



Major ion composition of rainwater in an agricultural locality of greater accra Region, Ghana

Juliet Osei, Shiloh Kwabena Osae, Joseph Richmond Fianko, Samuel Boakye Dampare, Samuel Ganyaglo and Cynthia Laar

Ghana Atomic Energy Commission (GAEC), Kwabenya, Accra, Ghana.

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ABSTRACT

Major ions as well as pH and conductivity were analysed in about 52 rainwater samples collected daily from the rain station of Ghana Atomic Energy Commission for a period of April, 2009- June, 2010. Results for the major cations analyses indicate a trend of $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$ and the major anions show a trend of $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$. The values of pH range from 4.62-8.64 and conductivity from 5.74-1274 $\mu S/cm$. Contribution to the acidity of rain in this area is mostly by SO_4^{2-} instead of NO_3^- due to the reason that the study area lies in the Accra Plains which is a highly industrialized area. Ratios of mean annual concentrations of major ions (Cl^- , K^+ , Mg^{2+} , Ca^{2+} and SO_4^{2-}) to Na^+ in the rainwater samples were higher in comparison to sea water. This suggests that there are other sources of these ions apart from the sea. High concentrations of most of the elements were recorded in months with smaller amounts of rainfall and so it was concluded that continuous rainfall may have washed away so many of the elements suspended in the atmosphere.

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Introduction

The study of the chemical composition of atmospheric aerosols is very significant due to the immediate influence on human health and the ecosystem in general. Increasing air pollution in urban areas as a result of emission of sulfur and nitrogen oxides from sources such as motor vehicles and industries is causing a sharp increase in the acidity of rains. Studies have shown that emission of sulfur and nitrogen oxides into the atmosphere in Asia, Europe and North America has resulted in widespread environmental effects such as acidification of soils, surface waters, ground waters, injury to vegetation, corrosion of building materials and decreased visibility (Singh et al. 2007).

Atmospheric deposition is not a just a domestic concern; it is also a regional environmental problem that transcends national boundaries. As emphasized in chapter 9 on Agenda-21 (on transboundary atmospheric pollution) adopted at the 1992 United Nations Conference on Environment and Development (UNCED) in Rio de Janeiro, acid deposition is a problem that requires international cooperative efforts for its solution. When acid rain hits the earth, nutrients such as potassium, calcium and magnesium which are essential for the trees in the soil are washed away and toxic metals are freed (Baird 1995). As a result, the trees absorb these toxic metals and die because they are deprived of their vital nutrients such as potassium, calcium and magnesium. Various pH values in rain have been reported throughout the world depending on the availability of acid precursors and neutralizing species in rain. For areas which are under the influence of SO_2 and NO_x gases, low pH values have been reported (Idrees et al. 1994).

However, neutralization of rain may occur in areas where there are enough $CaCO_3$ and or NH_3 in the atmosphere. These compounds may find themselves in the atmosphere as a result of agricultural, natural and industrial activities. When base cations

are present in rain, pH may be raised higher or neutralized even in the presence of acidifying SO_2 and NO_x .

Numerous studies on rainwater chemistry have been published for most of the developed regions (Kaya & Tuncel 1997, Negrel & Roy 1998; Singh et al. 2006; Panagiotis et al. 2007; Krawczyk et al. 2008). In contrast, there is limited information available for tropical regions, (Pelig-Ba et al. 2001; Dinrifo et al. 2010) where land-use changes are intense followed by rapid urbanization associated with large industrial expansion. This paper therefore seeks to present the chemical composition in rain water, with respect to major cations and anions in rain water collected from the rain water station of Ghana Atomic Energy Commission for the period of April 2009 – June 2010, and also identify potential sources which may contribute to the chemical composition of the rainwater.

Description of the study area

Ghana Atomic Energy Commission lies in the Accra plains. The Accra Plains contains the main industrial establishment of Ghana and provides one of the richest arable lands for large-scale agriculture in the country (Kortatsi et al. 2001). It is approximately 6000 Km^2 and lies between longitude $0^{\circ}20'W$ and $0^{\circ}40'E$ and latitudes $5^{\circ}30'N$ and $6^{\circ}15'N$, respectively. To its boundary on the west and the north-west are the Akwapim-Togoland ranges, on the east-northeast by the river Volta and on the south by the Gulf of Guinea. The Akwapim-Togoland range is made up of quartzite, phyllite, sandstone, shale, schist and silicified limestone (Kesse 1985). The Accra Plain is flat and undulating with a few isolated inselberg that seldom rise 70m above the mean sea level.

The climate is characterised by two main rainfall maxima. The major rainy season occurring between May and July with the peak occurring in June while the minor one occurs between September and October with the peak occurring in October. Generally the rainfall in the Accra Plains is low with mean

annual rainfall of approximately 900mm per annum. The mean annual rainfall on the Accra plain is not only very low for sub-equatorial latitudes, but is also of low reliability, varying from year to year. The mean temperature is 26°C.

Vegetation of the study area

There are 3 broad vegetation zones in the area which comprises shrub land, grassland and coastal lands. Only the shrub land occurs more commonly in the western outskirts and in the north towards the Aburi hills. It consists of clusters of small trees and shrubs which grow to an average height of five metres. The grasses are a mixture of species found in the undergrowth of forests. They are short and rarely grow beyond one metre. Ground herbs are found on the edge of the shrub. They include species, which normally flourish after fire.

The coastal zone comprises two vegetation types, wetland and dunes. The coastal wetland zone is highly productive and it serves as an important habitat for marine and terrestrial- mainly birdlife. Mangroves, comprising two dominant species, are found in the tidal zone of all estuaries and sand lagoons. Salt tolerant grass species cover substantial low-lying areas surrounding the lagoons.

Grasslands have an important primary production role in providing nutrients for prawns and juvenile fish in the lagoon systems. Protection of the coastal wetland zone is very important to the long-term sustainability of the fish industry, which the population of Accra depends upon for sustenance.

In addition to the natural vegetation zones, a number of introduced trees and shrubs thrive in the area. Neems, mangoes, cassias, avocados, palms are prominent trees on the Accra landscape. Introduced shrubs like bougainvillea are also prominent. These are being damaged from residential encroachment, bush fire, sand collection and illegal tree felling. Most of the open spaces in Accra are used for the cultivation of food crops like corn, okro, tomatoes and other vegetation. Fertilizers and insecticides are used in these areas. Constant felling of trees, bad farming practices and annual burning has altered the vegetation from 'dry forest' and greatly depleted the fertility of the soil.

Methodology

Daily rainwater samples were collected before 09:00 am each morning from a permanent station which is located on the Ghana Atomic Energy Commission Station (devoid of point sources and large settlements) between 16 April 2009 and 29 June 2010. The samples of rain were kept in clean polyethylene bottles (Panagiotis et al. 2007). The measurements of pH (pH meter pH 523 WTW) and conductivity (HACH senSion 5 conductivity meter) were done in-situ each morning during collection of rain water samples. The pH meter was calibrated in the range of 4-7 before every use. The remaining parts of the samples were filtered through a 0.45µm pore size membrane filter to remove all insoluble salts, and then collected in collection bottles. Collected samples were stored at 4°C until analyses of major ions (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , SO_4^{2-} , PO_4^{3-} , NO_3^-) were performed at the laboratories of the Chemistry Department of Ghana Atomic Energy Commission. A portion of the filtrate which has been acidified with nitric acid was analyzed for Na^+ and K^+ using flame photometer of Sherwood Model 420 and for Ca^{2+} and Mg^{2+} using Atomic Absorption Spectrophotometer (AAS) of Varian Model AA240FS. Argentometric titration was performed to determine chloride and bicarbonate was determined titrimetrically. A portion of the unacidified filtrate

was analyzed for SO_4^{2-} , PO_4^{3-} and NO_3^- using Shimadzu UV-VIS spectrophotometer Model UV-1201.

Results and Discussions

Meteorology

Rainfall data was recorded for the period of study from April, 2009 to June, 2010. During the study period, a total of 52 event samples were collected and analysed for major ion chemistry. Mean daily air temperature for the period was 26.9°C; the highest temperature was 31.3°C on 04/11/2009 and the lowest was 23.6°C on 17/06/2010. The total amount of rainfall recorded for the whole period was 1089.5mm.

The plot of monthly mean amount of rainfall records (Fig.1) shows that December recorded the lowest mean rain (12mm) whereas March had the highest mean amount of rainfall (36.5mm). However, the highest frequency of rainfall was recorded in June.

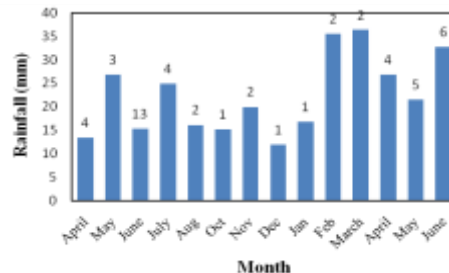


Figure 1. Mean monthly amount of rainfall (mm) in Ghana Atomic Energy campus from April, 2009-June, 2010. The numbers at the end of the bars show the number of times it rained in each particular month

Ion balance

The ratio of the total anions to that of the total cations is an indication of the completeness of measured parameters. If all the major anions and cations are included in the measurement, the ($\sum \text{anions} / \sum \text{cations}$) ratio is expected to be unity. Deviation from unity indicates that some of the major ions were excluded in the analysis (Idrees et al., 1994). The plot of the sum of cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) against the sum of anions (HCO_3^- , Cl^- , SO_4^{2-} , NO_3^- and PO_4^{3-}) is given in Fig.1 and the average ($\sum \text{anions} / \sum \text{cations}$) ratio was 0.98. Since the ratio was close to unity, it suggests that there was completeness in the measurement of anions and cations.

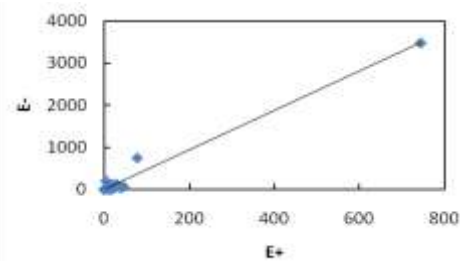


Figure 2. Ion balance in rainwater Acidity in rain from Ghana Atomic Energy Commission campus

The mean, minimum and maximum pH values were 6.75, 4.62 and 8.64, respectively. For a water solution that contains 325 ppm of CO_2 which is approximately the concentration of CO_2 in the atmosphere, the expected pH value should be approximately 5.6 (Panagiotis 2007). For rainfall figures smaller than the threshold value of 5.6 are associated with the effect of anthropogenic source of pollution such as transportation and industrial emissions. The acidity of the collected rain samples was highly variable. Almost 10% of the samples had pH values

less than 5.6. With reference to the examined period (16/04/2009-29/06/2010), episodes of acid rain ($\text{pH} < 5.6$) were reported especially in the month of June 2010. Out of the 13 rain samples collected in the month of June 2009, 4 rain samples recorded pH values smaller than 5.6. In June 2010, for the 6 different rain samples collected, only 1 sample recorded a pH figure smaller than 5.6. Also, July 2009 recorded the minimum pH value of 4.62. Acidity in rain depends on the concentrations of acid-forming ions as well as concentrations of alkaline species which neutralize the acidity. Weak acids dissolved in rain do not cause acidic conditions in the rain. Nitric oxide is not soluble in water and the sulfurous acid that sulfur dioxide produces upon dissolving in water is weak, therefore, the primary pollutants NO_x and SO_2 do not make rainwater acidic. However, some of the mass of these primary pollutants are converted over a period of hours or days into the secondary pollutants sulfuric acid, H_2SO_4 and nitric acid, HNO_3 , both of which are soluble in water and are strong acids (Baird 1995). Mostly, all the acidity in rain is due to the presence of these two acids. In our case, however, the pH values for the rain samples suggest predominantly neutral and alkaline pH figures (Table 1). This shows that the main process in the rain is neutralization. Bicarbonate concentrations were very high in the rain samples. However, the high pH values do not correspond to the high bicarbonate values. Waters with high bicarbonate content have the capacity to neutralize all strong acids present in the water as a result of dissolution of atmospheric CaCO_3 and MgCO_3 particles (Krawczyk et al. 2008). The results of the analysis indicate that the concentrations of SO_4^{2-} were higher than the concentrations of NO_3^- and their ratio ($[\text{SO}_4^{2-}]/[\text{NO}_3^-]$) in the rain was calculated equal 6.13. This is in agreement with the findings of Panagiotis et al. (2007) who had a ratio of 4.14 and thus concluded that the acidity of rain in Athens is due to H_2SO_4 and secondary to HNO_3 . Therefore, contribution to the acidity of rain in the study area is mainly due to H_2SO_4 . The mean conductivity of all the analyzed samples was estimated $221.29 \mu\text{S}/\text{cm}$ for Atomic Energy Commission campus. There is a positive correlation ($r = 0.47$, $p < 0.05$) between conductivity and pH of rain water for the area.

Major ion composition of rain and sources

The data presented in this work is from the first year of an on-going monitoring programme which will probably continue for a period of 5 years or more. Data treatment to understand sources of observed pollutants will be carried out when data for a longer period of time becomes available. The available data, however, may provide preliminary information on the major sources of ions in this study area.

The mean ratio of chloride to sodium is 1.72 and this value is similar to the ratio in sea water (i.e. 1.16) (Panagiotis et al. 2007). This may suggest that the chemical composition of the rain in this area may be influenced by the sea. This would not be far from right as the area is nearer coastal influence (Gulf of Guinea).

However, it may be concluded from Table 2 that the origin of Mg^{2+} , K^+ , Ca^{2+} and SO_4^{2-} may not be from the sea alone but other sources.

The concentrations of the mean of the major ions analysed (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , HCO_3^- , SO_4^{2-} , NO_3^- and Cl^-) are plotted in Figure 3 for about 52 rain samples collected from 04/2009-06/2010 and also shown in Table 3.

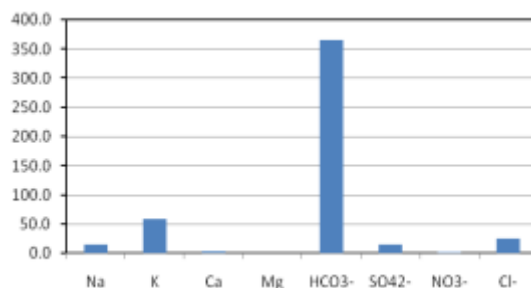


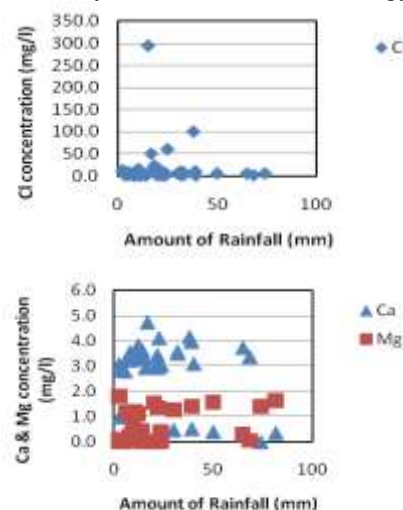
Figure 3. Mean concentrations of major species (mg/l)

The trend in magnitude of the major cations is as shown in Figure 3 is $\text{K} > \text{Na} > \text{Ca} > \text{Mg}$. The relative concentration of K which is higher than the other ions shows that the influence of sea spray in this environment is minimal. The ratio of K^+/Na^+ to that of normal seawater as determined by Galloway et al. (1983), as shown in Table 2 indicates a significantly higher value than its corresponding seawater value. This suggests other sources apart from the sea. Potassium salts are widely used in industry and fertilisers for agriculture (Chapman 1996). The high concentrations of K found in this study area is in accordance with a lot of farming activities that take place in the area and possibly the use of fertilisers during these activities.

For most of the rain samples analysed in the area, nitrate concentrations were relatively high although there were few ones which recorded as low as 0.09 mg/l . High nitrate values suggest human source (Pelig-Ba et al. 2000). There are also other sources such as inorganic nitrate fertilisers and atmospheric derived NO_3^- , from the oxidation of NO from the soil and or atmosphere.

Emissions of SO_2 produced both by natural (volcanoes) and as pollution (from power plants and smelters) become oxidized over a period of hours or days to sulfuric acids and sulfates in air (Baird 1995). High SO_4^{2-} observed in the study area is probably due to emissions from industries since Accra is endowed with a lot of chemical industries. Most soil Cl^- ions are normally derived from rainfall, as rocks and soils have very low concentrations except in areas where evaporite deposits are believed to be present and contamination by use of KCl fertilisers or from domestic wastes. However, the presence of chlorine in the atmosphere and its conservative nature makes it appropriate for use in groundwater recharge studies (Pelig-Ba et al. 2000).

Figure 4 depicts the relationship between the major ions and amount of rainfall daily from Ghana Atomic Energy campus.



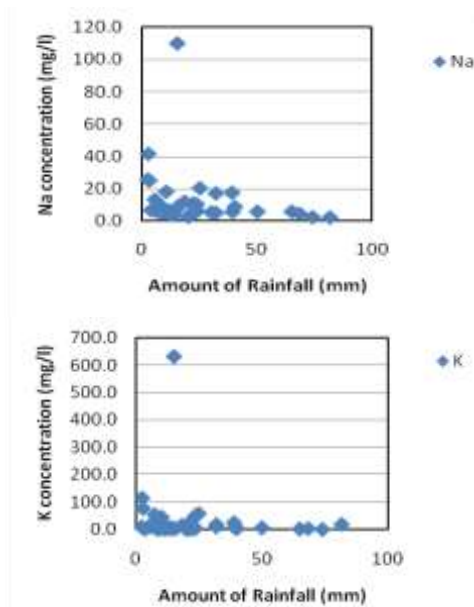


Figure 2. Relationship between major ions and rainfall amounts in Atomic Energy Campus

It is remarkable that a very high concentration of the ions, Cl^- , Ca^{2+} , Mg^{2+} , Na^+ and K^+ correlated with low amounts of rainfall.

This observation may suggest that continuous rainfall could result in the dilution of ions after the start of the rainy period, since most of the suspended particles in the atmosphere might have been washed out. Also observed in Table 3 is high concentrations of these ions evident during October. This is likely due to the accumulation of pollutants in the atmosphere combined with the absence of rainfall for a long time period before.

Conclusion

The concentrations of major ions (K^+ , Mg^{2+} , Ca^{2+} , Na^+ , SO_4^{2-} , HCO_3^- , NO_3^- , Cl^-), which were determined in 52 samples of rainwater at the Ghana Atomic Energy Commission campus during the period of April, 2009 to June 2010, were relatively high. Sources of these ions have been identified as the sea, industrial activities and agriculture. Relatively high concentrations of SO_4^{2-} determined in the rain samples means that it is the main cause of acidity in the rain. It is recommended that stringent measures are put in place to cut down the emission of SO_2 gas.

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Table 1. Statistical figures for pH and conductivity

		Mean	Std. Dev.	Minimum	Maximum
Ghana Atomic Energy Campus	pH	6.75	0.96	4.62	8.64
	Conductivity ($\mu\text{S}/\text{cm}$)	211.29	331.20	5.74	1274

Table 2. Ratios of mean annual concentrations of major ions Cl⁻, K⁺, Mg²⁺, Ca²⁺ and SO₄²⁻ to Na⁺, in rainwater and sea water

Ions ratio	Rainwater samples (from this work)	Sea water (Galloway et al., 1983)
[Cl ⁻]/ [Na ⁺]	1.72	1.16
[K ⁺]/ [Na ⁺]	3.98	0.02
[Mg ²⁺]/ [Na ⁺]	0.06	0.23
[Ca ²⁺]/ [Na ⁺]	0.23	0.04
[SO ₄ ²⁻]/ [Na ⁺]	1.04	0.12

Table 3. Results of mean monthly figures of major cations and anions (mg/l), along with their corresponding standard deviation s, in the collected rain samples at Ghana Atomic Energy Commission campus (April, 2009- June, 2010)

Month	April	May	June	July	August	Sept	Oct	Nov	Dec
pH	6.54±0.55	7.25±0.43	6.13±0.88	6.20±1.18	8.04±0.62	6.68	8.40	7.83	7.83
conductivity	27.70±17.87	323.76±495.14	103.38±238.57	29.74±50.78	796.00±140.01	32.00	n.d	115.40	30.40
[Na ⁺]	4.33±1.14	4.30±0.14	10.93±7.14	15.10±17.85	5.55±0.78	3.40	110.00	4.80	6.00
[K ⁺]	5.98±5.58	3.20±0.14	40.35±23.33	47.88±49.37	3.45±1.34	1.80	630.40	10.20	13.70
[Ca ²⁺]	3.45±3.65	3.38	6.12±0.43	0.68±0.45	3.14±0.14	5.50	3.30	3.51	3.83
[Mg ²⁺]	0.57±0.55	0.41±0.39	0.40	1.71±0.12	0.02	4.07	0.00	0.00	1.09
[HCO ₃ ⁻]	27.45±31.27	164.29±257.24	32.82±34.73	n.d	36.60	24.40	3050.00	122.00	73.20
[SO ₄ ²⁻]	41.57±39.65	2.71	6.26±6.86	n.d	32.86±45.46	3.29	63.82	0.49	0.57
[NO ₃ ⁻]	0.42±0.10	0.42	0.29±0.15	n.d	0.42±0.12	0.09	21.22	0.33	n.d
[Cl ⁻]	2.00	4.33±4.93	5.91±4.18	n.d	0.00	1.99	249.4	0.00	5.00

Month	Jan	Feb	March	April	May	June
pH	8.64	7.67±0.39	6.58±0.08	7.16±0.84	6.45±0.68	6.84±0.89
conductivity	1021.00	113.80±14.14	19.82±10.59	179.13±93.38	399.39±505.30	379.8±403.82
[Na ⁺]	n.d	17.10±0.28	5.30±0.42	5.50	13.00±7.97	4.58±1.67
[K ⁺]	n.d	21.45±4.88	6.90±6.79	6.20	29.78±21.71	14.05±13.32
[Ca ²⁺]	4.74	3.78±0.28	7.21±0.13	2.28±2.66	0.22±0.05	0.40±0.17
[Mg ²⁺]	0.00	0.00	0.27±0.04	1.55	1.35±0.06	1.35±0.06
[HCO ₃ ⁻]	854.00	42.70±8.63	54.90±8.63	93.53±42.84	240.45±280.02	290.77±242.95
[SO ₄ ²⁻]	20.36	1.75±1.41	0.99±0.50	3.08±3.98	24.46±23.39	n.d
[NO ₃ ⁻]	3.81	2.20±0.79	0.37±0.16	0.77	0.10±0.04	n.d
[Cl ⁻]	49.9	9.90	2.5±3.54	29.75±46.84	20.37±23.91	4.99±5.47