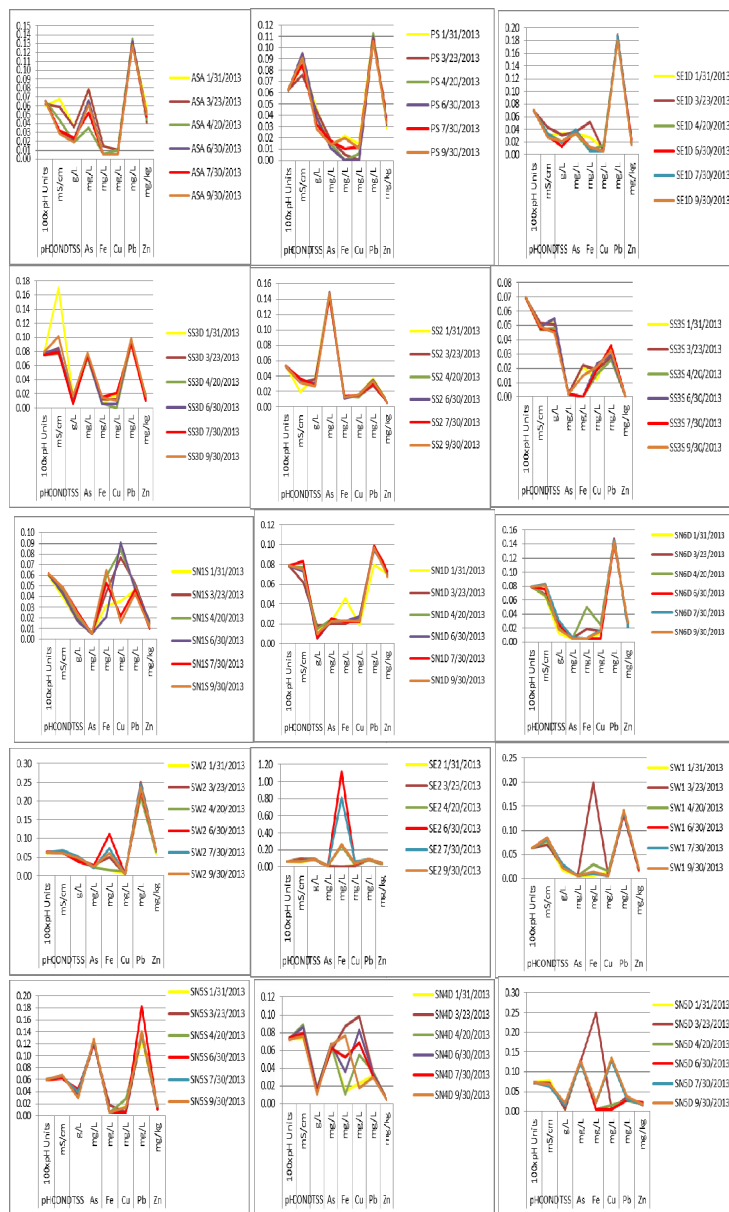


Figure 10: Seasonal Variations of Selected Parameters in MBHs of Obuasi Municipality

There are seasonal changes in arsenic content of the MBH in Arsenic-trioxide Storage Area (ASA) suggesting the mobility of arsenic with infiltrating water as an important transport pathway to groundwater. The seasonal mobility of arsenic in the ASA also indicates a possible break of the liner base of the buried arsenic and subsequent leakage of dissolved arsenic from the buried arsenic trioxide in the area. The overland flow and infiltrating water becomes an important transport pathway during heavy rainfall. The identified seasonal hydro-geochemical trend suggests the transport of dissolved organic and inorganic material from exposed surfaces as a result of road and building construction, galamsey, large scale mining, agriculture and other industrial and domestic activities in the study area may increase bacterial mediated activities that release arsenic from the arsenic-bearing minerals. It is noted that rainfall is a significant contributor to groundwater recharge in the study area and therefore is likely to significantly contribute to the transport of dissolved minerals and arsenic to groundwater resources. Higher temperature in the dry seasons is likely to increase thermodynamic activity on the host mineralogy. Except for MBH which are in close proximity to arsenic storage sources and will receive their arsenic from source, the temperature dynamics of the study area is likely to influence the distribution of arsenic in the order Rivers>Streams>Ponds>CBH>Wells>Springs. In general, the low temperatures suggest quick infiltration and a shallow flow-path. It also negates any possibility of magmatic heating and eliminates magmatic input in the arsenic mobilization process. The temporal distribution of arsenic in surface water follows a linear seasonal trend whereas all year round it generally follows a polynomial trend. Factors contributing to this trend are the seasonal rainfall pattern, the transport of dissolved organic and inorganic material from exposed and oxidized surfaces and the increase of bacterial mediated activities for release of arsenic from the arsenic-bearing minerals and high temperature required for bacterial growth. The dry season is a preparatory step significant for exposure of arsenic-rich minerals to air and increased dissolved oxygen in water for the oxidation of the minerals. Relatively higher temperatures and consequent evaporation during the dry season is likely to influence the oxidation process and increase arsenate in surface water. Mobilization of significant concentrations of arsenic into surface water through floods and storm water therefore commences during the rainy season. The depletion of dissolved oxygen due to flooding is likely to increase anaerobic activity in slow-flowing streams and ponds to mobilize arsenite.

C. Seasonal Hydro-geochemical Analysis of Surface Water and Groundwater

The surface water concentrations (mg/l) of selected ions analyzed in the wet season are Ca^{2+} from 8.23 to 67.11; Mg^{2+} , 3.02 to 51.13; Na^+ , 4.56 to 58.12; K^+ , 8.56 to 32.45; Cl^- , 8.19 to 56.52; SO_4^{2-} , 21.42 to 140.53; HCO_3^- , 11.55 to 382.8; Sr^{2+} , 4.11 to 17.09; and Ba^{2+} , 3.57 to 25.79. Likewise, the concentration of individual ions for surface water in the dry season varied as Ca^{2+} from 8.01 to 59.12; Mg^{2+} , 2.72 to 43.99;

Na^+ , 4.46 to 51.33; K^+ , 6.31 to 28.15; Cl^- , 9.64 to 48.58; SO_4^{2-} , 17.29 to 138.13; HCO_3^- , 13.42 to 363.53; Sr^{2+} , 3.23 to 16.94; and Ba^{2+} , 3.83 to 27.97.

The groundwater concentrations (mg/l) of selected ions analyzed in the dry season are Ca^{2+} from 6.14 to 31.12; Mg^{2+} , 0.89 to 11.32; Na^+ , 3.49 to 39.12; K^+ , 2.02 to 25.32; Cl^- , 7.65 to 54.45; SO_4^{2-} , 11.22 to 147.51; HCO_3^- , 12.98 to 332.53; Sr^{2+} , 4.12 to 18.96; and Ba^{2+} , 4.01 to 18.23. Likewise, the concentration of individual ions for groundwater in the wet season varied as Ca^{2+} from 7.52 to 38.54; Mg^{2+} , 0.97 to 14.21; Na^+ , 4.18 to 48.62; K^+ , 2.78 to 27.85; Cl^- , 9.12 to 65.32; SO_4^{2-} , 13.32 to 158.89; HCO_3^- , 13.79 to 385.81; Sr^{2+} , 4.56 to 19.67; and Ba^{2+} , 4.52 to 19.97. The concentration of Na^+ in the wet season is relatively higher than that of the dry season probably due to weathering of Na-feldspar. The concentration of K^+ in the wet season is relatively higher than that of the dry season probably due to weathering of K-feldspars and clay minerals from aquifer matrix. The concentration of Ca^{2+} in the wet season is relatively higher than that of the dry season probably due to dissolution of $\text{CaMg}(\text{CO}_3)_2$ or CaCO_3 during recharge. The concentration of Mg^{2+} in the wet season is relatively higher than that of the dry season probably due to dissolution of dolomite, gypsum, or magnesium calcite from source rock. The concentration of HCO_3^- in the wet season is relatively higher than that of the dry season probably due to bacterial action on organic matter coupled with action of CO_2 upon the basic material of soil and granitic rock. The concentration of SO_4^{2-} in the wet season is relatively higher than that of the dry season probably due to washing of the oxidized sulphides from the mineral surface. The order of relative abundance of major cations in surface water in the wet season was: Ca^{2+} (41.12%) > Mg^{2+} (24.21%) > K^+ (19.41%) > Na^+ (15.26%) while that of the anions was HCO_3^- (68.21%) > SO_4^{2-} (23.57%) > Cl^- (8.22%). In dry season, the order was: Ca^{2+} (38.41%) > Mg^{2+} (23.98%) > K^+ (21.56%) > Na^+ (16.05%) while that of the anions was HCO_3^- (67.80%) > SO_4^{2-} (22.69%) > Cl^- (9.51%). Likewise, the order of the relative abundance of major cations groundwater in the wet season was: Ca^{2+} (38.56%) > Mg^{2+} (26.91%) > Na^+ (19.12%) > K^+ (15.41%) while that of the anions was HCO_3^- (78.51%) > SO_4^{2-} (15.07%) > Cl^- (6.42%). In dry season, the order was: Ca^{2+} (35.45%) > Mg^{2+} (26.94%) > Na^+ (19.15%) > K^+ (18.46%) while that of the anions was HCO_3^- (72.53%) > SO_4^{2-} (14.06%) > Cl^- (13.41%). The general trend in the chemical composition reflects a low mineralization and mobilization of arsenic in both surface and groundwater in the dry season compared to the wet season. Unlike TDS, pH was observed to be lower in wet season (3.85 to 7.89) than that of dry season (3.93 to 7.99), perhaps because of additional leaching derived from sulphide minerals (acid mine drainage).

The minimum, maximum and mean values of $\text{HCO}_3^- / (\text{Na}^+ + \text{K}^+)$ ratio for dry and wet seasons are presented in Figure 5.64 which shows that generally $\text{HCO}_3^- / (\text{Na}^+ + \text{K}^+)$ ratio is greater than 1 for the wet season generally and less than 1 for the dry season indicating a strong potential for carbonate weathering as the main weathering process controlling the

surface water chemistry in the wet season as opposed to the dry season. The relationship between As concentration and $\text{HCO}_3^-/(\text{Na}^++\text{K}^+)$ ratio indicated a strong positive correlation for both surface and groundwater in both dry season (Figure 11) and wet season (Figure 12).

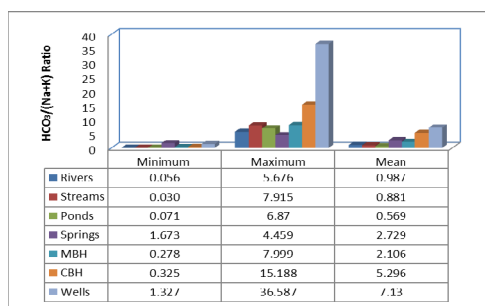


Figure 11: Minimum, Maximum and Mean Values of $\text{HCO}_3^-/(\text{Na}^++\text{K}^+)$ in (a) Dry Season

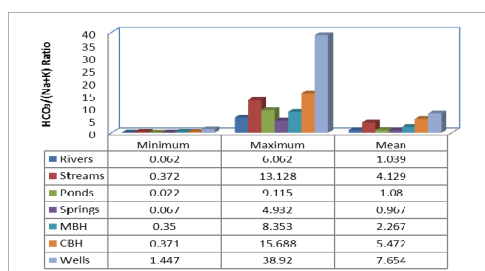


Figure 12: Minimum, Maximum and Mean Values of $\text{HCO}_3^-/(\text{Na}^++\text{K}^+)$ in (a) Dry Season and (b) Wet Season

The above results suggest that the transport of dissolved organic and inorganic material from exposed surfaces as a result of road and building construction, galamsey, large scale mining, agriculture and other industrial and domestic activities in the study area may increase bacterial mediated activities that release arsenic from the arsenic-bearing minerals. It is noted that rainfall is a significant contributor to groundwater recharge in the study area and therefore is likely to significantly contribute to the transport of dissolved minerals and arsenic to groundwater resources.

The TDS values of surface and groundwater in the study area ranged from 156.9 mg/l to 485.5 mg/l with a mean of 137.3 mg/l, and 121.6 mg/l to 489.8 mg/l with a mean of 185.1 mg/l for dry and wet seasons respectively. The higher mean value of TDS of surface water in the wet season suggest enrichment of salt due to lowering of flow rate, thermal action and evaporation (increased rate of reaction) in the dry season followed by subsequent dilution and flushing of dissolved salts up in the interstice or pores of clay and shale with rainwater in the wet season. This process will mobilize more arsenic into the surface water in the wet season compared to the dry season. The higher mean values of TDS of groundwater in the wet season could also be due to similar processes of groundwater drawdown to facilitate lowering of pH and acid drainage with a subsequent rise of the water table to flush the groundwater and release dissolved salt into the

water. This process will mobilize more arsenic into the ground water in the wet season compared to the dry season. TSS in surface water and groundwater was generally low in the dry season compared to the wet season. This can be due to higher infiltration and washing of metals from surfaces of oxides and release un-dissolved particles into the water. It can also be due to agitation from higher flow rate in both the surface water and groundwater. The concentration of Na^+ and K^+ in the wet season is relatively higher than that of the dry season probably due to weathering of K and Na feldspar or clay minerals from the aquifer matrix. The concentration of Ca^{2+} and Mg^{2+} in the wet season is relatively higher than that of the dry season probably due to dissolution of calcite, dolomite, gypsum, or magnesium calcite from the source rock. The concentration of HCO_3^- in the wet season is relatively higher than that of the dry season probably due to bacterial action on organic matter coupled with action of CO_2 upon the basic material of soil and granitic rock. The concentration of SO_4^{2-} in the wet season is relatively higher than that of the dry season probably due to washing of the oxidized sulphides from the mineral surface. The order of relative abundance of major cations and anions in surface water in the wet and dry season was $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$ and $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$ respectively. Likewise the order of relative abundance of major cations and anions in groundwater in the wet and dry seasons was $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ and $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$ respectively. This indicates replacement of Na^+ by K^+ probably as a result of precipitation. In groundwater during the wet season, there was relatively higher Ca^{2+} and lower K^+ as well as relatively higher HCO_3^- and lower Cl^- compared to the dry season. This indicates a stronger potential for carbonate weathering during the wet season as compared to the dry season. The general trend in the chemical composition reflects a low mineralization and mobilization of arsenic in both surface water and groundwater in the dry season compared to the wet season.

There seem to be significant seasonal relationship between TSS and Fe in the MBHs. This suggests infiltration of oxidized material into the borehole. Similarly, the same seasonal relationship seems to exist between Fe, Cu and Pb indicating mobility of metals from the host environment.

It is noted that rainfall is a significant contributor to groundwater recharge in the study area and therefore is likely to significantly contribute to the transport of dissolved minerals and arsenic to groundwater resources (Ewusiet *et al.*, 2013). According to Zhu *et al.* (2009), positive correlation of arsenic and trace metals such as Cu, Pb and Zn is a strong indication that arsenic and these trace ions are possibly derived locally from dissolution of host mineral as a result of water-mineralized rock interaction. If this is the case one would expect significant mobility of arsenic from the MBH unless a process is demobilizing the dissolved arsenic from solution.

There are seasonal changes in arsenic content of the MBH in Arsenic-trioxide Storage Area (ASA) suggesting the mobility of arsenic with infiltrating water as an important transport

pathway to groundwater. The seasonal mobility of arsenic in the ASA also indicates a possible break of the liner base of the buried arsenic and subsequent leakage of dissolved arsenic from the buried arsenic trioxide in the area. The overland flow and infiltrating water becomes an important transport pathway during heavy rainfall. The identified seasonal hydro-geochemical trend suggests the transport of dissolved organic and inorganic material from exposed surfaces as a result of road and building construction, galamsey, large scale mining, agriculture and other industrial and domestic activities in the study area may increase bacterial mediated activities that release arsenic from the arsenic-bearing minerals. It is noted that rainfall is a significant contributor to groundwater recharge in the study area and therefore is likely to significantly contribute to the transport of dissolved minerals and arsenic to groundwater resources. Higher temperature in the dry seasons is likely to increase thermodynamic activity on the host mineralogy. The temporal distribution of arsenic in surface water follows a linear seasonal trend whereas all year round it generally follows a polynomial trend. Factors contributing to this trend are the seasonal rainfall pattern, the transport of dissolved organic and inorganic material from exposed and oxidized surfaces and the increase of bacterial mediated activities for release of arsenic from the arsenic-bearing minerals and high temperature required for bacterial growth. The dry season is a preparatory step significant for exposure of arsenic-rich minerals to air and increased dissolved oxygen in water for the oxidation of the minerals. Relatively higher temperatures and consequent evaporation during the dry season is likely to influence the oxidation process and increase arsenate in surface water. Mobilization of significant concentrations of arsenic into surface water through floods and storm water therefore commences during the rainy season. The depletion of dissolved oxygen due to flooding is likely to increase anaerobic activity in slow-flowing streams and ponds to mobilize arsenite. This can be due to higher infiltration and washing of metals from surfaces of oxides and release un-dissolved particles into the water. It can also be due to agitation from higher flow rate in both the surface water and groundwater.

D. Influence of Water Temperature on Arsenic Concentration

Temperature readings were taken in the surface and ground water resources during the dry and rainy seasons. The temperatures of the surface and groundwater were observed to be generally higher in the dry season (Figure 13) than the wet season (Figure 14). Mean temperatures of the water in the dry season are in the order: Rivers>Streams>Ponds>CBH>MBH>Wells>Springs, whilst that for the wet season is in the order Rivers>Streams>Ponds>MBH>CBH>Wells>Springs. In-situ temperature of some mine water holding ponds in the study area were taken monthly and plotted against their arsenic concentration (Figure 15). There was moderate positive correlation between arsenic concentration and temperature.

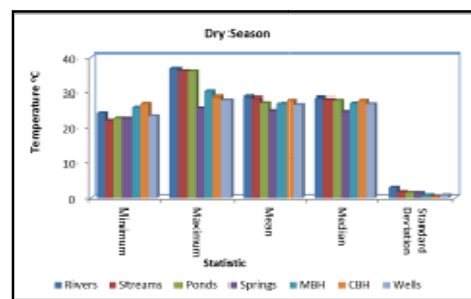


Figure 13: Temperature Statistics of Surface and Groundwater in Dry Season

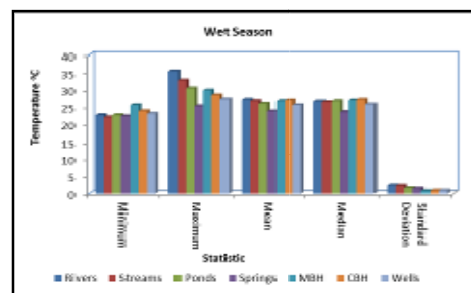


Figure 14: Temperature Statistics of Surface and Groundwater in Wet Season

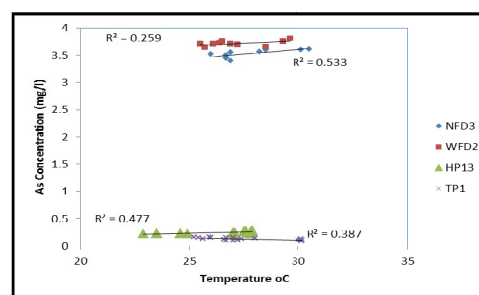


Figure 15: Arsenic Concentrations vs. Temperature in Mine Holding Ponds

IV. CONCLUSION

From the study it is concluded that the temporal distribution of arsenic in surface water follows a linear seasonal trend whereas all year round it generally follows a polynomial trend. It is not advisable to attempt to predict the concentration of arsenic in groundwater on the basis of the Fe contents alone. However, the presence of high Fe is a definite indication of high arsenic in groundwater. It is noted however that wells with low Fe will tend to have low arsenate concentration. There is a possible leakages or overflow of the Sansu Tailings Dam with subsequent transportation of arsenic by the groundwater current from east to west. There is a temporal nonlinear relationship between As and Fe concentrations which proposes a natural remediation of the polluted water source and indicates how long it may take for the water to revert to a compliant concentration when measures are taken to stop activities that mobilize arsenic. This suggests that if the current anthropogenic activities releasing arsenic is halted and with the appropriate concentration of iron in solution, the surface water may demobilize arsenic back into the host mineralogy. There are seasonal changes in arsenic content of the MBH in Arsenic-

trioxide Storage Area (ASA) suggesting the mobility of arsenic with infiltrating water as an important transport pathway to groundwater. The dry season is a preparatory step significant for exposure of arsenic-rich minerals to air and increased dissolved oxygen in water for the oxidation of the minerals.

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