Int. J. Environ. Res., 5(4):847-854, Autumn 2011
ISSN: 1735-6865

Chemical Composition of Rainwater over a Mining Area in Ghana

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Received 12 May 2009; Revised 19 Dec. 2010; Accepted 15 June 2011

ABSTRACT: A comprehensive study on the chemical composition of rainwater was carried out in Obuasi, a gold mining town in Ghana. Rainwater samples were analyzed for major ions (Ca^{2+},Mg^{2+}, K^+, Na^+, NH_4^+, Cl^-, NO_3^- and SO_4^{2-}) and trace metals (Fe, Al, Zn, Pb, Cr, and Cd). The rainwater was typically acidic with a mean pH of 4.76±0.47, which ranged from 4.0 to 5.6. The low pH found in the water suggests that the concentration of the alkaline particles in the rainwater were not high enough to neutralize acidic species present. SO_4^{2-} and Cl^- were the main anions, while Ca^{2+} and K^+ were the main cations. Concentrations of trace metals in this study were compared with those of other studies conducted at different sites in the world. The result of this study generally suggests that rainwater chemistry in the area is strongly influenced by local anthropogenic sources (mining). The pollutants in rainwater samples were mainly derived from mining activities. Concentrations of Pb in all the samples were above the WHO permissible limit of 0.01 mg/L for drinking water.

Key words: Chemical composition, Ionic species, Neutralization factor, Obuasi, Rainwater, Trace elements

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INTRODUCTION

Concentrations of many compounds present in the atmosphere have been significantly affected by human activities such as industry, agriculture, burning of vegetation and fossil fuel (Nègrel and Roy, 1998; Kohler et al, 1997). Quantification of these changes and their effect on terrestrial and aquatic ecosystems is important because of their potential adverse effects (Nriagu and Davidson, 1986). Rainwater functions as a major sink for both gaseous and particulate matter including trace metals in the atmosphere and therefore plays an important role in controlling the concentrations of these species. Scavenging of the atmospheric pollutants by rain affects the chemical composition and the pH of rainwater. The degree of acidity in rainwater depends on the neutralization effects of certain components such as ammonia and calcium carbonate and/or hydroxide on the acidic ions present in the water (Kulshrestha *et al.*, 1995a, b). Determination of rainwater composition reveals the relative importance of the different sources/types of gases and particulate matter present in the atmosphere.

Chemicals present in the atmosphere influence the chemical characteristics of rainwater whereas the material deposited by the rain affects soil, surface water and vegetation. Previous studies on the chemical composition of rainwater (Galloway *et al.*, 1987; Larssen *et al.*, 1999; Larssen and Carmichael, 2000; Feng *et al.*, 2001; Tang *et al.*, 2005) have revealed that the composition of rainwater depends on the local emission, pollutants transport, sea level elevation and drop size, which in turn influences the rainout (in-cloud scavenging) and the washout (below-cloud scavenging). Climatic conditions may also affect the levels of trace substances in rainwater.

Over the last 20 years, rainwater chemistry has been subjected to intense research and many studies on the chemical composition, long and short-term trends of precipitation have been conducted worldwide (Tu *et al.*, 2005; Rogora *et al.*, 2004; Sickles and Grimm, 2003; Avila and Roda, 2002; Seto *et al.*, 2002; Loye-Pilot *et al.*, 1986). However, in West Africa there are very few works concerning the chemical composition of rainwater (Uzomah and Sangodoyin, 2000; Yoboue *et al.*, 2005). Since atmospheric pollution is a problem of global concern, an in-depth study of the phenomenon in a developing country like Ghana is necessary. Monitoring the chemical nature of rainwater in Ghana is even more important due to the rapid growth in industrialization, intensive chemical usage in manufacturing processes, oil and mineral exploration and mining. Despite the possible environmental consequences of wet deposition, there

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is no report concerning the chemical composition of rainwater in Ghana.

The present study reports the chemical composition of precipitation in Obuasi, a gold mining town in Ghana. This is important because soil excavation and chemical use in mineral processes through mining operations have increased tremendously in the area. The objective of the present study is to examine the level of atmospheric pollution in Obuasi through the determination of chemical composition of rainwater. It is also aimed at determining the variation and distribution of rainwater composition based on prevailing activities from mining and residential areas. The data will significantly contribute to the very limited knowledge available on rainwater quality in West Africa.

MATERIALS & METHODS

The Obuasi municipality (Fig.1) hosts one of the richest gold mines in the world, which has been in operation for the past 110 years (Anonymous, 2006a). This municipality with a population of about 300,000 is located in the Ashanti Region of the Republic of Ghana. Obuasi is bounded by longitudes 5Ú35' N and 5Ú65' N, and latitudes 6Ú35' W and 6Ú90' W. The relief is slightly hilly, with average height of about 500 m above sea level and covers a total area of 162.4 km^2 (Anonymous, 2006b). The municipality experiences semi-equatorial climatic conditions with a mean annual rainfall of about 175 cm and average relative humidity of 78%. Temperatures are uniformly high all year with a mean annual value of 25.5 °C. The natural vegetation has been degraded largely due to mining activities. The area has a nucleated settlement pattern with narrow spaces in-between houses.

Three areas, Ramia, Wawasi and Antobuasi all within the Obuasi municipality were selected for this study. The sampling areas were chosen on the account of the presence of mining and other human activities which contribute heavily to the atmospheric load of pollutants in the municipality. Ramia has the Kwasi Mensah Shaft and the Sulphur Treatment Plant of the gold mining company. The Cote D'or Shaft, Adansi shaft, Ellis Turner Shaft and the Pompora Treatment Plant are also located in Wawasi area. Antobuasi has no mining activity but is located at the central part of Obuasi and has the central market. The locations of study areas are shown in Fig. 1.

Samples of rainwater were collected from the selected sites during the peak of the raining season (May to September) in 2007. In order to avoid collection of suspended soil particles, samples were collected at 1.5 m above the ground using high density polyethylene buckets. Samplers were placed on supports after the start of the rain to ensure that only wet depositions were collected. Samples were analysed for pH, electrical conductivity (EC) and turbidity immediately after collection. Samples that were meant for NO_3^-, Cl^-, SO_4^{2-} and NH_4^+ determinations were filtered through 0.45 µm pore size membrane filter to remove insoluble fractions which may be present. Filtered samples were kept in pre-washed high-density polyethylene bottles treated with chloroform to minimize microbial activities and were stored in refrigerator at about 4 ^{o}C. Other sample used for the determination of trace metal and major cations was kept in an acid-washed bottle. These bottles were soaked in 20% HNO_3 for 24 h, rinsed several times with deionized water and dried before use. Samples collected in acid-washed bottles were acidified with 1ml of 5% ultra-pure HNO_3 to prevent adsorption of the trace metals. All the samples were kept in well-labeled sealed containers and refrigerated until analysis. A total number of 15 rain events were sampled, and a total of 45 samples of rainwater were collected during the monitoring period.

A pH meter (Fisherbrand Hydrus 100 model) equipped with glass electrode was used for pH measurement. The pH meter was calibrated using standard buffer solutions of pH 4.01, 7.00, and 9.20 before each measurement. The EC measurements were made using a digital conductivity meter (Hi 9032 Microprocessor model). The instrument was calibrated before the measurements were started. Turbidity was measured using LP2000 Turbidity meter-Hanna Instrument. Metals analysis was done using Atomic Absorption Spectrophotometer (Unicam 929 model) with an air-acetylene flame. Calibration curves were drawn for each metal by running suitable concentrations of their standard solutions, from which the concentrations of the elements were obtained by extrapolation. Average values of three replicates were taken for each determination. After every five samples the standards were run to check peak response; if deviation was more than 2%, recalibration was done. The samples were digested using concentrated nitric acid according to (Zhang, 2007a). Concentrated nitric acid (5 mL) was added to 50 mL of sample of water in a 100 mL beaker. This was heated on a hot plate to boil until its volume reduced to 20 mL. Another 5 mL of concentrated nitric acid was added and then heated for another 10 min and allowed to cool. About 5 mL of nitric acid was used to rinse the sides of the beaker; the solution was quantitatively transferred into a 50 mL volumetric flask and made up to the mark with distilled water. Blank solutions were handled in exactly the same way as the samples and analyzed. Levels of all the metals in the blanks were below the detection limits of the equipment which was 0.001. NH_4^+, Ca^{2+},

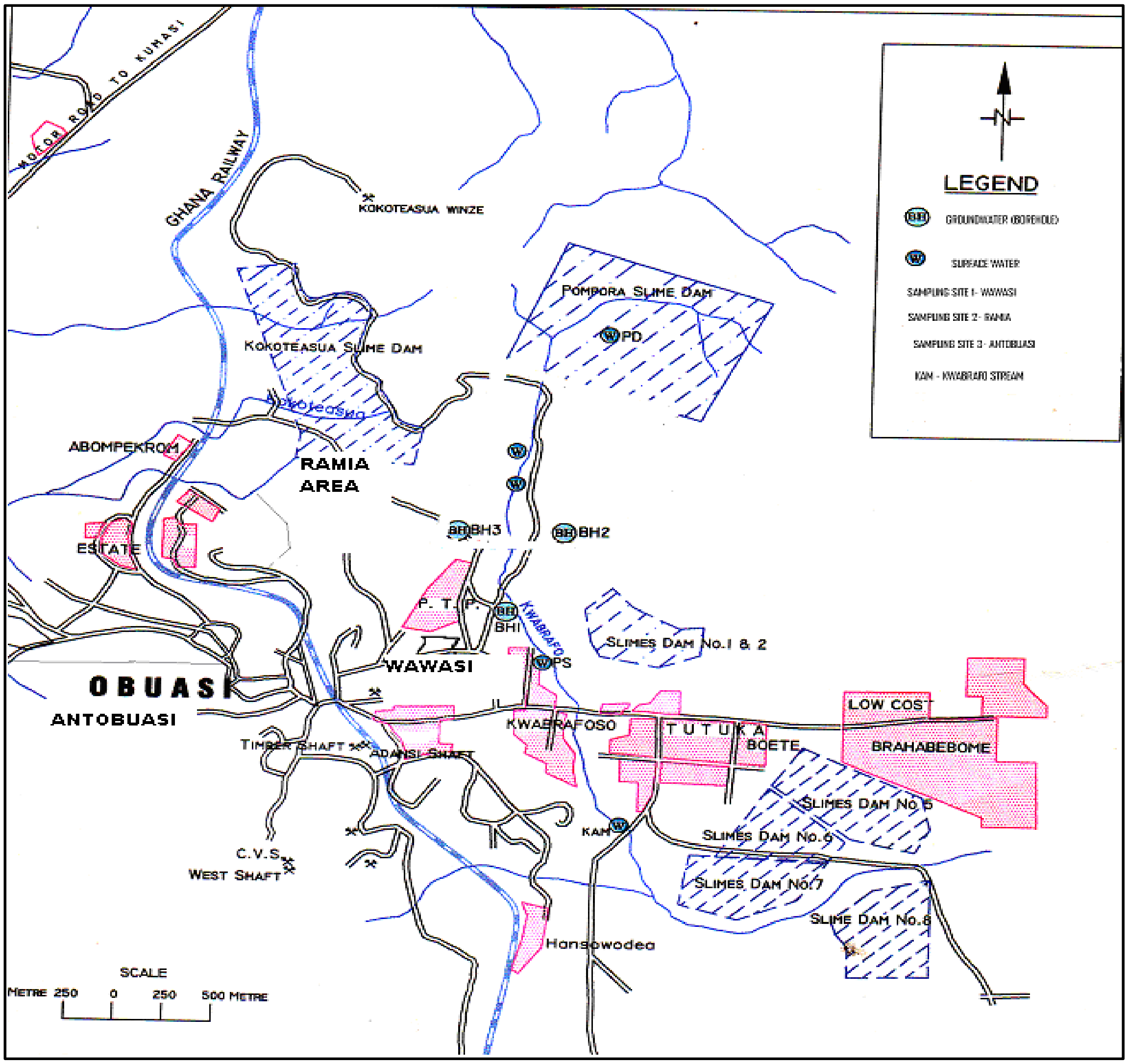

Fig. 1. Map of the study area showing the location of sampling sites

Mg^{2+}, NO_3^- and SO_4^{2-} were measured spectrophotometrically by using the procedure outlined in the Palintest photometer method. Alkalinity and chloride were measured by titrimetric measurements. Sodium and K^+ were determined by flame emission. All instruments/systems were properly standardized and calibrated before taken measurements.

RESULTS & DISCUSSION

The results obtained for pH, major cations and anions in the rainwater samples; their range, mean concentration and standard deviation are presented in Table 1. The pH values of individual precipitation ranged from 4.0 at Wawasi to 5.6 at Antobuasi with a mean value of 4.67 ± 0.47. The percent frequency distribution of pH for the rainwater samples is plotted in Fig. 2. The pH profile showed that of all the rainfall events, 40% of the rainwater had pH<4.5 indicating very acidic rainwater. About 95.4% of the total precipitation had a pH value less than 5.60, and about 4.6% of the precipitation had pH equal to 5.6. Over 90% of the samples had pH values less than 5.6, which is the pH value of unpolluted water at equilibrium with atmospheric CO_2 (Seinfeld, 1986; Charlson and Rodhe, 1982). These lower pH values consequently reflect a significant impact of anthropogenic activities on rainwater quality in the study area. The low pH values may be due to the presence of SO_2 gas in the atmosphere produced as a result of the mining of the sulphite ore and the extractive processes used in gold mining in the area. SO_2 gas can easily dissolve and get incorporated in the rain droplets and can easily affect the pH of rainwater. The use of strong acids for ore treatment can also contribute to the low pH values recorded in the area. Hence, a more detailed study is needed to highlight this point by considering the air quality data for this region (i.e., SO_2, HCl and NO_X compounds).

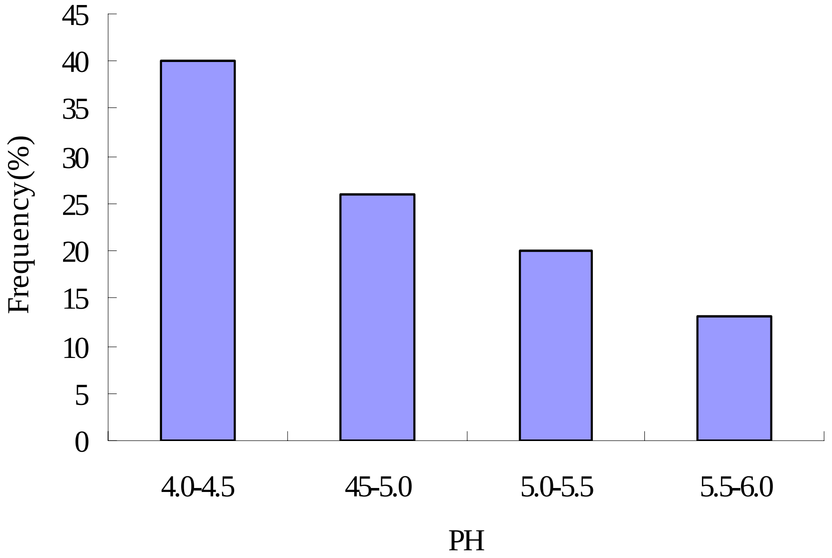

Fig. 2. Frequency distribution of pH of rainwater samples

Table 1. Mean and standard deviation of physicochemical parameters in rainwater at Obuasi (n=15)

Parameters/sites		**Ramia**	**Antobuasi**	**Wawasi**
PH	range	4.4-5.6	4.1-4.9	4-5.4
	mean ±St.D	4.79±0.51	4.49±0.39	4.77±0.51
Conductivity(μs/cm)	range	7.15-40.5	15.3-42.05	16.2-59.6
	mean ±St.D	19.84±14.52	24.18±11.99	39.75±21.66
TDS(mg/L)	range	6.8-20.4	9.4-21	10-24.1
	mean ±St.D	11.03±10.08	13.57±9.95	18.61±17.70
TSS(mg/l)	range	2.0-16.0	4-14	6.0-25.0
	mean ±St.D	8.8±9.03	8.57±9.00	17.14±15.63
Turbidity(NTU)	range	24.6-38.79	31-79	26.43-49.79
	mean ±St.D	33.84±12.26	51.43±19.11	38.28±16.14
Alkalinity(mg/L)	range	8-16	2-10	2.0-4.0
	mean ±St.D	11.14±11.82	5.71±18.23	3.143±16.69
Cl^- (mg/L)	range	4.25-6.22	3.22-5.16	4.0-4.65
	mean ±St.D	4.92±2.56	4.33±1.78	4.13±0.79
SO_4^{2-} (mg/L)	range	11.0-12.82	10.22-12.45	8.90-11.80
	mean ±St.D	11.79±2.39	11.46±1.65	10.04±1.23
NO_3^- (mg/L)	range	0.11-0.32	0.01-0.42	0.09-0.32
	mean ±St.D	0.29±3,20	0.28±4.66	0.23±5.76
Ca^{2+} (mg/L)	range	0.62-0.95	0.56-0.87	0.68-1.02
	Mean ±St.D	0.82 ±0.25	0.71 ±0.65	0.89 ±0.95
Mg^{2+} (mg/L)	range	0.15-0.36	0.21-0.29	0.19-0.25
	mean ±St.D	0.27 ±0.1.23	0.26±0.94	0.23 ±0.22
K^+ (mg/L)	range	0.52-0.74	0.43-0.57	0.48-0.61
	mean ±St.D	0. 66±0.51	0.52 ± 0.11	0.55 ±0.21
Na^+ (mg/L)	range	0.12-0.43	0.08-0.52	0.23-0.46
	mean ±St.D	0.31 ±1.27	0.38 ± 545	0.41 ±2.11
NH_4^+ (mg/L)	range	0.03-0.07	0.03-0.09	0.05-0.17
	mean ±St.D	0.06 ±0.13	0.07 ±0.12	0.12 ±0.25

*St.D = standard deviation

The mean EC values of the rainwater samples range from 19.84±14.52 at Ramia to 39.75±21.66 at Wawasi µs/cm (Table 1). The EC of precipitation is mainly attributed to the total soluble ionic components present in the rainwater samples. This observation, to a certain extent, reflects the impact of atmospheric particulate matter on the precipitation chemistry. It may also indicate a preferable dilution effect on the atmospheric pollution since heavy rainfall episodes are experienced in the study area. The EC values showed higher dispersions around their mean values according to the standard deviations.

From Fig. 3 it was observed that the dominant ionic species in the rainwater samples was sulphate (50%) followed by chloride (32%) and calcium (6%). The concentration of major ionic species had the following order; $SO_4^{2-} > Cl^- > Ca^{2+} > K^+ > Na^+ > NO_3^- = Mg^{2+} > NH_4^+$. The alkaline components namely, Ca^{2+}, Mg^{2+}, Na^+, K^+ and NH_4^+ contribute about 16% of the total ionic strength, whereas the acidic components comprising of SO_4^{2-}, Cl^-, and NO_3^- made up 84%. The high concentration of SO_4^{2-} observed may be due to the processing of ore with high content of pyrite resulting in the emission of high amount of SO_2 into the atmosphere in the area (Jetuah, 1997).

The anionic and cationic composition of the rain water is given in Figs 4a and 4b. Among the anions the dominant species was SO_4^{2-} contributing 60% to this group and 50% to the total ions composition. This was followed by Cl^- (33%) and NO_3^- (2%). In the cation category (Fig. 4b) Ca^{2+} was dominant, contributing 39% in the group and 6% to total ions in the rainwater samples. The mean concentrations of Ca^{2+} in the study area were much lower than those recorded in Jinhua city in China (Zhang, *et al.*, 2007), rural regions surrounding a coal plant in the city of Figueira, Brazil (Fleus *et al.*, 2002), Lagos and Ibadan in Nigeria (Uzomah and Sangodoyin, 2000). Based on this result, it is thought that the relatively low concentration of Ca^{2+} is not sufficient to cause neutralization of the acidic species present as the highest pH recorded was 5.6 indicating acidic precipitation. The study area does not have many construction activities and other works involving the use of calcium containing materials. K^+ ions make 28% of the cation mass which is the highest contribution after Ca^{2+}. This was followed by Na^+ (18%), Mg^{2+} (12%) and NH_4^+ (4%). NH_4^+ concentrations were found to be very close in Ramia and Antobuasi samples but doubled in Wawasi samples to a mean value of 0.12 ±0.25 m/L. These values are exceptionally low when compared to other literature values from rural areas (Fleus *et al.*, 2002). High concentrations of NH_4^+ in rainwater are usually an indication of agricultural activities. Therefore, it is thought that the fertilizers put in the field within the study area might have been very small resulting in the release of small quantities of ammonia into the atmosphere. Fig. 3 showed that SO_4^{2-} and Cl^- concentrations were much higher than the other ions concentrations measured in the study.

Chemical properties of rainwater depend on its acidic and alkaline ions compositions and the acidic neutralization capacity of the alkaline species such as Ca^{2+}, Mg^{2+}, Na^+, K^+ and NH_4^+ (Singh *et al.*, 2007). The pH values obtained in the rainwater were low indicating that alkaline species [NH_3, $CaCO_3$ and $Ca(OH)_2$] are probably not high enough to neutralize the acidic effect of sulphate. To verify which cations more frequently neutralize the sulphates, neutralization factors (NF) for Ca^{2+}, Mg^{2+}, Na^+ and NH_4^+ were determined (Kulshrestha, 1995a). NF for the species was derived as a mean of the averages recorded from the three sample sites, using the equation

$$NF_X = \frac{X}{SO_4^{2-} + NO_3^-}$$

*Where X denotes the concentration of chemical component of interest

The order of the neutralization factors is 0.07 for Ca^{2+}, 0.04 for K^+, 0.03 for Na^+ and 0.02 for Mg^{2+}. The mean concentration of NH_4^+ was insignificant therefore its NF value was not determined.

Mining activities in the area discharge lots of trace metals in nimble forms into the atmosphere. The types and levels of metals present in water may depend on the type ore being mined, the metallurgical processes used to separate the precious metals from the ores and other human activities concentrated in the area. Based on these assumptions, the concentrations of six trace metals were measured in the rainwater samples. The concentrations together with statistical analyses of values obtained for these metals in rainwater sampled at Obuasi area is presented in Table 2. The mean values recorded for Pb, Zn, Fe, Cr, Al, and Cd were 0.17±0.08, 0.11±0.17, 0.11±0.36, 0.05±0.12, 0.03±0.16 and 0.03±0.08 mg/L respectively.

The variation in concentration values of trace metals between different rainfall events could be related to the source of pollutant emissions. The high concentrations of metals were measured in wet deposition after periods of dryness, while low values of metals were measured when rain had continued for a few months. The relatively high concentration values recorded at the beginning of the raining season may be due to the fact that there was a large amount of pollutants in the atmosphere before the rains set in.

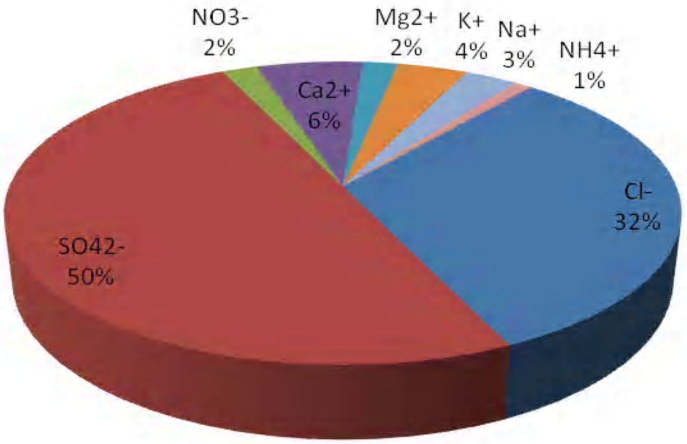

Fig. 3. Percentage distribution of the ionic composition in the rainwater samples

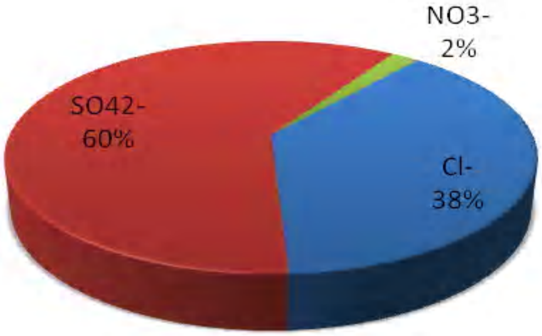

Fig. 4a. Percentage anion composition

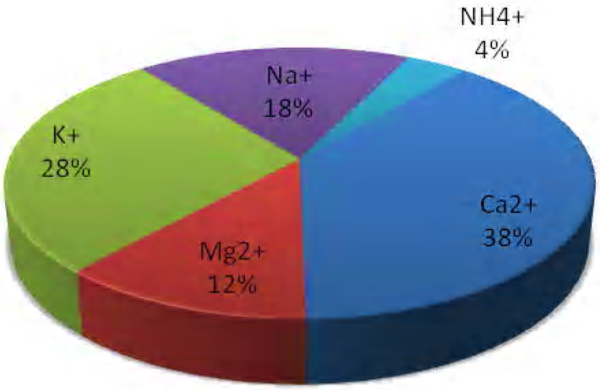

Fig. 4b. Percentage cation composition

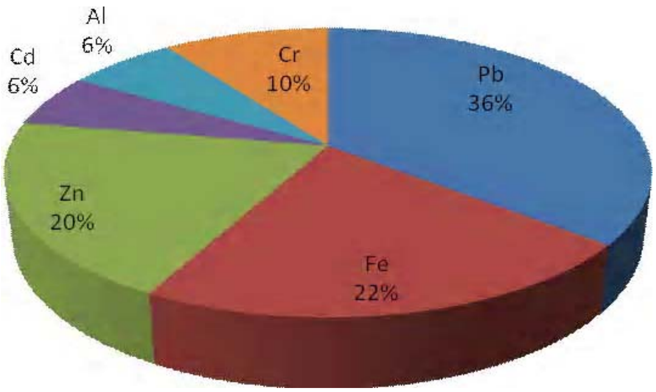

Fig. 5. Mean contribution of metals in the rainwater samples

Table 2. Mean values and Std. Deviation for total metal concentration in rainwater samples (n=15)

Parameter/site		Pb (mg/L)	Fe (mg/L)	Zn (mg/L)	Cd (mg/L)
Remia	range	0.15-0.19	0.07-0.13	0.05-0.15	ND-0.1
	mean± St.D	0.17 ± 0.02	0.1 ± 0.02	0.09 ± 0.04	0.04±0.05
Antobuasi	range	0.11-0.17	0.06-0.18	0.05-0.23	0.01-0.02
	mean± St.D	0.15 ± 0.04	0.12 ± 0.05	0.13 ± 0.07	0.02±0.02
Wawasi	range	0.15-0.19	0.07-0.12	0.05-0.22	ND-0.02
	mean± St.D	0.18 ± 0.01	0.1 ± 0.02	0.09 ± 0.07	0.02±0.09

*St.D = standard deviation
*ND = not detected

The concentrations of each metal in rainwater are shown in Fig. 5. It clearly shows that the mean concentration of the trace metal species in the rainwater follows the order Pb > Fe > Zn > Cr > Cd = Al. The high values of metals in rainwater samples may be due to local point sources of atmospheric pollution and the soil dust from mining and other anthropogenic activities which affect the composition of wet atmospheric deposition. Trace element concentrations in precipitation collected world wide has been studied by Dasch and Wolff (1989), Heaton et al (1990), Al-Momani et al. (1998) and Al-Momani (2003) for metals commonly analyzed in rainwater. In most cases the concentrations of some metals (Zn, Cr, Al and Cd) in our samples were in good agreement with those of Dasch and Wolff (1989), Heaton et al. (1990), Al-Momani et al. (1998). However the concentrations of Pb and Fe were high in our samples than those reported by these workers. Although the concentrations of the metals, except that of Pb, were below the WHO allowable limit of 0.01 mg/l for drinking water.

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CONCLUSION

In this investigation into the chemical composition of rainwater in Obuasi, we have been able to establish a database on the quality of rainwater around one of the riches gold mining towns in the world. The study revealed that rainwater in the area is acidic. The mean pH of rainwater was well below the reference pH of unpolluted rainwater which is at equilibrium with CO_2. The acidity in the rainwater is not significantly neutralized by Mg^{2+} and NH_4^+ whereas Ca^{2+} played a minor role. Sulphate and Cl^- were the major acidifying ions in rainwater of the study area. The chemical composition of rainwater in the study area is influenced by local activities such as mining. The concentration of trace metals (Fe, Al, Zn, Pb, Cr, Pb and Cd) that were determined in the rainwater samples was relatively low except that of Pb.

ACKNOWLEDGEMENT

We would like to acknowledge the staff of the Analytical Laboratory of Anglogold Ashanti Ltd, Obuasi, for their support in carrying out the analyses.

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