

The Geochemistry of some Ground and Surface water Systems in the East Gonja District of Northern Ghana

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Abstract

East Gonja District is located at the South-eastern section of the Northern Region of Ghana and known to have the highest density of boreholes in the country. A total of 38 water samples derived from 26 boreholes, 7 hand-dug wells, 2 dams and 3 rivers were studied by determining the physicochemical, trace elements and major ions compositions of these ground and surface water samples. Among the physicochemical parameters determined were pH, EC, ORP, TDS and hardness while the trace elements included F, Fe, Cu, Ni and Zn. Major ions determined were Mg, Ca, Na, K, Cl, HCO₃, NO₃ and SO₄. The values of the physicochemical parameters largely revealed the samples are fresh water. The major ions and their concentration distributions in the ground waters showed that the hydrochemistry of the waters is dominated by bicarbonates, calcium, magnesium and sodium ions. Saturation indexes (SI) with respect to carbonate (dolomite, calcite, fluorite and apatite) and evaporate (gypsum, anhydrite and halite) minerals, as well as activities of soluble species were also determined using the hydrochemical modelling from PHREEQC. This revealed that most of the considered ground waters are saturated with respect to calcite, dolomite, fluorite and hydroxyapatite but unsaturated with respect to gypsum, anhydrite and halite.

Keywords: Surface and ground water, geochemistry, major cations and anions, trace elements

1. Introduction

The analysis of trace element concentrations in the environment is of great importance in the interest of reducing all pollutants that can affect man's well-being. Water samples are among the most important materials to be tested during investigations of environmental pollution; this is especially true in the case of subsurface waters because of their widespread use as drinking water. Furthermore, the amount of pollutants in subsurface waters cannot be detected, as in surface waters (lake or river water), by analysing aquatic plants which, due to their elevated concentration factors, contain higher amounts of trace elements (Clemente and Mastinu, 1974). It is well known that trace elements are produced from a variety of natural and anthropogenic sources. In aquatic systems, metal pollution can result from direct atmospheric deposition, geologic weathering or through the discharge of agricultural, municipal, residential or industrial waste products (Dawson and Macklin, 1998).

Metals that are naturally introduced into the river come primarily from such sources as rock weathering, soil erosion, or the dissolution of the water-soluble salts. Naturally occurring metals move through aquatic environments independent of human activities, usually without any detrimental effects (Garbarino et al. 1995). While trace metals and major ions usually present in water are essential for proper metabolism in all living organisms; toxicity may result when they occur in concentrations above acceptable thresholds. Other metal ions are non-essential but are toxic even at relatively low concentrations. For example, iron and manganese have been found in elevated concentrations in water in Ghana. Iron is not a health concern in itself, however elevated levels of both iron and manganese affect the taste and quality of drinking water, leading to colouration of cooking utensils and food. This has caused hundreds of wells to be abandoned in favour of surface waters that are likely contaminated with harmful microorganisms (Gyau-Boakye and Dapaah-Siakwan, 1999; Smedley, 1996, as quoted in Schafer et al, 2010).

East Gonja District is located at the South-eastern section of the Northern Region of Ghana and water supply is mainly by mechanized pipe systems, boreholes and hand-dug wells fitted with/ without hand pumps. The area has the highest density of boreholes in Ghana but, these often dry-up in the dry season making people to result to surface water use. The use of surface water sources has in the past resulted in high levels of guinea worm and other water borne diseases. The provision of boreholes and other groundwater supply sources which are of good quality (chemically and biologically) have led to an almost total eradication of guinea worm with only one confirmed case in 2010. However, waters are barely monitored following bore construction for the presence of inorganic and organic contaminants such as arsenic, nitrate, and fluoride etc. The assessment of the quality of water (subsurface and surface) in the eastern Gonja district for domestic and agricultural use has therefore been of major concern for this research.

2.0 Methodology

2.1 The study area

East Gonja lies between latitudes 8°N and 9.29°N and, longitudes 0.29°E and 1.26°W in Northern Ghana (Figure 1). It covers a total land area of 10,787 km². The area is drained by the Volta River and some of its major tributaries including

the White Volta, Daka and Oti rivers. The topography of the area is mostly low-lying, with an average elevation of 91 m above sea level. The area lies in the tropical continental climatic zone with influence from the wet South-West Monsoon and the dry North-East Trades winds. Two distinct seasons are observed in the area namely, the rainy season and the dry harmattan conditions. Rainfall is characterized by irregularity and variability in terms of timing of onset, duration and total amount of rainfall. The total annual rainfall ranges between 1050 mm to 1500 mm. Temperatures are fairly high ranging between 29°C and 40°C. Maximum temperature is usually recorded in April, towards the end of the dry season. Minimum temperatures are also recorded around December-January, during the Harmattan period.

The natural vegetation in the district is the Guinea Savannah woodland with few grooves. The tree cover consists of semi-deciduous trees such as oil palm trees, raffia palm, acacia, shea-nut trees and Dawadawa trees among others. In addition, high grasses that characterize savannah areas extensively spread throughout the district. The land is drained by rivers Nasia, Daka, Oti and the Black and White Volta. Kwei (1997) reported that the water table generally varies from ground surface to about 45 m below land surface.

The region is underlain predominantly by the Voltaian rocks consisting mainly of sandstone, shale, mudstone, sandy and pebbly beds and limestone (Kesse, 1985). Three major groups of soils developed over this geological formation are alluvial soils, ground water laterites and savannah ochrosols. The alluvial soils classified as 'glycols' are medium textured and moderately well drained in parts and fertile. Bulk of the area is covered by ground water laterites, developed mainly from Voltaian sandstone materials and highly concretional with frequent exposures of iron pan and boulders. Borehole yields in the Voltaian System range between 0.1 and 2.4 l/s, with an average of 1.7–2.4 l/s for the various sub-provinces.

The local economy is supported by agriculture as 81.8% of the economically active labour force (PHC Report, 2000) is either engaged in subsistence agriculture and irrigations carried out in the dry seasons at small dam sites. Small-scale industries or petty trade, charcoal burning are other ways by which the inhabitants derive their livelihood. Crops produced are mostly roots and cereals.

2.2 Water sampling and analysis

The ground and surface water samples made of 26 boreholes, 7 hand-dug wells, 2 dams and 3 rivers were collected in October 2010. A total of 38 samples were collected per the Monsoon season. After 10-15 minutes of pumping, water samples were collected into 1 L polyethylene bottles. Then, the bottles were sealed, and stored properly (at 4°C) until analysed at the chemistry laboratories of the National Nuclear Research Institute, Ghana Atomic energy Commission and School of Nuclear and Allied Sciences, Kwabenya, Accra . The samples were analysed using standard procedures (APHA, AWWA, WEF, 1998). Flame emission photometry was used for determining sodium and potassium whilst EDTA titration was used for calcium and total hardness. Chloride contents were also determined by argentometric titration, but total alkalinity was determined by strong acid titration. Calcium and magnesium hardness, on the other hand, were determined by calculation. Total iron and manganese were also determined using an atomic absorption spectrophotometer and fluoride (F) was analysed using fluoride ion selective electrode. Electrical conductivity (EC) and pH were determined on the field using electrodes (Eutech). Total dissolved solids (TDS) were also measured in-situ with a TDS portable electrode (Hach 6 ion).

2.3 Calculations

Statistical analysis was performed using the Statistical Programme for Social Sciences (SPSS) version 16.0 software for the computation of Pearson's correlation matrix analysis on the data. The second stage of the analysis involved geochemical modelling using the PHREEQC (Parkhurst and Appelo, 1999) package. Both the major and trace elements were used in the simulation. The package was used to determine mineral saturation index (SI) using the specific ionic concentrations in the water. PHREEQC uses the mass balance approach to calculate all the stoichiometrically available reactions that are responsible for the observed chemical changes between end member waters (Plummer and Back, 1980). The package calculates the SI of minerals using the concentrations of the major ions and trace elements in the system. The saturation index of a mineral is obtained from Eq. 1 (Appelo and Postma, 2005).

$$SI = \log \left(\frac{IAP}{K_t} \right) \quad (1)$$

where IAP is the ion activity product of the dissociated chemical species in solution, K_t is the equilibrium solubility product for the chemical involved at the sample temperature. SI of minerals is very useful for evaluating the extent to which water chemistry is controlled by equilibrium with solid phases (Appelo and Postma, 2005). When the SI is below 0, the water is termed undersaturated with respect to the mineral in question. An SI of 0 means the water is in equilibrium with the mineral, whereas an SI greater than 0 means a supersaturated solution with respect to the mineral in question.

3.0 Results and discussion

3.1 Physico-chemical properties

The physicochemical and trace element compositions of ground and surface water samples collected from the East Gonja district are shown in Table 1. Figures 2 and 3 show the distribution of temperature, electrical conductivity, total dissolved solids, redox potential and pH in the water samples. The temperatures have been found to be generally close to ambient temperatures, 29 – 40 °C, with a mean value of 33 °C. The temperature range for the waters is 28.10 °C and 31.80 °C with a mean of 29.24 °C. Temperature of the Volta River, the main surface water body that could possibly contribute to groundwater recharge in the area has been between 30.5 and 31.8 °C. In general, the ground waters found close to this river body have temperatures that ranged between 29.8 and 30.6 °C.

Temperature plays a key role in the health of a stream's aquatic life, both in the water column and in the benthic habitat of stream bed sediments. Analyses of subsurface temperature patterns provide information about surface-water/groundwater interactions (Constantz and Stonestrom, 2003). A possible connection between the aquifers and the river seems to exist and could be exploited further in future investigations.

The frequency distribution plots showed pH values 5.08 - 8.44 with a mean of 7.34. This means that the ground waters in the area exhibit slightly acidic to slightly alkaline conditions. The low pH values of 5.08 to 5.88, recorded for these boreholes are principally attributed to natural biogeochemical processes (CO₂ generation in the soil zone through root respiration and the effect from leaching of organic acids from the decay of organic matter).

Redox potential values ranged from -80 to 119 mV with an average of -20±45.73 mV. Most of the groundwater samples (68%) show reduction potential between -102 to -14 mV while others exhibit values of oxidation between 0 and +119 mV. Redox potential values of +118 to -414 mV are generally classified as anaerobic conditions where oxygen depletion is observed. Oxygen depletion can result from a number of natural factors, but is most often a concern as a consequence of pollution and eutrophication in which plant nutrients enter a river, lake, or ocean, and phytoplankton blooms are encouraged. For the groundwater, these redox potentials are expected but this condition is likely to endanger the life of fish in the surface water body.

The EC values of groundwater from the area are generally low, ranging from 158 to 1421 µS/cm with a mean of 533.62±370.69 µS/cm. The mean conductivity value is less than 1,500 µS/cm, the guideline value set by the World Health Organization (WHO, 1996). The samples from the area contain fresh water since the TDS values evaluated are less than 1,000 mg/l (Davis and De Wiest, 1966). The mean TDS is 351.04±246.37 mg/L with a range between 94.00 and 846.00 mg/L. The low-TDS content observed could either be a result of the slow decomposition of most rocks or short residence time of the groundwater.

3.2 Water type

A Box plot (Fig. 4) indicates the concentration distribution of the various major ions in the groundwater and shows that the hydrochemistry is dominated by bicarbonates, calcium, magnesium and sodium ions. The ion concentration percent - frequency diagrams (Fig. 5a & 5b) were used to determine the frequency of the groundwater samples falling within a certain percentage of values for a particular ion. This diagram defines the relative content of a cation or an anion as a percentage of total cations and anions, respectively (Sen and Al-Dakheel 1986).

Figures 5a & 5b indicate that, in this groundwater system, there is Na+K cation and HCO₃⁻ anion dominance in most of the waters. In few cases Mg²⁺ and Ca²⁺ cations also extend to the zone of dominance (meq/l% > 50%). Since Na+K cations constitute as much as 50% of the totals, water in the area can be recognized as a (Na/K, Mg and Ca) cation type and identified by the names of all the important cations. For most of the boreholes, HCO₃⁻ is the only anion that extends to the zone of dominance (meq/l% > 50%), whereas in some cases, the Cl⁻ ions extend to the zone of dominance. Sulphate ions are considerably well below the dominance level (meq/l% > 50%) (Fig. 5b). Hence, a bicarbonate and chloride type of water is seen in the area.

3.3 Water – rock interaction processes

Most transformations on the earth's surface are controlled by interactions between water and rocks. The minerals that make up the rocks react with aqueous solutions; primary minerals are dissolved, thus freeing ionic species in solution and secondary minerals precipitate at thermodynamic equilibrium or in over saturated domain (Helena et al, 2000). The alteration processes are usually very complex and for this reason, geochemical models have been developed to understand and simulate the reactions occurring between a set of minerals, constituting a rock and an aqueous solution at thermodynamic disequilibrium (Clement et al. 1994).

In the present study, saturation indexes (SI) with respect to carbonate (dolomite, calcite fluorite and apatite) and evaporate (gypsum, anhydrite and halite) minerals, as well as activities of soluble species were calculated by using the chemical program PHREEQC (Parkhurst and Apello, 1999), the expression of Debye and Huckel is used for computation of coefficient activities, because all investigated groundwaters have generally low total dissolved solids.

Figures 6a and 6b show the plots of SI against equivalent concentrations of the minerals for all the investigated groundwater samples. We may assume that SI values falling within range ± 0.5 units from 0 indicate the equilibrium state (Plummer et al. 1976). Most of the considered groundwaters are saturated with respect to calcite, dolomite, fluorite and hydroxyapatite indicating that these carbonate mineral phases may have influenced the composition of groundwater for the period (Fig. 6a). Calcite precipitation could result from two main sources; the weathering of limestone and the incongruent weathering of silicate minerals whereby bicarbonate and calcium ions are liberated. Calcite precipitation kinetics may be retarded as a result of the blockage of precipitation sites or the presence of precipitation inhibitors such as magnesium, phosphorus and organic matter (Doner and Pratt 1968; Suarez 1977; Levy, 1981), leading to calcite supersaturation. On the other hand, groundwater samples are found to be unsaturated with respect to evaporate minerals (Fig. 6b) indicating phases undergoing dissolution for halite and gypsum. This explains the high concentration of evaporate elements in the groundwaters.

The pH and Oxygen Reduction Potential (ORP) play significant role in minerals dissolution process. Apatite and carbon dioxide CO_2 (g) saturation are strongly influenced by increasing pH of groundwater in the study area (Figure 7), while, fluorite saturation is not affected. The decrease in carbon dioxide saturation with increasing pH could be due to the absence of hydrogen ions in solution which are necessary for CO_2 (g) production from carbonate species in solution resulting in less carbon dioxide dissolution in such waters. Redox potential measurements also show no effects on the SI of the mineral species.

3.4 Trace elements

The accumulation of some of these metals in the aquatic environment has direct consequences for humans and the ecosystem. Interest in metals like Zn and Cu, which are required for metabolic activity in organisms, lies in the narrow 'window' between their essentiality and toxicity (Skidmore, 1964; Spear, 1981).

The water presents wide variations in trace element concentration values. Fluoride concentrations vary from below limits of detection to 44 mg/l. The same observations were made for Cu (nd – 1.7 mg/l) and Zn (nd – 0.1 mg/l). Iron values in most of the water samples range from 0.1 – 1.3 mg/l. Except for fluorite which has values far above the WHO threshold of drinking water (WHO, 1996), all the measured trace element concentrations are within acceptable ranges. In order to explore the effect of pH on the water samples in the area; the scatter diagram modified from Gray et al. (2000) of the total metal concentration in groundwater has been plotted (Figure 8). The figure shows the relationship between total metal contents and pH for the water samples. All the samples are near neutral and low to high metal content waters.

In order to explore the possible associations among the measured variables, simple statistical analysis was performed on the data. The Pearson correlation coefficients of pH, EC, TDS and heavy metals in the surface water are summarized in Table 2. Moderate positive correlations exist between elemental pairs Zn–Cu ($r=0.50$). Also similar relationships are exhibited between the ions of Fe–EC ($r=0.66$) and the physico-chemical parameters of pH–EC ($r=0.55$). The relationships between ORP–TDS ($r= 0.72$), TDS–Fe ($r=0.72$), EC - TDS ($r= -0.78$) and pH- ORP ($r= -0.79$) are regarded as strong relationships.

The lack of significant correlation between pH and the elemental ions could be inferred as the pH of the waters show no significant contribution to the dissolution of the ions of Fe, Cu, Ni and Zn in the area. This could be as a result of the slightly acidic to neutral pH ranges within which most of the waters in the area fall.

4.0 Conclusions

The ground and surface water resources in the East Gonja district were evaluated for their chemical composition and suitability for domestic and agricultural uses. Frequency distribution plots for some of the physicochemical parameters for example; pH showed values between 5.08 - 8.44 with a mean of 7.34 for the groundwaters. This means that the ground waters in the area exhibited slightly acidic to slightly alkaline conditions. The low pH values of 5.08 to 5.88, recorded for the boreholes can be principally attributed to natural biogeochemical processes such as CO_2 generation in the soil zone through root respiration and the effect from leaching of organic acids from the decay of organic matter.

With regards to the groundwater systems, there is Na+K cation and HCO₃ anion dominance in most of the waters. Nonetheless in few cases, Mg²⁺ and Ca²⁺ cations also extend to the zone of dominance (meq/l% > 50%). Since Na+K cations constitute almost 50% of the total water system studied, the area can be said to contain Na/K, Mg and Ca cation types of water system. For most of the boreholes, HCO₃⁻ is the only anion that extends to the zone of dominance (meq/l% > 50%), that notwithstanding, Cl⁻ ions are also found in certain cases to extend to the zone of dominance. The water types in the study area can therefore be classified as bicarbonate and chloride type of water with regards to anions. Given the water types noticed in the study area, they can be said to be suitable for domestic and agricultural uses.

5.0 Acknowledgements

The authors are very grateful to the National Nuclear Research Institute, Ghana Atomic energy Commission and School of Nuclear and Allied Sciences, Kwabenya, Accra for equipment and expertise support.

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Table 1: Physico-chemical and trace element compositions of water from the East Gonja area

Sample ID	pH	ORP, mV	EC, $\mu\text{S}/\text{cm}$	TDS, mg/l	TH, mg/l	F-, mg/l	Fe, mg/l	Cu, mg/l	Ni, mg/l	Zn, mg/l
VL1	8.3	6.0	107.2	75.6	88.0	1.2	0.9	0.3	0.4	0.1
BR2	6.9	-16.0	804.0	571.0	352.0	1.7	0.3	0.1	0.3	0.1
BJ3	5.1	119.0	31.6	22.6	64.0	nd	0.5	0.3	0.3	nd
BJ4	7.4	-32.0	739.0	524.0	208.0	28.2	0.1	nd	0.1	nd
LN5	7.8	-52.0	874.0	623.0	80.0	0.7	0.2	0.2	0.7	0.1
LN6	7.1	28.0	140.1	99.7	96.0	44.2	0.5	0.4	0.5	0.1
NG7	7.3	-33.0	877.0	620.0	216.0	33.5	0.2	0.7	0.2	nd
IP8	6.5	46.0	221.0	158.0	184.0	9.6	0.3	0.2	0.3	nd
IP9	7.0	25.0	83.0	59.0	88.0	1.1	1.3	1.7	0.5	0.2
KB10	7.7	-66.0	1040.0	738.0	56.0	1.5	0.2	1.5	0.5	0.2
KB11	7.4	-42.0	850.0	603.0	144.0	1.5	0.2	0.3	0.1	0.2
KB12	6.1	27.0	61.3	43.5	80.0	nd	0.4	0.6	0.2	0.3
KW13	7.5	-50.0	1192.0	846.0	104.0	0.9	0.2	0.8	0.7	0.2
VL14	8.4	8.0	48.6	35.1	56.0	nd	0.4	0.1	0.6	0.1

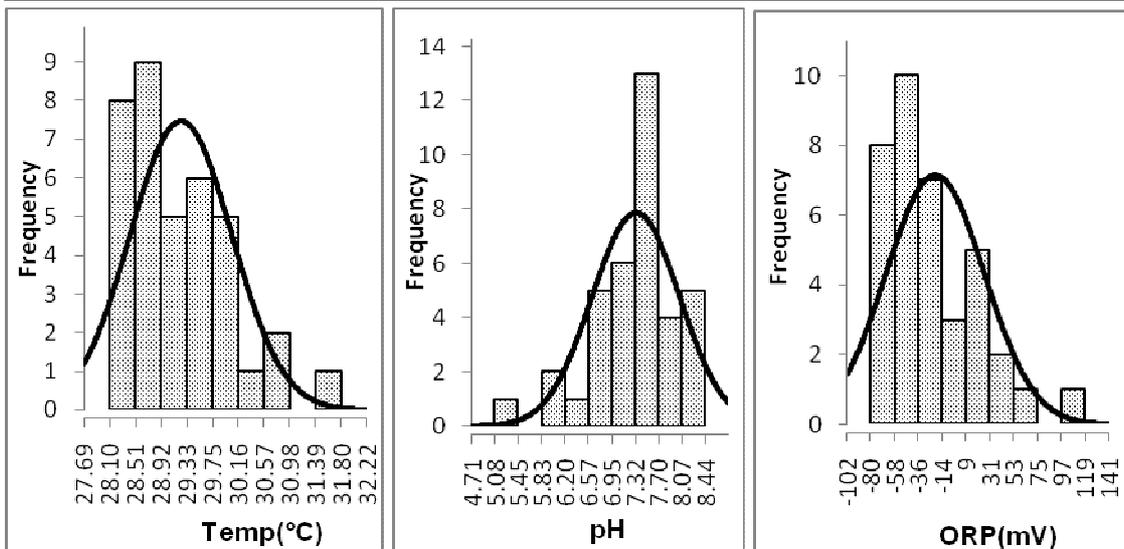


Figure 2: Distribution of Physico-chemical properties: temperature, pH and redox potential of water samples from the East Gonja area.

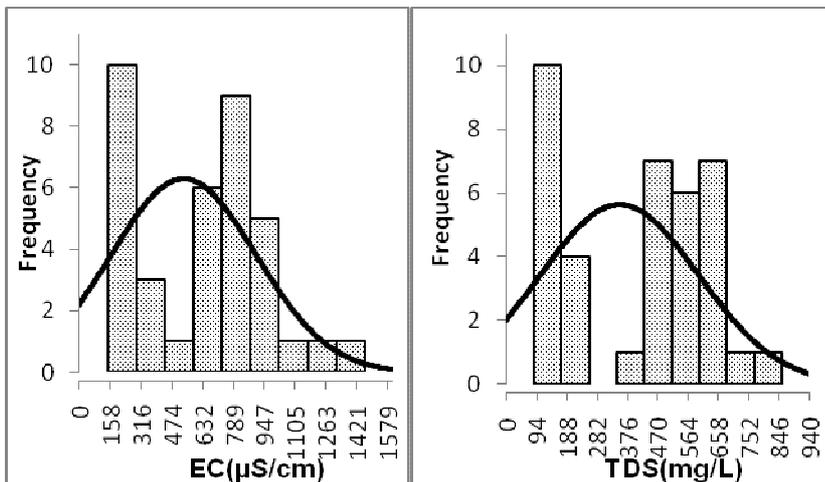


Figure 3: Distribution of Physico-chemical properties: EC and TDS of water samples from the East Gonja area.

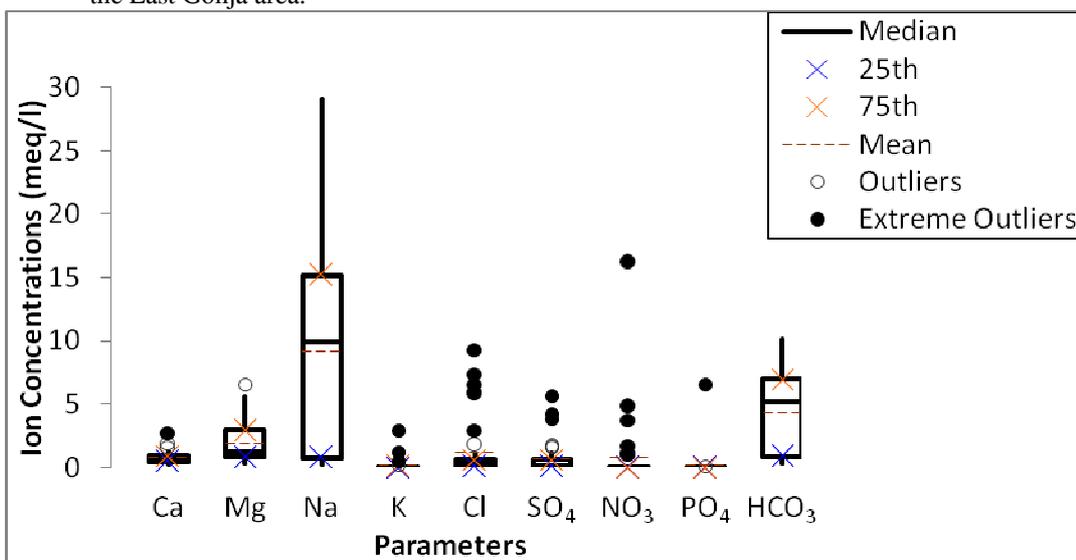


Figure 4: Box plots of the major ions: nitrate and phosphate

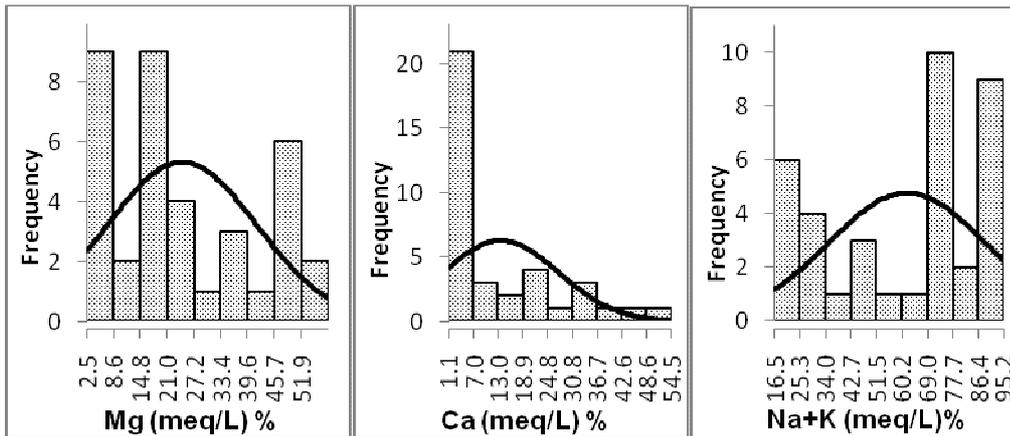


Figure 5a: A frequency distribution of the percentage contributions of major cations

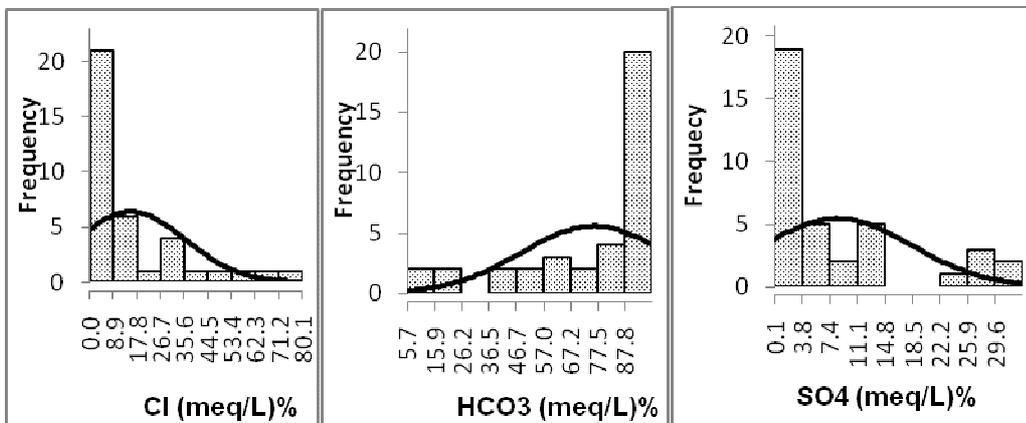


Figure 5b: A frequency distribution of the percentage contributions of major anions

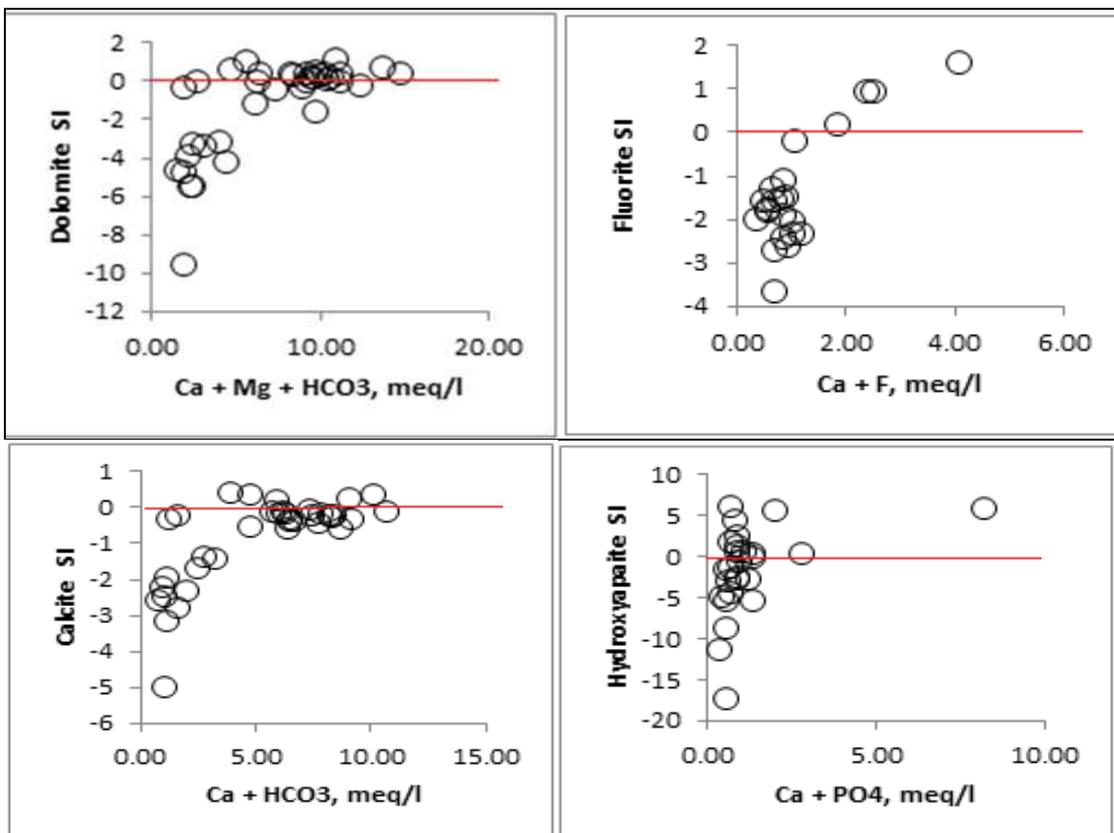


Figure 6a: Plots of saturation indices with respect to some carbonate minerals.

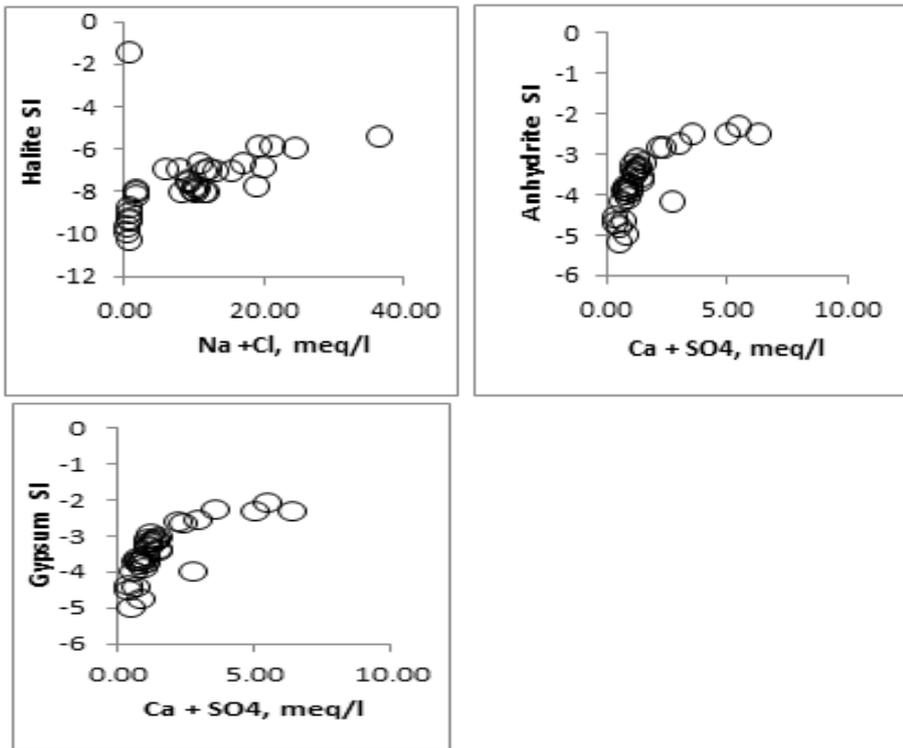


Figure 6b: Plots of saturation indices with respect to some carbonate minerals.

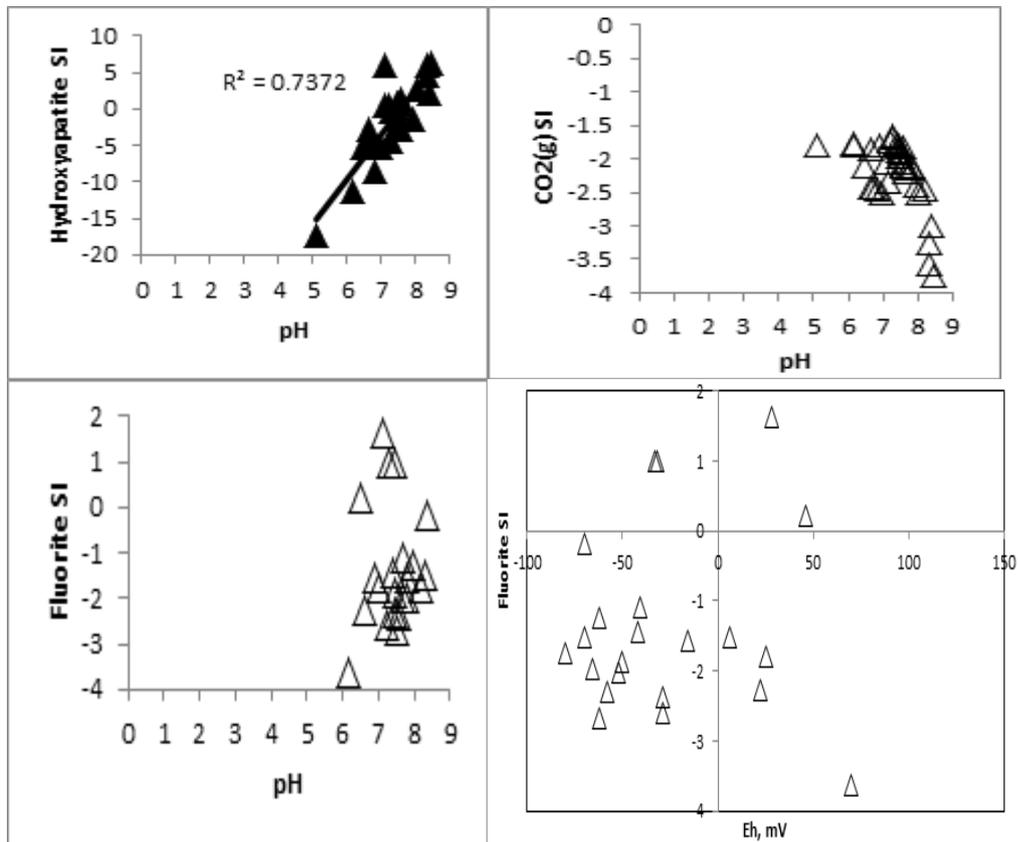


Figure 7: Eh/ pH effect on SI

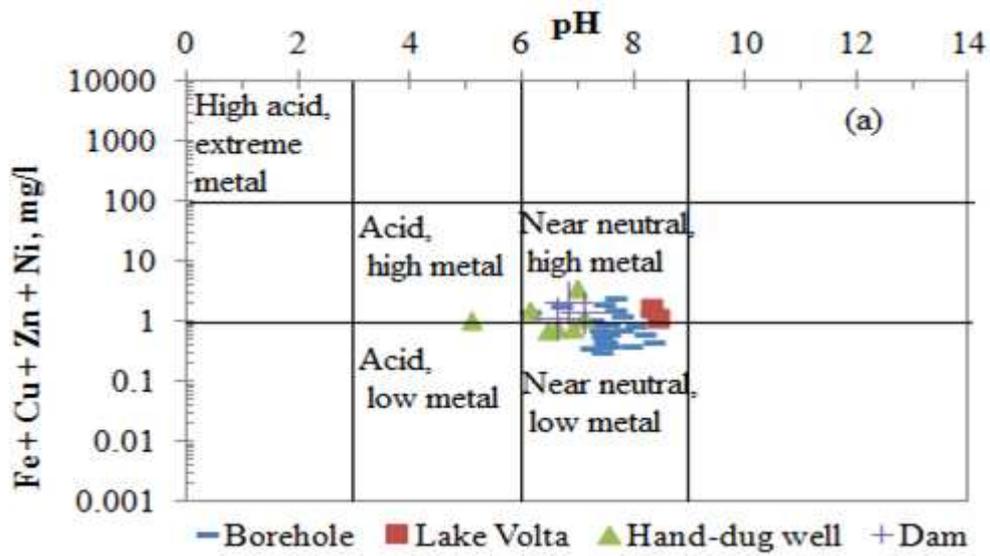


Fig. 8: Scatter diagram of the total metal concentration in ground and surface water versus pH

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