Scientific Research Publishing

Hydrochemistry of Surface and Groundwater in the Vicinity of a Mine Waste Rock Dump: Assessing Impact of Acid Rock Drainage (ARD)

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Abstract

Acid Rock Drainage (ARD) is a well-known problem related to the mining industry due to its hazardous environmental effects. Metal-rich drainage and acid effluent transmitted from mine waste dumps compromise environmental quality of groundwater and surface water systems destroying aquatic life and increasing human health risks. This study was aimed at assessing the acid and metal drainage potential from the Subriso East Rock Dump (SERD) located in the Wassa East district of Ghana on ground and surface water quality in the catchment using a system of monitoring boreholes, reference boreholes and river samples. Water samples were collected from deep and shallow monitoring boreholes and surface water within the immediate environs of the SERD from August 2012 to February 2013 for laboratory and statistical analysis. Parameters analyzed include sulphate, alkalinity, Arsenic (As), Manganese (Mn), Iron (Fe), Zinc (Zn), Copper (Cu), Cadmium (Cd), Mercury (Hg), Aluminum (Al), Silver (Ag) and lead (Pb) and their concentrations compared with Ghana Standards Authority (GSA) GSB (2009) and WHO (2017) standards. Results indicate that surface and groundwater were not impacted by the SERD possibly because there was no generation of acid or metal-loaded effluent from the SERD into the environment. Physicochemical variables between monitoring boreholes did not differ significantly from conditions in the reference boreholes. Similarly, comparison of upstream and downstream river conditions did not yield any statistical significance ($p > 0.05$). Mn and Fe concentrations were above the WHO (2017)/GSB (2009) standards. Heavy

metal concentrations in surface and groundwater were below detection limits except manganese and iron whose concentrations exceeded the recommended guidelines. No significant environmental impacts exist that could be attributed to the waste rock dump and may be as a result of engineering designs and mechanisms which prevent acid generated water from reaching the external environment. Furthermore, the geology of the study area potentially could be slightly inert having the potential to generate ARD under appropriate conditions. Again, the young age of the waste rock dump is a factor that may contribute to ARD generation under appropriate condition. Routine monitoring of groundwater and surface water sources is required to determine future acid generation of the SERD and its environmental impacts. The results of this study will assist decision makers and environmental managers to plan effectively to mitigate future impacts as mining waste rock dumps are known to increase in acid generation potential with age.
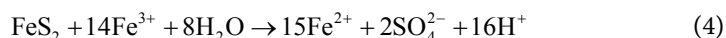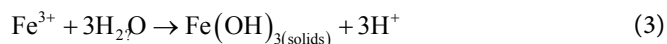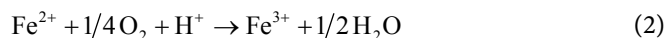
Keywords

Waste Rock Dump, Acid Rock Drainage, Surface Water, Ground Water, Wassa East District, Water Quality

1. Introduction

Acid Rock Drainage (ARD), or otherwise referred to as Acid Metalliferous Drainage (AMD) is a prevalent environmental problem in the mining and extractive industry in developed and developing countries and is associated with numerous active and abandoned mine sites (Ezeigbo & Ezeanyim, 2006, Gaikwad & Gupta, 2008). Acid leachate emanating from mine waste rock dumps and tailings can potentially contaminate groundwater, surface water and soils often with deleterious consequences for ecological systems and even human health (Peppas et al., 2000). According to (Lengke et al., 2010) the appropriate disposition and management of waste rock are a critical function of hard rock mining considering the significant potential that some materials may be acid-generating and hence increasing environmental stewardship within the mining sector. Sources of AMD are varied but generally include tailings deposits, waste rock dumps, surface runoffs from open pit mine, ore stockpiles and seepage from underground workings (Ackcil & Koldas, 2006). However, the greatest contributors to ARD are residue deposits and spoil heaps (Sullivan & Yelton, 1998). Characterized by low pH, high acidity, toxic elements, heavy metals and cyanide content, ARD is detrimental to aquatic habitats and biodiversity, undermines ecological integrity and increases human health risks (Azapagic et al., 2004). ARD is formed through the occurrence of Potentially Acid Generating (PAG) materials containing sulphide minerals in excess of neutralizing minerals which when oxidized in the presence of water and oxygen, produce acidic water that is discharged into the environment (Peppas et al., 2000). Despite the fact that ARD is a natural occurring process, the amount of acidity generated can be aggravated

by mining activities that increase the surface area and exposure of sulphur-bearing rocks to air and also bacteria that breakdown suphide minerals (Jennings et al., 2000). In many instances the occurrence of ARD at operating and decommissioned mines is unavoidable unless the oxidation of waste is prevented (Kuyucak, 2012) which further indicates the important role of oxygen in the acid generating process. ARD typically has low concentrations of toxic heavy metals, high concentrations of iron, aluminium and manganese and low pH which can increase the rate of dissolution of metals that come into contact with the effluent (Galvez-Cloutier & Le Francois, 2005).

A variety of chemical, biological and physical factors whose relative importance differ from various mining sites and from the natural geology and mineralogy of the area may determine the rate of acid generation (Sprynsky et al., 2006). Key ingredients for acid generation include pH, temperature, oxygen content, chemical activity of Fe^{3+}, surface area of exposed metal sulphide, chemical activation energy for acid generation and bacterial activity (Ackcil & Koldas, 2006). The time interval between exposure and peak rate of acid generation of any PAG material may be from days to years depending on environmental factors and the neutralization potential of the rock (Ackcil & Koldas, 2006). Iron sulphides such as pyrites and pyrrhotite have been identified as the predominant precursors responsible for ARD generation (Fox et al., 1997). The oxidation of iron sulphides is a complex set of reactions giving rise to oxidized irons, sulphate anions and a strong acidity as illustrated from Equations (1)-(4) (Pozo-Antonio et al., 2014).

$$FeS_2 + 7/2\,O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \tag{1}$$

$$Fe^{2+} + 1/4\,O_2 + H^+ \rightarrow Fe^{3+} + 1/2\,H_2O \tag{2}$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3(solids)} + 3H^+ \tag{3}$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \tag{4}$$

The process is initiated by the oxidation of sulphide mineral (e.g. Pyrite) to yield dissolved iron, sulphate and acidity. The dissolved products (Fe^{2+}, SO_4^{2-}, H^+) increase the total dissolved solids and acidity of the water. In the presence of sufficient oxygen, "Fe^{2+}", is oxidized to "Fe^{3+}". The rate of this reaction is by the presence of a bacterium called *Acidothiobacillus ferroxidans*. This is the rate determining step of the overall reaction.

The next step involves the hydrolysis of ferric irons to produce iron hydroxide precipitate leaving little ferric iron in solution whilst further decreasing the pH. The iron hydroxide formed is commonly called yellow boy. This reaction is pH dependent and will occur only in the pH range of 2.3 to 3.5. As the acidity increases, the reaction reinitiates because ferric iron remains in solution from Equation (2) and Equation (3) and is reduced by pyrite. Acid generation may be represented by a combination of the above reactions.

ARD formation is dependent on local conditions such as geomorphology, climate and extent of distribution of ARD (Plumlee, 1999) and discharges from

mine-operations are generally determined by mineral and chemical composition of metallic ore deposits and geology (McCarthy, 2011). ARD formation can occur at faster reaction rates and may be difficult to arrest under treatment until the source of pyritic sulphur is exhausted or depleted (Gandy, 2009). Once formed and released, AMD acidifies the environment with its low characteristic pH and high levels of Total Dissolved Solids (TDS), electrical conductivity, concentrations of iron and other toxic and non-toxic metals (Valente & Gomes, 2009). The acidified environment further enhances the mobility and bioavailability of potentially toxic heavy metals (Galvez-Cloutier & Le Francois, 2005).

Waste rock dumps from which ARD potentially emanates are typically composed of porous, highly permeable undersaturated mixture of silt, sand, gravel, cobble and boulder-sized detritus which may interact with perched water tables and manifest as seeps bleeding along the slopes of waste rock piles (Gandy et al., 2009). The physical, geochemical and mineralogical properties of waste rock dumps are determined by the physical configuration, geochemical distribution, temperature and transport of air and water through the waste rock dump (Tran et al., 2003). The period of storage is an important factor determining the potential and viability of mine waste rocks to produce ARD as studies by (Abrosimova et al., 2015) indicated that 26% of rock samples produced acidic effluent following a long-term storage period in the laboratory.

Within a mine establishment are systems for monitoring ARD and effluent transmission through a bouquet of infrastructure consisting of various types of instrumentation to detect discharges and flows into soil, surface and groundwater environments from its operations. These installations are either mounted on embankments to detect rise in water and phreatic levels or downstream to detect potential seepages. Such instruments include boreholes which detect downstream seepage from Tailings Storage Facilities (TSF's) and waste rock dumps. Downstream sumps and secondary confinement channels collect and hold discharge and seepages to measure environmental quality prior to discharge into the external environment. The sitting and location of these monitoring systems are influenced by the hydrogeology and topography of the area influencing surface and groundwater.

Studies dealing with the incidence and environmental effect of ARD in Ghana have been reported in literature. Ankomah-Appiah (2011) found severe deterioration in water quality of underground and surface water from high concentrations of Fe, Cu, Mn, Zn, Cd, Pb and As above Ghana EPA regulatory limits. New techniques of Acid Base Accounting (ABA) have been used to examine the environmental impacts of ARD on the river systems and mining belts (Akabaza et al., 2007; Afriyie-Debrah et al., 2010; Foli et al., 2011). There is however very limited scientific information and understanding of the effect of the Subriso East Waste Rock Dump (SERD) on groundwater and surface water systems in the Wassa East District specifically to communities within and outside of the large mining enclave in Ghana. A large population of local commu-

nities in the large mining district depend on groundwater and surface water resources for their drinking water supply and therefore any contamination of these vital resources could have profound consequences on human health. This study is therefore relevant to ascertain the environmental risk associated with the SERD and to assist decision makers to design effective mitigation plans in anticipation of potential future impacts of the SERD on water resources. The aim of this study was to investigate the potential effect of the SERD on groundwater and surface water systems with a view to identify any indicators of contamination.

2. Materials and Methods

2.1. Study Area

The study was conducted at the Subriso East Rock Waste dump area located in the Hwini-Butre and Benso (HBB) mined out areas (**Figure 1**). Major communities within the catchment include Subriso, Ningo, Akyaakrom, and Awonakrom.
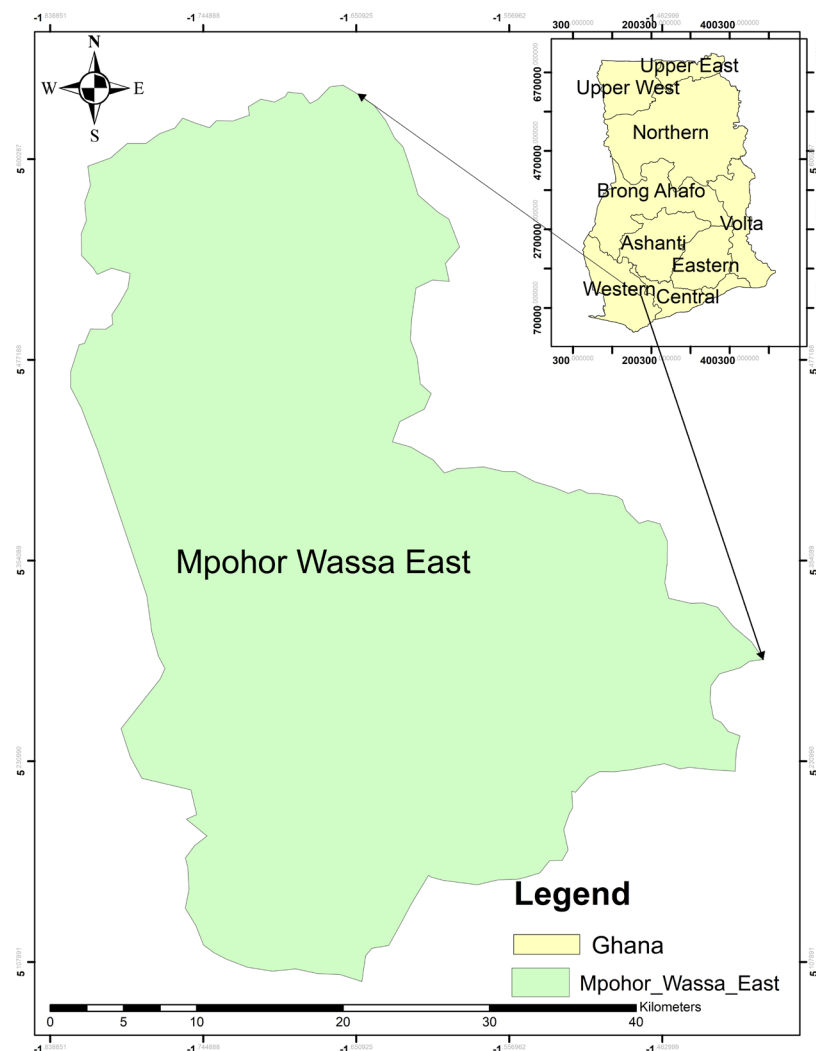

Figure 1. Map of Ghana showing study area.

The HBB area is hosted within mafic intrusive rocks of gabbroic to dioritic composition, which intrude a thick volcano-sedimentary sequence mainly composed of mafic volcanic flows. The geology consists of approximately 10 - 40 saprolite (clayey silt) overlying a meta-volcanic basement rock. Mean annual rainfall is approximately 1874 mm with maximum and minimum values of 1449 mm and 2608 mm, respectively. Topography is quite variable and results from the erosion of extensive peneplain (old weathered) surface with the broad valleys of Hwini and Butre reaching up to 10 m above sea level (ASL) and gradual elevation to the north of about 20 m. The area is drained by the Bonsa River which is connected to two important tributaries, Ben and Subri Tuntum Rivers.

2.2. Sampling

Fifteen water quality parameters were analyzed in water samples collected from August 2012 to February 2013 from boreholes and river monitoring points (Figure 2). A system of monitoring boreholes (MB) made up of four pairs of
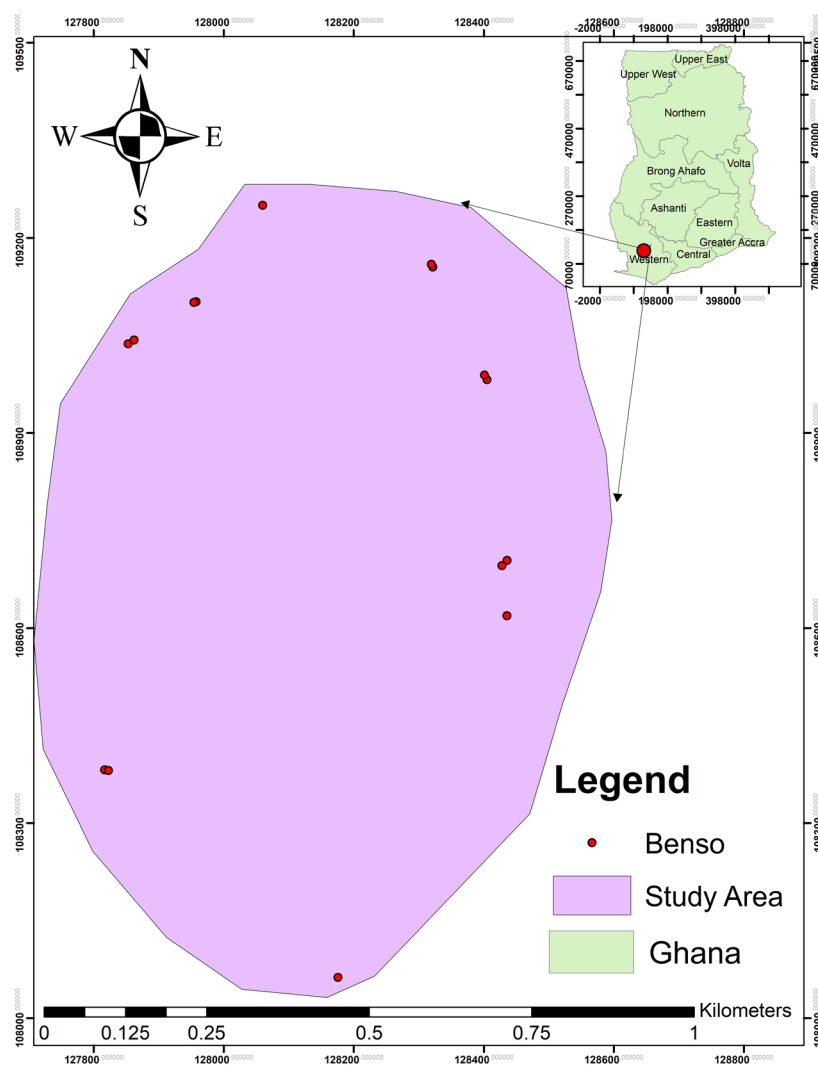

Figure 2. Map of study area showing sampling points.

deep and shallow wells were evenly installed at approximately 500 m around the toe of the Subriso East Rock Dump (SERD). Each pair of twin MB, installed at 1.2 m apart, was 60 m and 30 m deep respectively. Reference boreholes located at 500 m from the SERD were used as control and sampled for the same set of water quality variables. Sampling from the Subri River located 50 m east of the SERD, involved collection of water samples at upstream and downstream points. Overall, water samples were collected from fourteen (14) locations comprising ten (10) monitoring boreholes, two upstream points and two downstream points of the surface water (Table 1). Water sampling was preceded by pre-treatment of 500 ml HDPE sample bottles with HNO_3 and purging of the MB's. In the field, sample bottles were rinsed three times with the water to be sampled before collecting the final sample. An HDPE bailer was used to sample water from the MB's by lowering it down the bore and collecting a column of water. Surface water was sampled by directly fetching from the Subriso river. Electrical conductivity, pH and TDS were measured *in situ* with Orin 5-star multi-parameter analyzer and Insite IG 3150 TDS meter. Water samples were collected for analysis of Total Suspended Solids (TSS), Nitrate, Sulphate, Alkalinity, Arsenic (As), Manganese (Mn), Iron (Fe), Zinc (Zn), Copper (Cu), Cadmium (Cd), Mercury (Hg), Aluminum (Al), Silver (Ag), Cobalt (Co), Chromium (Cr) and lead (Pb). Samples for heavy metal analysis were acidified with 50% HNO_3 to attain a pH of 2 in order to maintain metal ions in the dissolved state and also to inhibit microbial activities. The samples were transported to the laboratory within 24 hours where they were refrigerated for subsequent analysis. All samples were collected in duplicate.

Table 1. GPS coordinates of sampling locations.

No.	ID for sampling	Description	Northings/ Longitudes (UTM)	Eastings/ Latitudes (UTM)
1.	SEMB-01A	Deep Monitoring Borehole	624,791	575,152
2.	SEMB-02A	Deep Monitoring Borehole	624,846	575,516
3.	SEMB-03A	Deep Monitoring Borehole	624,673	575,600
4.	SEMB-04A	Deep Monitoring Borehole	624,387	575,624
5.	BRMB-01A	Deep Reference Borehole	624,071	575,014
6.	SEMB-01B	Shallow Monitoring Borehole	624,790	575,149
7.	SEMB-02B	Shallow Monitoring Borehole	624,850	575,514
8.	SEMB-03B	Shallow Monitoring Borehole	624,680	575,596
9.	SEMB-04B	Shallow Monitoring Borehole	624,395	575,632
10.	BRMB-02B	Shallow Reference Borehole	624,070	575,020
11.	SW-SE-01	Subri at diversion Channel	624,940	575,254
12.	SW-SE-02	Subri down South East Pit	624,310	575,632
13.	SW-SE-03	Subri on bridge to Subriso	623,753	575,374
14.	SW-SE-07	Subri upstream (control)	624,940	575,254

2.3. Laboratory Analysis

Each surface and ground water sample was analyzed for the following: pH, Electrical Conductivity, Sulphate, Alkalinity Arsenic (As), Manganese (Mn), Iron (Fe), Zinc (Zn), Copper (Cu), Cadmium (Cd), Mercury (Hg), Aluminum (Al), Silver (Ag) and lead (Pb). Chemical analysis of samples followed standard protocols outlined in Table 2.

2.4. Statistical Analysis

One-way analysis of variance (ANOVA) was used to test for variation between deep monitoring boreholes, shallow monitoring boreholes and upstream and downstream points of surface water at 95% confidence level using SYSTAT 10 statistical software (SYSTAT Inc.).

3. Results

3.1. Surface Water Quality Characteristics of the Subri River

The Subri River can generally be characterized as moderately acidic with pH values ranging between 5.47 ± 0.23 - 5.73 ± 0.12 (Table 3). The low acidity was associated with particularly, high concentrations of iron and aluminum. The low alkalinity levels of the river indicated low buffering capacity corresponding with the level of acidity of the water. Surface water conditions across the channel of the Subri River from upstream and downstream locations can be characterized as uniform due to the reduced spatial variation in pH and consequently low acidic conditions ($p > 0.05$). These values were below (GSB, 2009) and (WHO, 2017) permissible ranges of 6.5 - 8.5 for drinking water. The low variability in

Table 2. Methodological references of techniques applied in laboratory analysis.

Parameter	Methodology	Reference
pH	Geotechnical test method GTM24	Geotechnical engineering bureau
Electrical Conductivity	Standard method 2510	APHA, 1992
Arsenic (As)	USEPA Method 3050, AAS	USEPA
Manganese (Mn)	USEPA Method 3050, AAS	USEPA
Iron (Fe)	USEPA Method 3050, AAS	USEPA
Zinc (Zn)	USEPA Method 3050, AAS	USEPA
Copper (Cu)	USEPA Method 3050, AAS	USEPA
Cadmium (Cd)	USEPA Method 3050, AAS	USEPA
Mercury (Hg)	USEPA Method 7473	USEPA
Lead (Pb)	USEPA Method 3050, AAS	USEPA
Alkalinity	Standard Method 2320	APHA, 1992
Ag	USEPA Method 3050, AAS	USEPA
Al	USEPA Method 3050, AAS	USEPA
Sulphate	USEPA Method 9038	USEPA

Table 3. Mean (±SD) of physico-chemical parameters of surface water of the Subri River. Units for Electrical Conductivity (μs/cm) and all other parameters (mg/L).

Parameter (mg/l)	SW-SE-01A	SW-SE-02	TS-SE-01	TS-SE-02	SW-SE-07
pH	5.47 ± 0.23	5.73 ± 0.12	6.38 ± 0.19	6.17 ± 0.21	5.48 ± 0.12
Alkalinity	14.00 ± 7.18	14.33 ± 7.61	107.5 ± 55.49	93.17 ± 70.27	14.67 ± 8.57
EC	6.65 ± 0.88	6.88 ± 0.81	59.08 ± 16.95	44.68 ± 10.10	6.73 ± 1.06
TDS	57.0 ± 7.64	57.2 ± 13.76	362.0 ± 155.43	250.0 ± 33.15	47.0 ± 4.86
SO$_4$	1.67 ± 0.58	5.00 ± 2.16	130.83 ± 95.09	72.00 ± 29.15	7.00 ± 1.42
Fe	1.30 ± 1.71	1.38 ± 1.59	2.78 ± 2.34	3.50 ± 2.65	1.50 ± 1.86
Cu	0.02 ± 0.00	<0.02 ± 0.00	0.03 ± 0.00	<0.02 ± 0.00	<0.02 ± 0.00
Mn	0.24 ± 0.32	0.12 ± 0.02	0.52 ± 0.32	0.64 ± 0.48	0.74 ± 1.11
Zn	0.34 ± 0.28	0.14 ± 0.01	0.2 ± 0.01	0.45 ± 0.18	0.06 ± 0.06
Al	0.30 ± 0.33	0.32 ± 0.37	0.45 ± 0.41	0.54 ± 0.43	0.61 ± 1.00
Cd	<0.002 ± 0.00	<0.002 ± 0.00	<0.002 ± 0.00	<0.002 ± 0.00	<0.002 ± 0.00
Pb	<0.01 ± 0.00	<0.01 ± 0.00	<0.01 ± 0.00	<0.01 ± 0.00	<0.01 ± 0.00
Ag	<0.02 ± 0.00	<0.02 ± 0.00	<0.02 ± 0.00	<0.02 ± 0.00	<0.02 ± 0.00
As	<0.002 ± 0.00	0.002 ± 0.00	0.002 ± 0.00	0.002 ± 0.00	0.002 ± 0.00

pH across the river channel is a general reflection of the low concentrations and variation in most physicochemical parameters measured. Generally, alkalinity, electrical conductivity, TDS, sulphate, copper, manganese, zinc, cadmium, lead, silver and arsenic all showed remarkably low values relative to the reference guideline concentrations for chemicals in drinking water (WHO, 2017). Distinctively, aluminum and iron concentrations measured were above the threshold levels. The tested variance of the various parameters between upstream and downstream sampling points of the Subri River showed uniform and less variable water quality conditions that were not significant at $p < 0.05$.

3.2. Physicochemical Characteristics of Deep Monitoring Boreholes (DMB)

The hydrochemical characteristics of DMB was similar to the water quality conditions of natural waters inferred from the remarkably low concentrations of all measured parameters which were far below the guideline values considered permissible for drinking water (WHO, 2017) (Table 4). Water quality in the DMB featured neutral pH, high alkalinity and well-buffered groundwater containing extremely low levels of heavy metals (Table 4). However, groundwater in the DMB showed overall higher levels of water quality than surface water in the Subri River (Table 3 and Table 4). Variation between water quality parameters among DMB and the reference borehole was not significant at $p < 0.05$ probability level.

Table 4. Mean (±SD) of physico-chemical parameters of deep monitoring boreholes. Units for Electrical Conductivity (μs/cm) and all other parameters (mg/L).

Parameter	SEMB-01A	SEMB-02A	SEMB-03A	BRMB-01A
pH	6.90 ± 0.28	6.88 ± 0.20	6.95 ± 0.12	6.73 ± 0.21
Alkalinity	208.80 ± 4.83	238.00 ± 18.97	241.67 ± 23.45	131.50 ± 61.69
EC	48.8 ± 4.66	54.37 ± 4.32	60.03 ± 2.86	26.90 ± 3.25
TDS	237.5 ± 116.34	253.8 ± 123.17	302.7 ± 174.74	166.0 ± 82.05
SO_4	1.00 ± 0.00	5.17 ± 1.33	38.17 ± 6.05	6.17 ± 1.33
Fe	0.10 ± 0.00	0.10 ± 0.00	<0.01	0.06 ± 0.06
Cu	<0.02	<0.02	0.03 ± 0.00	<0.02
Mn	0.10 ± 0.13	0.27 ± 0.20	0.33 ± 0.16	<0.02
Zn	<0.05	<0.05	<0.05	<0.05
Al	<0.03	<0.03	<0.03	0.10 ± 0.06
Cd	<0.002	<0.002	<0.002	<0.002
Pb	<0.01	<0.01	<0.01	<0.01
Ag	<0.02	<0.02	<0.02	<0.02
As	0.005 ± 0.001	0.003 ± 0.001	0.002 ± 0.00	0.002 ± 0.00

3.3. Physicochemical Characteristics of Shallow Monitoring Boreholes (SMB)

Shallow Monitoring Boreholes showed similar characteristics to DMB and its designated reference borehole (Table 4 and Table 5). No clear differences could be found between water samples from the two groundwater sources. Mean pH of samples from shallow boreholes varied between 6.30 ± 0.13 and 6.88 ± 0.19. pH values were within (GSB, 2009, WHO, 2017) permissible limit of 6.5 - 8.5 for drinking water. Statistically, there was no significant difference between values of parameters in monitored and reference boreholes ($p > 0.05$).

3.4. Seasonal Patterns and Temporal Variations of Physicochemical Variables and Heavy Metal Concentrations in Surface and Groundwater

Majority of physiochemical parameters had no detectable seasonal patterns related to wet and dry climatic periods. The temporal variations in the concentrations of various parameters were clearly distinct from each other in regards to the surface water and boreholes monitored (Figure 3 and Figure 4). However, high levels of turbidity and TSS in surface water were recorded in September during the secondary rainfall peak of the year (Figure 3 and Figure 4). Highest nitrate concentrations were recorded in DMB and SMB but not surface water in January during the dry season. Mean values recorded for most parameters showed very high variability in surface and monitoring boreholes throughout the study period as indicated by the magnitude of the associated error bars (Figure 3 and Figure 4). Electrical conductivity, pH, alkalinity, TDS and
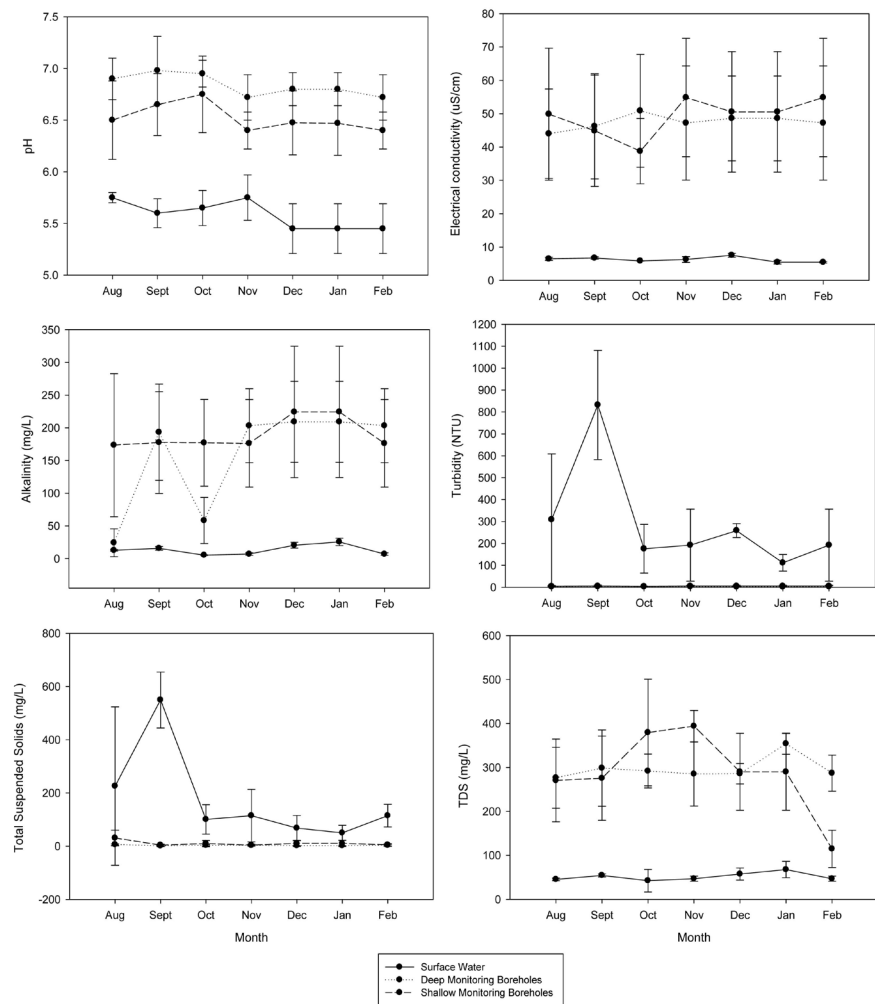
Figure 3. Temporal variation in mean pH, electrical conductivity, alkalinity, turbidity, TSS and TDS in surface water, deep and shallow monitoring boreholes.

Table 5. Mean (±SD) of physico-chemical parameters of shallow monitoring boreholes.

| Parameters	SEMB-01B	SEMB-02B	SEMB-03B	BRMB-01B
pH	6.30 ± 0.13	6.30 ± 0.17	6.68 ± 0.20	6.88 ± 0.19
Alkalinity	116.67 ± 13.37	140.17 ± 15.94	270.83 ± 34.17	240.83 ± 93.61
EC	28.48 ± 2.43	43.87 ± 3.79	61.03 ± 8.44	59.57 ± 15.30
TDS	196.4 ± 36.7	245.3 ± 160.06	292.2 ± 174.3	295.6 ± 173.7
SO_4	2.00 ± 0.00	54.50 ± 16.22	22.17 ± 4.36	16.00 ± 4.52
Fe	<0.01	1.00 ± 0.00	1.00 ± 0.00	0.20 ± 0.00
Cu	<0.02	<0.02	<0.02	0.03 ± 0.00
Mn	0.06 ± 0.00	2.01 ± 0.38	0.21 ± 0.15	0.04 ± 0.00
Zn	<0.05	<0.05	<0.05	<0.05
Al	0.03 ± 0.01	0.11 ± 0.00	0.04 ± 0.02	0.06 ± 0.00
Cd	<0.002	<0.002	<0.002	<0.002
Pb	<0.01	<0.01	<0.01	<0.01
Ag	<0.02	<0.02	<0.02	<0.02
As	0.002 ± 0.00	0.002 ± 0.00	0.002 ± 0.001	0.003 ± 0.001
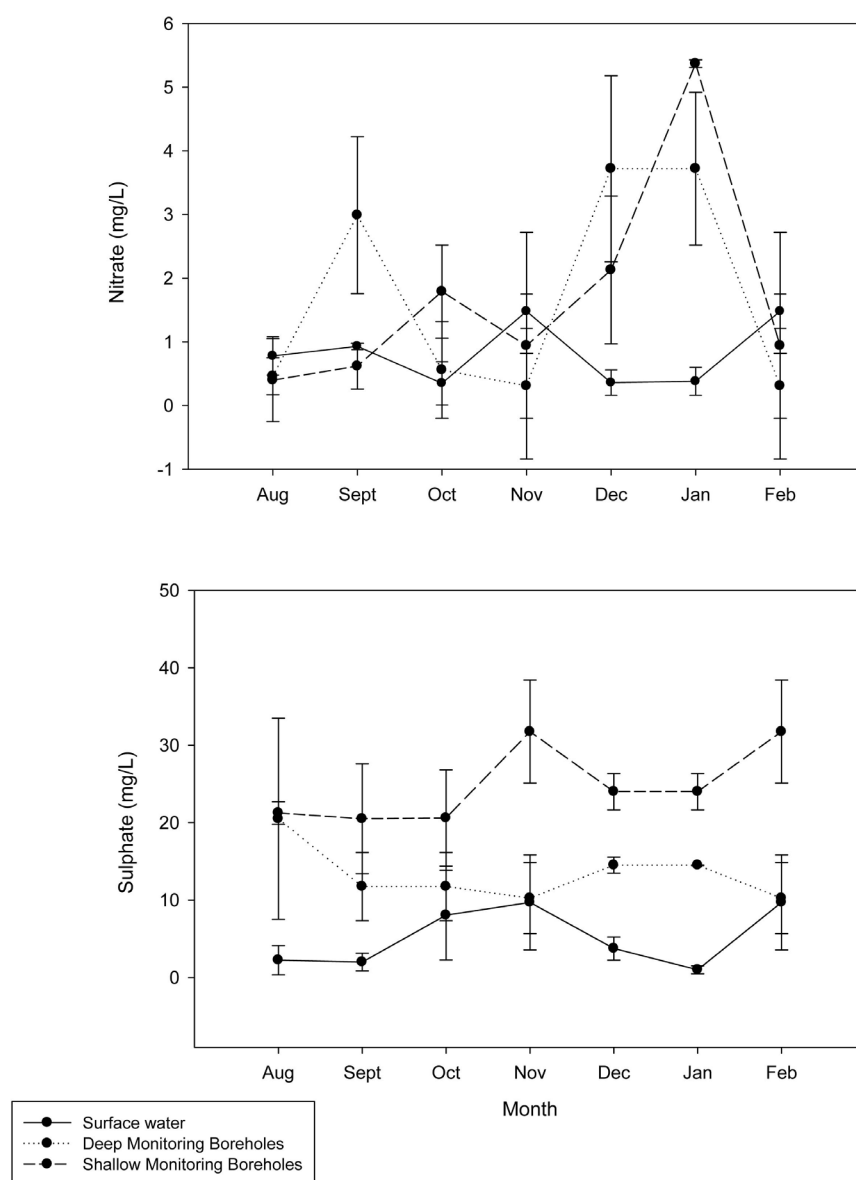
Figure 4. Temporal variation in mean nitrate and sulphate in surface water, deep and shallow monitoring boreholes.

sulphate content of surface water showed consistently lower values compared with both deep and shallow monitoring boreholes (**Figure 3** and **Figure 4**). pH of surface water remained moderately acidic whilst monitoring boreholes were neutral throughout the study period.

With the exception of iron and manganese, heavy metal concentrations monitored in the river and groundwater systems were less variable and largely below the detection limits to trigger toxicity (WHO, 2017). Iron (Fe) concentration in surface water varied between 1.30 ± 1.71 mg/l and 1.50 ± 1.86 mg/l but upstream iron content of surface water was higher than downstream concentrations. Fe concentration of all the samples exceeded the (GSB, 2009; WHO 2017) permissible limit of 0.3 mg/l for drinking water. Statistically, the variation be-

tween Fe concentration of the upstream point and the downstream sampling points was not significant ($p > 0.05$). Mean Mn concentrations reported for all sampling points in surface water and boreholes were 0.24 ± 0.321 mg/l; 0.21 ± 0.02 mg/l; 0.74 ± 1.11 mg/l; 0.52 ± 0.32 and 0.64 ± 0.48 mg/l. Overall, downstream sampling points reported marginal Mn concentrations below the upstream point. Statistical analyses showed that variation between Mn concentration measured in the upstream point and each of the downstream points was not significant ($p > 0.05$).

4. Discussion

Surface water, monitoring and the reference boreholes were mainly characterized by neutral pH, low acidity, low TDS, low electrical conductivity, low sulphate and low concentrations of heavy metals which varied little between dry and wet seasons. The results from the study showed that the monitored boreholes and surface water diverged considerably from the chemical characteristics typical of systems that have been impacted by ARD which usually are expressed by low pH, high acidity, high TDS, high electrical conductivity, high iron and high concentration of heavy metals (Azapagic, 2004; Akcil & Koldas, 2006). Thus, the Subriso East Rock Dump (SERD) did not appear to be acid generating. This may be explained as the SERD could be a designed and engineered facility to control seepage. An engineered waste rock dump (WRD) according to (Yankful et al., 1993) will have placement of an impermeable membrane which will collect seepage at the base of the pile, preventing discharge into the natural environment. The physical and chemical heterogeneities and internal structure of a waste-rock pile affect internal chemical weathering patterns, as well as physical transport processes, including gas (oxygen), water, and heat transport which facilitate oxidation for ARD generation. Additionally, according to (Singhal & Gupta, 1999), the water discharge in a WRD follows a dual porosity model consisting of porous block and channels. In relation to SERD, it can be inferred that the porous blocks have high primary porosity, a low hydraulic conductivity and molecular diffusion whiles the channels present a high hydraulic capacity, low storage capacity and transport processes which are controlled by advection and mechanical dispersion, all of which do not allow for ARD to reach the external environment.

Analysis of surface water indicated acidity below pH of 6 which may be indicative of impairment of a river system by ARD. The slightly acidic nature of water from Subri river in the study area conforms to the baseline assessment conducted prior to commencement of the HBB mine operations indicating that the level of acidity is due to natural geochemical properties of the area and not attributable to AMD. The trend in pH of surface water may be due to high rate of organic matter decomposition in the Subri River resulting from runoff or direct input of riparian vegetation into the channel. The process of organic matter decomposition may produce slightly acidic water due to the presence of dissolved carbon dioxide and organic acids (Brady et al., 1990). Frequent and con-

tinuous rinsing of seepage by precipitation could contribute to the low pH values recorded due to the high dilution and rapid flushing rates of high volumes of discharge (Smith et al., 1995).

Drainage water quality in a mine environment is highly influenced by factors such as water saturation level, particle size distribution and soil permeability, but may also be influenced by the mineral composition of the soil, which in turn controls the distribution of metals. Discharge of sulphate is controlled by mineral solubility. The recorded low levels of sulphur can be attributed to the absence of water-soluble sulfates (Jambor et al., 2000), which are among the most definite indicators of ARD. These sulfates are among the first products of sulfide oxidation and occur above the water table, closest to oxidizing pyrite, and in areas where the exposure of pyrite by erosion and the evaporation of AMD fluids create extremely low pH values (Jambor et al., 2000).

5. Conclusion and Recommendations

The study indicated that no significant impacts to surface and ground water contamination are attributable to SERD. Nevertheless, depending on the site topography, geology and engineering inputs and functions of waste rock dumps containing acid-generating or potentially acid generating material, high precipitation pattern as in the case of the study site may promote erosion and facilitate infiltration of water in rock dump leading to subsequent discharge of acidic water harmful to the environment.

Acknowledgements

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

Abrosimova, N., Gaskova, O., Loshkareva, A., Edelev, A., & Bortnikova, S. (2015). Assessment of the Acid Mine Drainage Potential of Waste Rocks at the Ak-Sug Porphyry Cu-Mo Deposit. *Journal of Geochemical Exploration, 157,* 1-14.
https://doi.org/10.1016/j.gexplo.2015.05.009

Afriyie-Debrah, C., Obiri-Danso, K., & Ephraim, J. H. (2010). Acid Mine Drainage-Effect on Creeks or Streams in a Mining Community in Ghana and Treatment Options. In *2010 International Conference on Environmental Engineering and Applications* (pp. 285-290). Piscataway, NJ: IEEE.

Akabzaa, T. M., Banoeng-Yakubo, B. K., & Seyire, J. S. (2007). Impact of Mining Activities on Water Resources in the Vicinity of the Obuasi Mine. *West African Journal of Applied Ecology, 11,* 101-109.

Akcil, A., & Koldas, S. (2006). Acid Mine Drainage (AMD): Causes, Treatment and Case

Studies. *Journal of Cleaner Production, 14,* 1139-1145.
https://doi.org/10.1016/j.jclepro.2004.09.006

Ankomah-Appiah, E. (2011). *Assessment of Acid Rock Drainage Dissolved Trace Metal and Its Impact on Water Quality in Mining Areas.* Department of Theoretical and Applied Biology, Kwame Nkrumah University of Science and Technology.

Azapagic, A., Perdan, S., & Clif, R. (Eds.) (2004). Sustainable Development in Practice. In *Case Studies for Engineers and Scientists*, Chichester, England: John Wiley and Sons. https://doi.org/10.1002/0470014202

Brady, L., Smith, M. W., Beam, R. L., & Cravotta, C. A. (1990). *Effectiveness of the Use of Alkaline Materials at Surface Coal Mines in Preventing or Abating Acid Mine Drainage: Part 2. Mine Site Case Studies* (pp. 227-241).

Ezeigbo, H. N., & Ezeanyim, B. N. (2006). Environmental Pollution from Coal Mining Activities in the Enugu Area Anambra State, Nigeria. *Mine Water Association, 11.*

Foli, G., Apeah, O. B., & Amedjoe, C. G. (2011). Pre-Mining Water Quality Prediction from Non-Weathered Sulphide Ores along the Ashanti Metallogenic Belt in Ghana Using Acid-Base Accounting Procedure. *American Journal of Scientific and Industrial Research, 2,* 827-833. https://doi.org/10.5251/ajsir.2011.2.5.827.833

Fox, D., Robinson, C., & Zentili, M. (1997). Pyrrhotite and Associated Sulphides and Their Relationship to Acid Rock Drainage in the Halifax Formation, Meguma Group, Nova Scotia. *Atlantic Geology, 33,* 87-103.

Gaikwad, R. W., & Gupta, D. V. (2008). Review on Removal of Heavy Metals from Acid Mine Drainage. *Applied Ecology and Environmental Research, 6,* 81-98. https://doi.org/10.15666/aeer/0603_081098

Galvez-Cloutier, R., & Lefrançois, P. J. (2005). Soils Contaminated by Metals Heavy: Geochemical Distribution and Restoration Techniques (Part I). *Vector Environment, 38,* 30-38.

Gandy, C. J., Younger, P. L., & Lindsay, P. (2009). Modelling Waste Rock Leaching at an Opencast Coal Mine in New Zealand: The Effects of Mineral Grain Size on Long-Term Contamination. *Journal of Environmental Geology.*

Ghana Standards Board Limits for Drinking Water (GS 175-1:2009, 3rd ed.). https://www.gsa.gov.gh/wp-content/uploads/2018/08/2018-Catalogue-of-Ghana-Standards.pdf

Jambor, J. L., Nordstrom, D. K., & Alpers, C. N. (2000). Metal-Sulfate Salts from Sulfide Mineral Oxidation. *Reviews in Mineralogy and Geochemistry, 40,* 303-350. https://doi.org/10.2138/rmg.2000.40.6

Jennings, S. R., Neuman, D. R., & Blicker, P. S. (2008). *Acid Mine Drainage and Effects on Fish Health and Ecology: A Review.* Bozeman, MT: Reclamation Research Group Publication.

Kuyucak, N. (2012). Acid Mine Drainage Prevention and Control Options. *IWMA Proceeding 1999*, Sevilla: International Mine Water Association.

Lengke, M. F., Davis, A., & Buckman, C. (2010) Improving Management of Potentially Generating Acid Waste Rock. *Journal of Mine Water and Environment, 29,* 29-44. https://doi.org/10.1007/s10230-009-0097-1

McCarthy, T. S. (2011). The Impact of Acid Mine Drainage in South Africa. *South Africa Journal of Science, 107,* 1-7.

Peppas, A., Komnitsas, K., & Halikia, I. (2000). Use of Organic Covers for Acid Mine Drainage Control. *Minerals Engineering, 13,* 563e74. https://doi.org/10.1016/S0892-6875(00)00036-4

Plumlee, G. S. (1999). The Environmental Geology of Mineral Deposits. In G. S. Plumlee, & M. J. Logsdon (Eds.), *The Environmental Geochemistry of Mineral Deposits, Part A. Processes, Techniques, and Health Issues: Society of Economic Geologists, Reviews in Economic Geology* (Vol. 6A, pp. 71-116). Littleton, CO.

Pozo-Antonio, S., Puente-Luna, I., Lagüela-López, S., & Veiga-Ríos, M. (2014). Techniques to Correct and Prevent Acid Mine Drainage: A Review. *DYNA, 81,* 73-80. https://doi.org/10.15446/dyna.v81n186.38436

Singhal, B. B. S., & Gupta, R. P. (1999). *Applied Hydrogeology of Fractured Rocks* (pp. 129-150). London: Kluwer Academic Publishers. https://doi.org/10.1007/978-94-015-9208-6

Smith, L. A., López, D. L., Beckie, R., Morin, K., Dawson, R., & Price, W. (1995). *Hydrogeology of Waste Rock Dumps*. British Columbia Ministry of Energy, Mines and Petroleum Resources and CANMET.

Sprynskyy, M., Boguslaw, B., Terzyk, A. P., & Namiesnik, J. (2006). Study of the Selection Mechanism of Heavy Metal ($Pb^{2+,}$ Cu^{2+}, Ni^{2+} and Cd^{2+}) Adsorption on Clinoptilolite. *Journal of Colloid and Interface Science, 304,* 21-28. https://doi.org/10.1016/j.jcis.2006.07.068

Sullivan, P. J., & Yelton, J. L. (1998). An Evaluation of Trace Element Release Associated with Acid Mine Drainage. *Journal of Environmental Geology and Water Sciences, 12,* 181-186. https://doi.org/10.1007/BF02574730

Tran, A. B., Miller, S., Williams, D. J., Fines, P., & Wilson, G. W. (2003). Geochemical and Mineralogical Characterization of Two Contrasting Waste Rock Dumps—The INAP Waste Rock Dump Characterization Project. In *ICARD 2003 Proceedings from the 5th International Conference on Acid Rock Drainage* (pp. 939-947). Melbourne: The Australasian Institute of Mining and Metallurgy.

Valente, T. M., & Gomes, C. L. (2009). Occurrence, Properties and Pollution Potential of Environmental Minerals in Acid Mine Drainage. *Science of the Total Environment, 407,* 1135-1152. https://doi.org/10.1016/j.scitotenv.2008.09.050

World Health Organization (WHO) (2017). *Guidelines for Drinking Water Quality* (4th ed., Vol. 1). Geneva: WHO. http://apps.who.int/iris/bitstream/handle/10665/254637/9789241549950-eng.pdf;jsessionid=E817FD2914FC36AB0065638DB4F6547E?sequence=1on

Yankful, E. K., Bell, A. V., & Woyshner, M. R. (1993). Design of a Composite Soil Cover for an Experimental Waste Rock Pile near Newcastle, New Brunswick, Canada. *Canadian Geotechnical Journal, 30*, 578-587.