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Major ions and trace elements partitioning in unsaturated zone profile of the Densu river basin, Ghana and the implications for groundwater

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Soil solution samples were extracted from a vertical unsaturated zone profile and groundwater samples were obtained from the Densu river basin, Ghana. Major ions and trace metals in the soil solution, groundwater samples and solid soil (Ca^{2+} , Na^+ , Mg^{2+} , K^+ , NO_3^- , SO_4^{2-} , Cl^- , HCO_3^{2-} , PO_4^{3-} , Fe, Mn, V, Cu, Zn, Cr) were analyzed along with other hydrochemical parameters. Impact of the unsaturated zone soil solution chemistry on the groundwater and metal mobility and potential of leaching into the groundwater system have been evaluated. The groundwater were characterized by slightly alkaline pH (6.22 to 6.67), EC (98.8 to 382.0 $\mu\text{S}/\text{cm}$), TDS (49.7 to 192.4) and total alkalinity (43.63 to 149.14 mg/L). Calcium was the dominant cation, with major amounts of sulphate, chloride, nitrate and carbonate species present. Na/K cations dominated the leached soil-solution with SO_4^{2-} and Cl^- anions. Soil-liquid partitioning coefficients (K_d) for the metals Fe, Cu, Mn, Cr, V and Zn evaluated after experimental determinations showed wide variability within the profile. The relationships between the calculated values were explored relative to variations in soil solution pH, soil organic carbon (SOC), and concentrations of total soil metal. The results of the empirical linear regressions showed K_d values were best predicted with total soil metal contents (with R^2 values of 0.04 to 0.69).

Key words: Unsaturated zone, groundwater, major ions, trace elements, partitioning coefficient.

INTRODUCTION

In Ghana about 74% of the total population of 18.4million people lives in rural areas (Ghana Statistical Services, 2000 Population and Housing Census provisional results). Water delivery to these rural settings is mainly through the collection of surface water, rain and groundwater by boreholes and hand-dugwells. The Densu river basin lies between latitude 5°30'N to 6°20'N and longitude 0°10'W to 0°35'W in the southern part of Ghana. The basin has one of the highest rural human population densities of more than the 10 river basins in the country (WRC, 2003).

Understanding the behavior of major and trace metals

in the unsaturated zone is becoming increasingly important, especially in the basin, as growing cities and communities struggle with problems of environmental contamination, waste storage and land use, and dwindling water supplies from surface water bodies (Asante and Ansah-Asare, 1998; Fianko et al., 2010). Groundwater sources became the best alternative source of portable water. For this reason the quality of the groundwater then needs to be sustained. With this in mind, it has become imperative to critically examine the chemistry of the soil in unsaturated zone and water chemistry of underlying groundwater in evaluating the impacts of ion behaviour in soils on the groundwater chemistry.

Solutes in aquifer systems generally originate from reaction of water with the solid framework of the aquifer, from advective or diffusive transport from underlying or

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adjacent aquifers, or from atmospheric precipitation (Wood et al., 2003). Fordyce et al. (2000) and Siegel (2002) have shown that the occurrence and geographical distribution of certain diseases could be correlated with the presence of toxic elements in the geologic environment as well as input from anthropogenic sources. Quantifying the amounts of these elements in soil, water and air gives an indication of the potential hazard(s) they are likely to pose to the environment and the living organisms in events where they exceed thresholds. For example, nitrate is a major problem for bottle-fed infants, in whom the risk of methaemoglobinaemia ("blue-baby syndrome") increases as the concentration of nitrate rises above 50 mg/L. The risk is increased by the presence of nitrite, which is a much more potent methaemoglobinemic agent than nitrate, and by the presence of microbial contamination, which can lead to gastric infections in infants (WHO 2004; WHO 2006).

Although significantly high levels of iron and manganese are not suspected of causing direct health effects through their presence in drinking-water, they can cause severe discolouration of water, which may lead to consumers turning to other, microbially unsafe sources of drinking-water. High concentrations of sulfate, in association with cations, such as magnesium, may have a laxative effect on people not accustomed to the water. Similarly, chloride in high concentrations can contribute to a salty taste, although neither sulfate nor chloride is harmful in moderate concentrations.

Health hazards from algal toxins are primarily associated with overgrowth (bloom) events. Algal blooms may develop rapidly and be of short duration; they are generally seasonal and are frequently associated with the presence of nutrients, particularly phosphate (WHO, 2004; WHO, 2006; Thompson et al., 2007).

It has been recognised, however, that total soil metal contents alone are not good measure of mobility and bioavailability, and do not provide a useful tool to assess potential risks and toxicity from contamination of trace elements especially in soils and to groundwater sources (Lee, 2006; Sauve et al., 2000a,b; Chen et al., 2009). Solid-solution partitioning is critical to assess mobility and bioavailability in soils and the potential of leaching of metals from soil to groundwater (Sauve et al., 2003).

The solid-liquid partitioning is often expressed with an empirical distribution coefficient or K_d , which gives the ratio of the concentration in the solid phase (mg/kg) to that in the solution phase (mg/L). Mathematically, the solid-solution partition coefficient K_d is defined in linear form as:

$$K_d = \frac{C_{total}}{C_{soil\ solution}} \quad (1)$$

Where C_{total} (mg/kg) and $C_{soil\ solution}$ (mg/L) refer to the total and solution concentration of the trace element in solution respectively. The K_d value of a metal (l/kg)

reflects the net effect of various reactions in the solid and liquid phases and varies in orders of magnitude among soils (Sauve et al., 2003). It also normalizes the mineralogical and chemical differences of soils and expresses the trace element of the soils in the soluble form that is mobile and bioavailable of the total pool (Lee, 2006).

The objectives of this study were to:

- (i) Investigate impact of major ion chemistry of the unsaturated zone soil on the shallow groundwater.
- (ii) Investigate partitioning of trace metals between the soil solution and soil solids in the unsaturated zone.
- (iii) Assess mobility and potential leaching and contamination of trace elements Fe, Mn, Cu, Cr, Zn and V in the soil to the shallow groundwater tables.

MATERIALS AND METHODS

Sample collection and preparation

Fourteen soil and five groundwater samples were collected from a profile and five locations (Figure 1) in the Densu river basin of Ghana between June and July 2008. The soil samples were obtained from 0 to 500 cm deep section representing the depth of the shallow groundwater table in the area. Samples were taken at every 25 cm interval depth to the water table with a truck mounted drill auger. The incorporated organic debris deposited on the soil surface if any was excluded. The samples collected were stored in clean polythene bags and transported to the laboratory. After air-drying at $29 \pm 2^\circ\text{C}$ in a dust free area for 7 days, each of the samples was disaggregated with a porcelain mortar and pestle to pass 2 mm openings and approximately 350 g of screened soil were gathered and stored. The subsamples were then grounded and homogenized by pulverizing to $>100\ \mu\text{m}$ and $>30\ \mu\text{m}$ using a Retch MM200 ball mill with sample compartment and balls made of agate.

A 5.0 g aliquot each of the pulverized, homogenized powdered soils ($>30\ \mu\text{m}$ fraction) was placed into a die and pressed with a manual press (at a pressure of 15 tons) into 32 mm diameter pellet for total elemental concentration analyses by energy dispersive X ray fluorescence (EDXRF).

Water samples collected were in two sets of 250 ml filtered and unfiltered. The unfiltered bottles were acidified with 10% nitric acid to keep ions in dissolved state. The samples were kept in ice-chest containers at 4°C and later transferred to the laboratory for chemical analysis.

Laboratory analysis

The soil solution concentrations of Fe, Cu, Cr, Mn and V were determined by mixing an aliquot of 1.0 g each of the dried, homogenized soil samples ($>100\ \mu\text{m}$) with 30 ml de-ionised water in the ratio 1:30 (w/v) in pre-conditioned Teflon containers and leached after modified method described by Sheppard et al. (2000). The mixture was agitated vigorously by mechanical shaker (at 20 rpm) to ensure mechanical mixing and equilibration for 16 h and released to settle for 1 hour. The supernatant collected was centrifuge in an IEC Centra GP8R centrifuge model at 3500 rpm for 15 min. The eluted soil-water was then filtered through a 0.45 μm filter membrane (Gelman Inst. Co., London).

The concentrations of the cations, anions and trace elements in the water samples and the soil-solutions were analyzed by Atomic Absorption Spectrometer (Varian AA24OFS), flame photometer

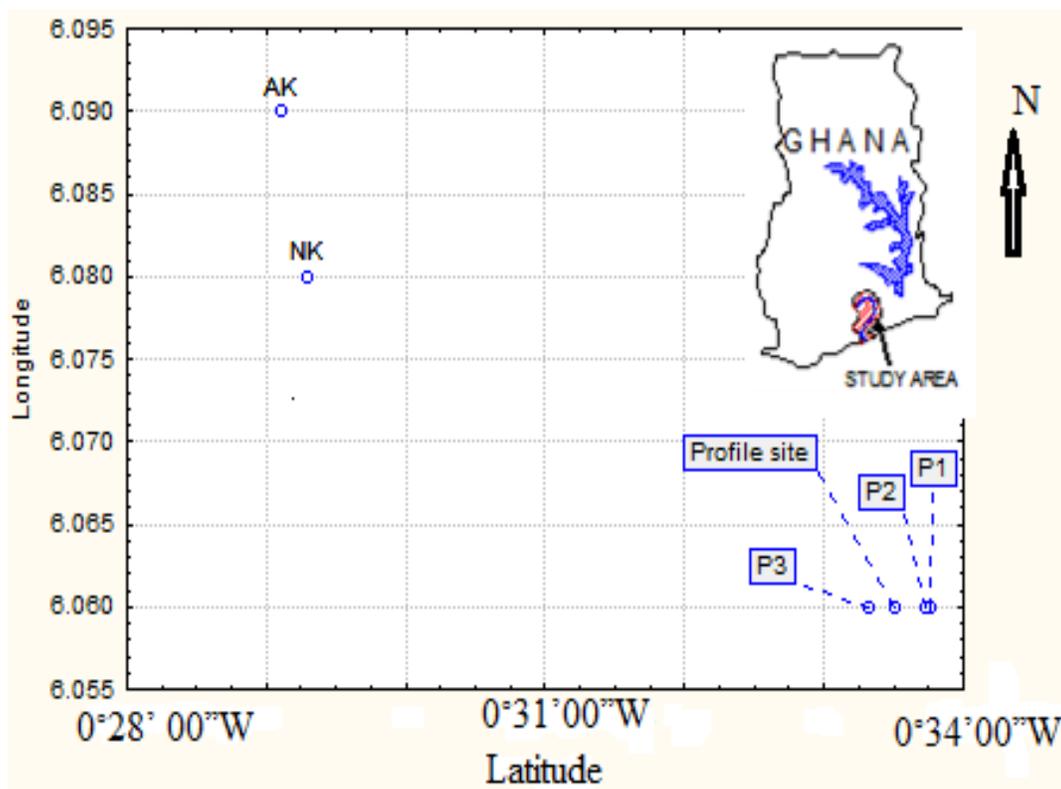


Figure 1. Location map of boreholes and soil sample site within the basin. Index map depicts Ghana with an outline of the Densu river basin. AK-Akoko; NK-Nkronso; P-Potroasi.

(Sherwood Model 420) and Ion Chromatograph (Dionex ICS-90) at the Ghana Atomic Energy Commission laboratories following the procedures described in APHA (1989).

Specific conductance (EC), temperature, TDS and pH were determined in the field using calibrated meters; total alkalinity as ($\text{CO}_3^{2-} + \text{HCO}_3^-$) was determined by titration of a 10 ml aliquot of the solution with 0.73 N hydrochloric acid for water samples, while those of the solutions were determined in the laboratory. Soil pH, Eh and moisture contents were measured after the procedures of Blakemore et al. (1987), using Ion Selective Electrode, Ion 6 (Eutech Instruments Pte Ltd/ Oakton Instruments), and Marshall et al. (1999) respectively.

Replicate extractions of separate sample aliquots were reproducible generally within 10 relative percent for all analytical methods (Table 3), indicating that the 1 g sample was representative. Soil organic carbon was analyzed using loss on ignition (LOI) with a 1 h preliminary drying step at 105°C, weight is then recorded, followed with heating at 450 to 550°C for 3 h and allow to cool in a desiccator, and weigh accurately. Mass loss is calculated as LOI in %. This analysis was carried out at the geochemistry laboratory of Geological Survey Department, Accra-Ghana.

The soil total metal concentrations of Ca, K, Fe, Cu, Cr and V of samples were determined using EDXRF technique. EDXRF provides a rapid and non-destructive method for the analysis of trace and major elements in soil samples. An X-ray generator tube, Compact 3K5 X-ray Generator (Ital IS Structures, Italy) was used for the production of the X-rays. The energy dispersive X-ray fluorescence has a maximum power of 3000 W (60 kV and 50 mA). The samples were irradiated at 800 W (40 kV and 20 mA) with Mo secondary target as the anode for 10 min. A Canberra Si(Li) detector, model SL30165(Canada) with energy resolution of 160 eV

for Mn K α energy peak at 5.895 keV, coupled to a preamplifier and amplifier operating at -500 V, was used to detect the resulting fluorescent X-ray lines. Off-line data analysis of the intensities and concentrations of the selected elements were accomplished with Maestro32 and the AXIL software package developed by the IAEA.

Single metal targets of Fe ($K\alpha = 6.400$ keV), In ($K\alpha = 24.139$ keV), Mo ($K\alpha = 17.433$ keV) and standard reference material ESTUARINE SEDIMENT 1646a (NIST, USA) and reference material, IAEA SOIL-7(Austria) were analyzed to calibrate the instrument and these were again analyzed intermittently during sample irradiation for analytical precision and accuracy.

Statistical analysis and graphical representations

Graphical representation of the major cations and anions to delineate the relation between the soil solutions and the waters was accomplished by plotting a Piper diagram and Microsoft office excel 2007 for Windows.

RESULTS AND DISCUSSION

Soil characteristics

Soil strata was classified using Munsell soil colour chart and texture and wetness determined after Faniran and Areala (1978). The classification was based on the unified soil classification system of the United States Department of Agriculture (USDA) 1995. Details are

Table 1. Soil characteristic as determined from the profile.

Depth (cm)	Moisture content and texture description	Strata description at Potroasi
0 – 20	Slightly moist: Less cohesive can slightly or not be moulded.	SP: Gravely sand, with little or no fines, non plastic Blackish, loose, homogeneous residual.
20 –125	Dry to slightly moist: cohesive soils friable and powdery, cohesion less and free running.	SM: Silty sand, low plasticity, Blackish Brown to Red stiff, homogeneous, residual.
125 – 245	Slightly moist to moist: soil feels cool. a cohesive soil hence can be moulded.	CL: Gravely Silty clay, low to medium plasticity Brownish to Yellowish Red, stiff, homogeneous, residual.
245 – 350	Moist to wet: cohesive can be moulded within the fingers, free water forms on hand when handling.	CL: Silty clay, low to high plasticity, Reddish, Brownish to Yellowish Grey, soft, homogeneous residual .

presented in Table 1.

The total organic carbon content of the soils ranged between 20.0 to 25.0% with a standard deviation of 2.2%, this decreases down the profile.

Moisture content, pH and redox potential conditions of the unsaturated zone

The moisture content of the soils based on the weight loss upon heating at 105°C ranged from 10 to 30%. This water likely includes free water, water adsorbed to minerals surfaces, water within the interlayer of expansive clays and some water of crystallization in some hydrated salts (Breit et al., 2009). The amount of water lost increased with depth. The lowest water content was measured in near surface samples, with similarly low concentrations at the 350 cm depth. The low water content between 25 and 50 cm for the profile is consistent with the low matric potentials of the silty sand and gravely sands (with no fines particles) identified in this depth range. The fluctuations encountered in the water content of the profile in the intervals of 50 to 350 cm may be due to the soil texture differences. Soil pH is the most important parameter influencing metal-solution and soil-surface chemistry. The dependence of heavy metal adsorption on, example, clays on soil pH has been noticed early. In general, heavy metal adsorption is small at low pH values. At high pH values, the metal ions (example, Zn, Cd and Cu) are completely removed (Bradl, 2004). pH values for the profile ranged between 5.6 to 8.3 pH units. This pH range may not support effective leaching of the heavy metals from the soil surface to the groundwater system by rainfall events. The soil depth of 25 to 100 cm registered the highest pH values. The soil pH decreased down the profile. Soil pH is affected by the changes in redox potential which occur in soils that become waterlogged periodically. The redox potentials Eh (mV) recorded for the entire profile ranged

between -107.1 (pe= -1.6) to +50.2 (pe= 0.8). Eh (mV) values become more positive down the profile. The soils can be classified as anaerobic soils. The anaerobic nature of the soils is attributed to the fact that the area usually experience stagnation of water during the wet seasons and this led to the depletion in atmospheric oxygen, O₂ resulting in reducing properties of the soils (Vepraskas and Faulkner, 2000). The relationship between soil pH and soil Eh (mV) is obvious, that as high alkaline pH are responsible for high negative reducing potentials encountered in the profile. Figure 2 shows the variation of the pH, Eh and the moisture content with depth.

Ground water composition

Selected compositional parameters measured on water samples from boreholes are presented in Table 2. The groundwater is characterized by slightly alkaline pH (6.22 to 6.67), Electrical conductivity (98.8 to 382.0 µS/cm), TDS (49.7 to 192.4) and total alkalinity (43.63 to 149.14 mg/L). Calcium is the dominant cation, with major amounts of sulphate, chloride, nitrate and carbonate species present. Cu, Fe, Mn, Cr, V and Zn are commonly considered as trace elements in groundwater but Cu and Mn are present in significantly high concentrations in the basin. The trace elements are likely derived from the weathering of the aquifer framework. Chromium in solution (Cr⁶⁺) almost certainly represents the weathering of pyroxene (Wood et al., 2003). The absence of Cr may be due the likely absence of weathered Cr-rich pyroxene. Dissolved Zn is probably derived from the weathering of the mineral sphalerite (ZnS) in the heavy mineral fraction of the soils. Calcium and V are associated with weathering of silicate bearing minerals for example, calcic-rich component of the plagioclase feldspars, pyroxenes, anorthite and amphiboles found in the study area (Alloway, 1995; Ganyaglo et al., 2010).

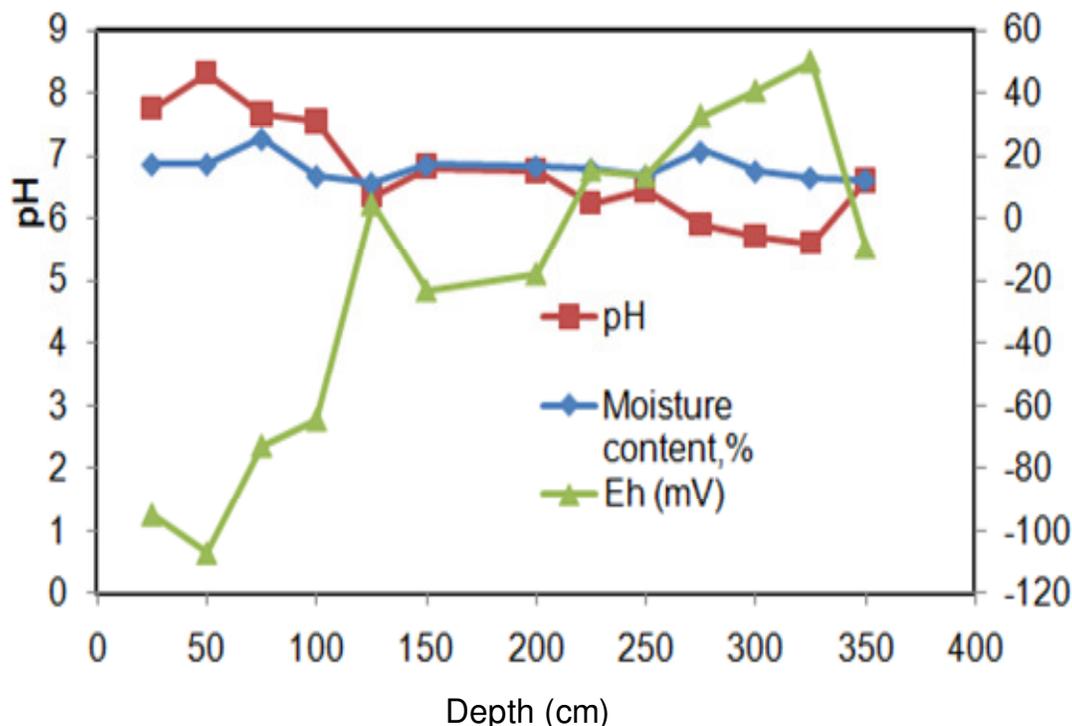


Figure 2. The depth profile of pH, Eh and moisture content.

Table 2. Chemical composition of groundwater sampled from boreholes in the Densu basin near the soil sampling site.

Parameter	P1	P2	P3	AK	NK
pH	6.37	6.67	6.58	6.44	6.22
EC ($\mu\text{S}/\text{cm}$)	300.00	382.00	188.80	121.30	98.80
Na^+ (mg/L)	55.30	55.70	35.10	46.80	30.80
K^+ (mg/L)	23.00	39.10	18.40	80.50	46.0
Ca^{2+} (mg/L)	160.60	197.00	63.00	56.80	58.00
Mg^{2+} (mg/L)	87.00	92.28	54.96	22.68	27.00
Cl^- (mg/L)	119.00	1242.50	241.500	255.5	297.50
NO_3^- (mg/L)	39.50	28.46	22.35	7.16	1.59
SO_4^{2-} (mg/L)	488.16	775.68	1280.60	463.20	237.60
HCO_3^- (mg/L)	108.40	180.80	92.00	76.00	50.80
PO_4^{3-} (mg/L)	0.15	0.02	0.08	0.18	0.14
Fe (mg/L)	0.255	0.251	0.298	0.289	0.02
Mn (mg/L)	5.69	2.46	8.86	11.91	7.37
V (mg/L)	0.22	<0.08	0.018	0.17	0.10
Cr (mg/L)	<0.001	<0.001	<0.001	<0.001	<0.001
Cu (mg/l)	0.90	11.21	3.99	9.06	9.57
Zn (mg/l)	3.20	<2.00	<2.00	2.10	<2.00
TDS (mg/l)	150.6	192.4	96	60	49.7

The presence of some dissolved iron and manganese in the water samples (Table 2) are interpreted to indicate that the water has a high reducing potential. The nitrate levels of 1.59 to 39.50 mg/L in the groundwater then

raises concern for its mechanism of incorporation. Nitrite and nitrate are inorganic ions produced during various stages of the nitrogen cycle. Nitrate is predominant ion in well-oxygenated water, because of the rapid oxidation of

Table 3. Chemical composition of water-extract solutions prepared by reacting 1g of dried sediment from the Densu River Basin with 30 ml of de-ionised water for the profile.

Depth (cm)	pH	EC ($\mu\text{S/cm}$)	HCO_3^- (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	PO_4^{3-} (mg/L)
0- 25	7.42	115.0	60	129	180	66.3	38.7	199.86	172.65	41.46	<0.001
25-50	7.52	109.1	60	153	237	65.7	38.1	242.34	140.55	45.09	0.81
50-75	7.34	77.7	40	84	291	37.8	39.6	62.61	109.02	34.86	<0.001
75-100	6.88	51.6	30	75	291	27.3	46.5	38.58	203.04	35.91	<0.001
100-125	6.82	48.0	30	81	306	22.5	48.3	55.15	286.26	40.17	<0.001
125-150	6.9	50.8	30	87	168	24.6	46.5	157.38	489.84	5.08	0.48
150-175	6.52	31.6	20	90	45	9.6	41.4	101.58	927.78	6.00	<0.001
175-200	6.41	44.8	20	342	36	5.7	39.6	404.79	235.68	16.17	<0.001
200-225	6.45	39.8	20	87	75	6.3	39.9	36.12	571.65	20.01	<0.001
225-250	6.14	22.2	10	93	120	2.1	35.1	78.42	118.74	12.87	<0.001
250-275	6.22	15.3	10	174	693	10.5	47.7	60.69	79.38	11.76	<0.001
275-300	6.33	16.0	10	141	675	11.4	45.0	24.06	94.44	7.65	6.36
300-325	6.51	25.5	10	180	798	15.3	47.4	190.05	140.07	12.51	0.66
325-350	7.04	32.7	20	207	1035	23.4	54.0	21.45	81.45	14.4	<0.001

nitrite. Nitrate is used mainly in inorganic fertilizers. Therefore, its concentration in groundwater and surface water is normally low; nitrate can reach high levels as a result of leaching or runoff from agricultural land or contamination by human or animal wastes (Ekmekci, 2005). Owing to its negative charge (NO_3^-) is not held in the soil, the majority being leached to the saturated zone (Canter, 1996; Novais et al., 2008). It was found that nitrate concentration in waters in the study area comprises NO_3^- , and NO_2^- and NH_3 are absent or below detectable levels. This indicates that the pollution is not actual and that the areas from which the waters recharge are oxygen rich and feature an oxidizing environment, that is sufficient to perform the transition of NH_3 to NO_3^- ($\text{NH}_4^+ + 2\text{O}_2 = \text{NO}_3^- + \text{H}_2\text{O}$). This indicates that rain water, which is one of the main sources of recharge in the basin (Ganyaglo et al., 2010, Gibrilla et al., 2010) does not reach the groundwater rapidly and

therefore the permeability of recharge areas of the waters is not very high as indicative of the clayey layers found in the unsaturated zone lithologic log as one moves down. However, the leaching of nitrate from the surface through the soil zone could mean that shallow wells could be at risk of pollution from soil surface activities.

Impact of major ion chemistry on groundwater in the unsaturated zone

Presentation of chemical analysis in graphical form makes understanding of complex groundwater system simpler and quicker. The objective is to discuss the major ion chemistry of the leached soil solution and the groundwater samples within the catchment of the profile using the method proposed by Piper (1953).

The Piper plot (Figure 3) for leached soil- solution

and groundwater, indicates the groundwater were of 80% $(\text{Ca}+\text{Mg})\text{SO}_4/\text{Cl}_2$ and 20% $(\text{Na} +\text{K})\text{SO}_4/\text{Cl}$ water types consistency with the earlier findings of Ganyaglo et al. (2010).

The dominant cations obtained from the leached soil-solution are Na/K. The dominant anions are SO_4^{2-} and Cl^- . The leached soil solution were of $(\text{Na}+\text{K})\text{SO}_4/\text{Cl}$ water type. The difference in the groundwater types and the leached soil-solution can be attributed to the fact Na^+ ions are easy to leach out since Na forms soluble salts that easily dissolves in water, while Ca^{2+} salts are not soluble as Na. The exchange of the cation Na^+ for Ca^{2+} is however possible in geochemical environments where weathered calcic-rich component of the plagioclase feldspars, pyroxenes and anorthite are found. This may account for the variations in the cation compositions. The interaction of the groundwater with the aquifer materials has been longer than the soil solution, hence the dominance

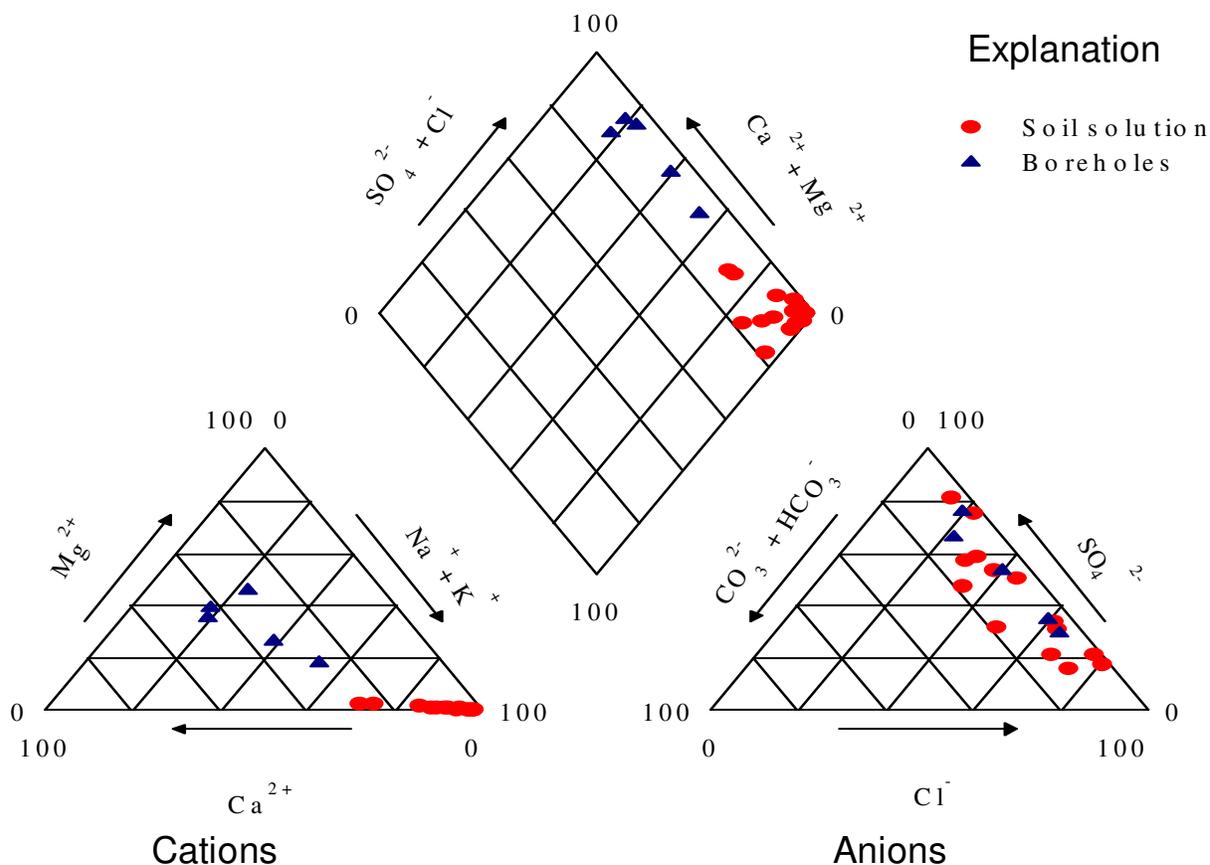


Figure 3. Groundwater samples from the profile catchment and soil-solution plotted in Piper Tri-linear diagram.

of Ca^{2+} over Na^+ ions. The dominance of the anions SO_4^{2-} and Cl^- in both groundwater and the soil solutions were indication of the direct influence the unsaturated zone chemistry have on the groundwater chemistry in the area (Chebotarev, 1955; Driscoll, 1995).

The nitrate levels were high (between 41.6 to 40.0 mg/L) at the topmost 0 to 125 cm and decreases down the profile to 14.4 mg/L at 350 cm depth. This observation was attributed to the input of nitrogen derivatives applied to soils in the area and shows anthropogenic pollution, an indication of leaching were observed in nitrate levels in the groundwater.

Solid soil-solution partitioning of trace elements

The K_d concept is frequently adapted in sorption studies and it represents the ratio between dissolved and adsorbed metal, rather than total metal of contents. However, it is the proportion of dissolved metal that is of concern and the K_d from the total metal content were appropriate for this study (Lee, 2006). The values of K_d varied from 4,016.47 to 25,277.89 for Fe, 114.89 to 514.32 for Cu, 239.59 to 2588.67 for V and Mn 18.64 to 699.44. For Cr and Zn, dissolved metal concentrations for

some samples were too low and therefore, K_d values could not be evaluated. Generally, K_d values increased with depth. The increase in K_d values is in the order $\text{Cu} < \text{V} < \text{Mn} < \text{Fe}$; indicating a decreasing solubility in the same sequence. The decrease in solubility of the metals with depth implies groundwater is less susceptible to contamination through leaching of these trace elements.

From earlier works of Bradl (2004), Sauve et al. (2003) and Lee (2008) where pH, total metal contents and SOM contributed significantly to metal ions in solution, the linear relationship between the K_d values and soil properties as pH, soil organic carbon represented by LOI and the total metal content in establishing which components contributes most in solubility of the trace metals was explored. The linear relationship between K_d and soil solution pH indicate between 8 to 52% for the variation of V, Mn and Cu. For Fe, the dissolved metal concentration was so low that R^2 value was less than 0.01. The linear relationships between K_d and total metal contents explained more about the variation, with 69% for Mn, 62% for Fe, 24% for Cu and 4% for V. The K_d – LOI relationship reveal similar trend as observed for pH- K_d relationship with Fe recording the least 1%, V with 5%, 29% for Cu and 32% for Mn. Total soil organic carbon

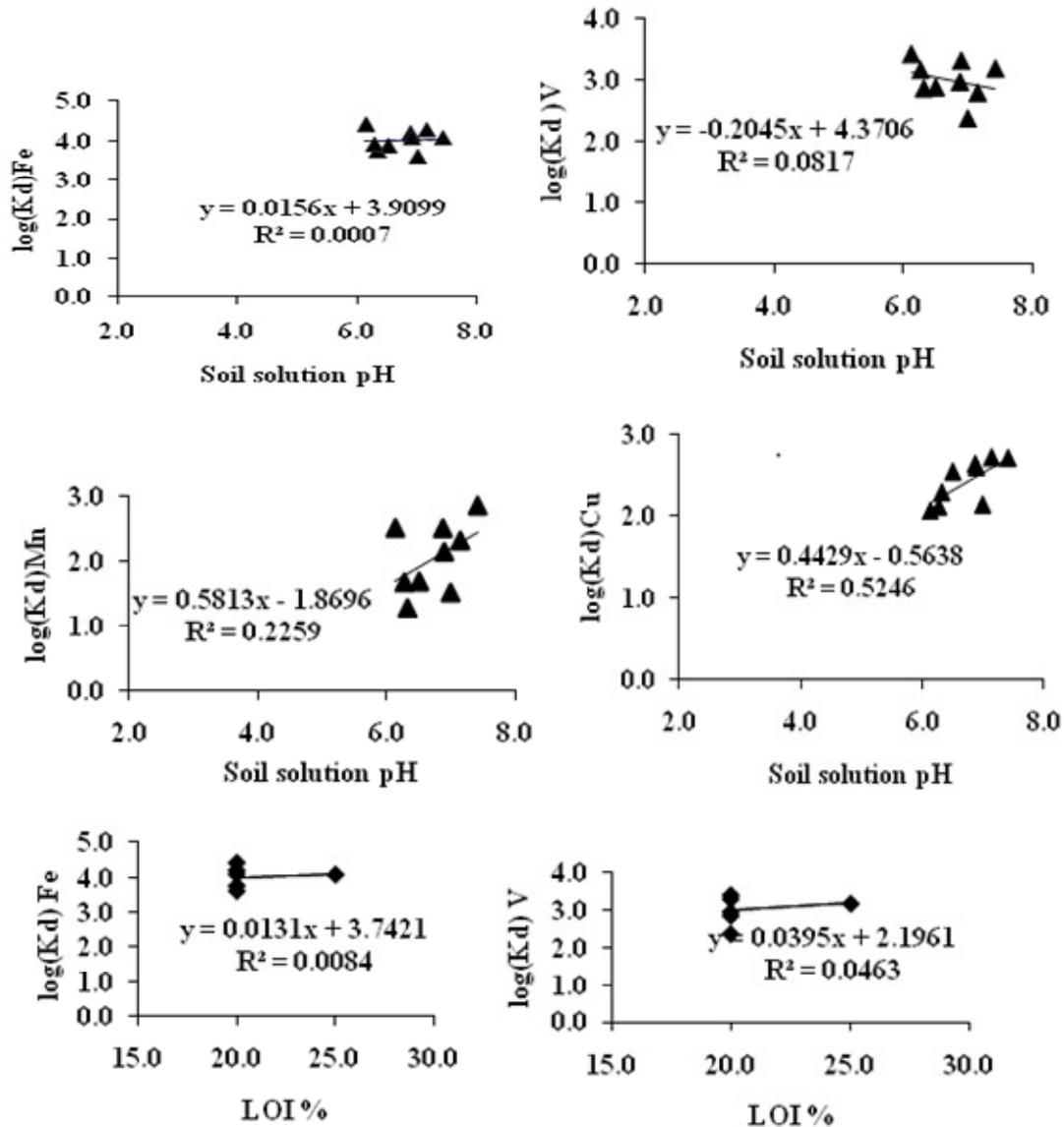


Figure 4. Correlation of K_d with pH and soil organic carbon (LOI).

contents (LOI) of the soils were used in accounting for the impact of soil organic matter as the conversion was a scalar factor.

Although some metal specific behaviour were observed (Figures 4 and 5), the dissolved metals in the soil solution were total metal contents dependent to a greater degree but; this alone does not predict the dissolved metal contents of the soil solution. However, in this study, the total metal contents control more of the dissolved metals contents in the soil solution, which implies that land use activities like farming which tills the land could lead to the release of trace elements into solution.

Conclusion

The vertical profile of the unsaturated zone solution

chemistry of the Densu river basin has some direct impact on the groundwater chemistry and this were controlled by the weathering of silicate bearing minerals for example, calcic-rich component of the plagioclase feldspars, pyroxenes, anorthite and amphiboles found in the area. The permeability of water through the unsaturated zone is not very high as indicative of the clayey layers found in the unsaturated zone lithologic log as one moves down. However, the leaching of nitrate from the surface through the soil zone could mean that shallow wells could be at risk of pollution from soil surface activities.

A large variability is observed among the reported values of K_d for the soils at different depths and the general order of solubility of trace elements in the soil profile is $Fe < V < Mn < Cu$. The relationships between

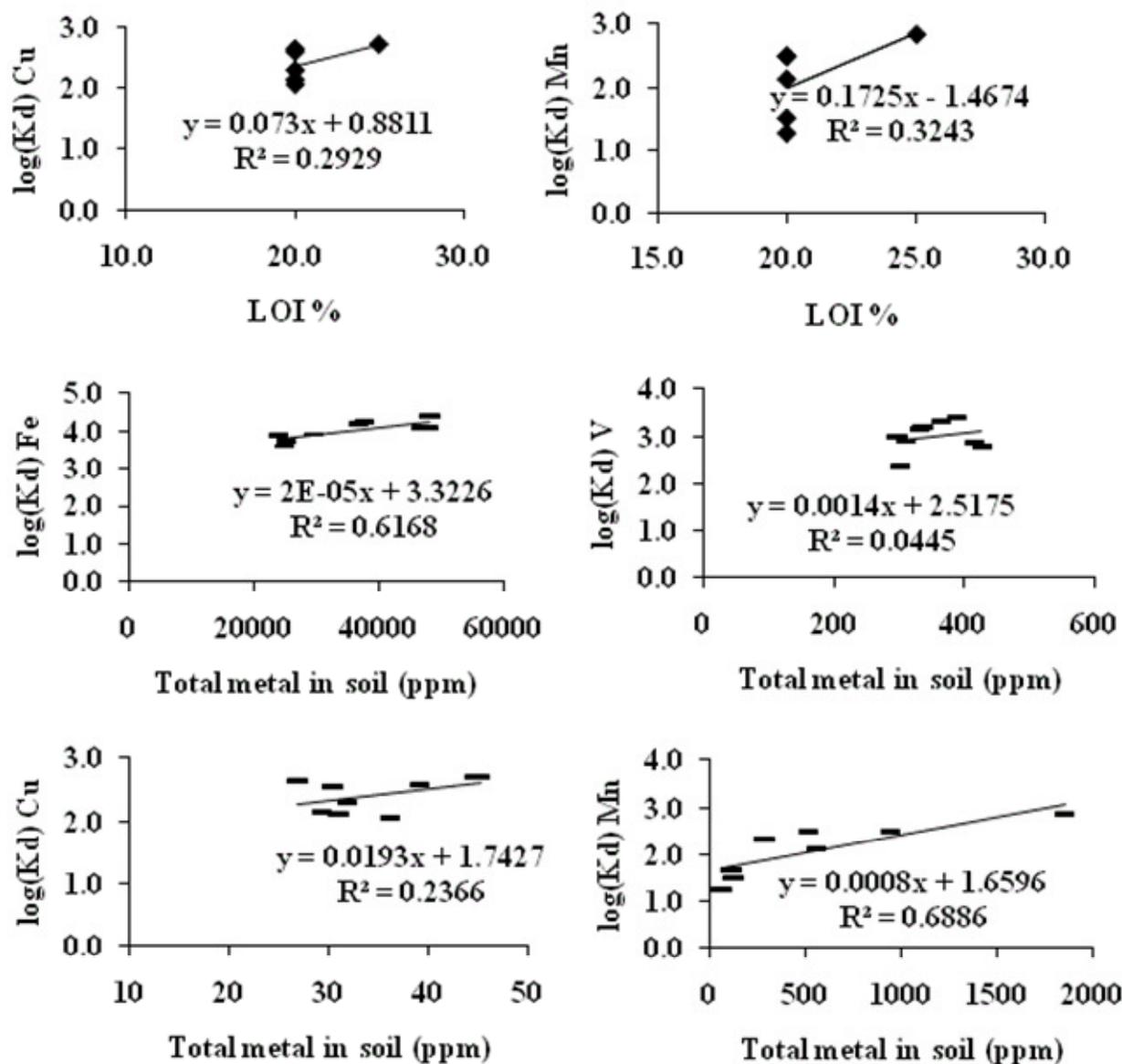


Figure 5. Correlation of K_d with soil organic carbon (LOI) and total metal contents.

the reported values of K_d explored relative to variations in soil solution pH, soil organic carbon (LOI), and concentrations of total soil metal predicted using empirical linear regressions shows that K_d values are best predicted with total soil metal (with R^2 values of 0.04 to 0.69).

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