

## Controls on groundwater chemistry in a highly urbanised coastal area

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Received 7 Oct. 2009;

Revised 29 Aug. 2010;

Accepted 5 Sep. 2010

**ABSTRACT:** Douala metropolitan city located in the littoral province of Cameroon, has experienced a rapid urbanisation and industrialisation. The city depends heavily on groundwater as a resource. Due to ubiquitous sources of pollution, groundwater quality and contamination has become an important issue for this urban groundwater supply. This study uses the major ion chemistry of groundwater together with the mineralogical and chemical composition of sediments to investigate the chemical characteristics and contamination of groundwater. An attempt has been made to identify the different factors controlling the chemical composition of groundwater. Groundwater is acidic (4.1-6.9) and the chemistry is more influenced by atmospheric inputs and anthropogenic activities than by aquifer water reactions. The ionic content of groundwater shows a large variation with electrical conductivity ranging from 34.3-1021  $\mu\text{S}/\text{cm}$ . However, Cl and  $\text{HCO}_3^-$  are dominant anions meanwhile Na and Ca are dominant cations. Groundwater from natural low residential areas has low electrical conductivity and Ca-Na- $\text{HCO}_3^-$  type whereas the chemical composition of groundwater is shifted to Ca-Na-Cl ( $\text{NO}_3^- + \text{SO}_4^{2-}$ ) downstream with maximum electrical conductivity and high nitrate levels above the guide limits occurring in the highly urbanised, settlements at the Centre of the study area. Groundwater is vulnerable to acid deposition due to the resistant nature and the low level of base forming cations in the aquifer sediments, which provides very little buffer for acid inputs.

**Key words:** Groundwater chemistry, Urbanisation, Sea spray, Shallow groundwater, Groundwater demand

## INTRODUCTION

Shallow aquifers with poor and doubtful water quality are major sources of water supply for drinking and other domestic purposes in many urban cities in developing countries, especially in the sub-urban centre (Howard *et al.*, 1999; Pedley and Howard 1997; Tanawa *et al.*, 2002; Zingoni *et al.*, 2005; Ousmane *et al.*, 2006; Kulabako *et al.*, 2007). Because these aquifers are viable complementary solution to water supply problems in urban areas, and equally because these aquifers are exposed to many sources of anthropogenic pollution, there is a need for adequate protection and sustainable management. Groundwater chemical quality is mainly controlled by natural processes- precipitation, mineral weathering and evaporation-crystallisation (Chebotarev, 1955; Gibbs, 1970; Palmer and Cherry 1984). Many studies world wide have shown that the hydrochemistry of urban groundwater is significantly influenced by anthropogenic processes (Lerner and Barrett, 1996; Barrett *et al.*, 1999, Lawrence *et al.*, 2000; Zilberbrand *et al.*, 2001; Foppen, 2002; Lerner, 2002;

Cronin *et al.*, 2003; Powell *et al.*, 2003; Eiswirth *et al.*, 2004; Ellis and Rivett, 2007). In particular, contamination of groundwater by trace elements and nutrients: (Leong and Jiao, 2006; Zingoni *et al.*, 2005; Foster, 2001; Kulakabo *et al.*, 2007; Al-Kharabsheh *et al.*, 2003; Elhasadi, 2008) have been identified from anthropogenic processes in many developing countries. In urban cities therefore, there is a necessity to have a sound knowledge of the sources of the various constituents of groundwater so as to identify elevated concentrations originating from natural sources, from pollution due to anthropogenic activities. This is very essential if environmental imposed changes are to be identified (Edmunds *et al.*, 2003), and also one of the vital aspects of the EU Directives (Onorati *et al.*, 2006) for protection and sustainable management of groundwater. The coastal low-lying urban city of Douala, the economical capital of Cameroon in West Africa, host more than 80% of industries in the Country. The city, which rests directly on unconsolidated alluvial deposits, host the largest

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urban population in the country (3000000 inhabitants) with a population density of 350 persons per KM<sup>2</sup>. In addition to this, each year the area receives about 120.000 migrants from the rural areas (Guévert *et al.*, 2006). This town has faced a rapid growth in population, intensive urban and industrial development which has not been matched by the provision of basic infrastructures (drainage, sanitation, waste disposal, pipe-borne water). Inadequate supply of pipe-borne water with only 65.000 persons connected out of 3 million inhabitants (Guévert *et al.*, 2006), pushes the population to depend on groundwater. According to the recent field study, 80% of the low income populations in informal settlements use spring and bore-well water for part or all of their drinking and other domestic water needs. Despite its importance as a source of water supply and intensive use of groundwater for both urban and industrial purposes, the knowledge of the hydro chemistry of groundwater in this area remains very poor. Previous studies have mostly focused on the bacteriological aspects (Takem *et al.*, 2009). This makes it difficult to determine not only the presence, but more importantly the origin of current/future anomalous concentrations of substances in groundwater.

This study therefore aims to contribute to the protection and sustainable management of the shallow aquifer, through providing information on the factors that control the chemistry of groundwater. The specific objectives include

To describe the chemistry of ground water in the shallow aquifer;

To determine the factors that contributes to the chemistry quality of groundwater

To determine the spatial and temporal distribution of the physico-chemical parameters and identify the extent of any pollution event.

The study area is located 60m, above mean sea level, in Douala in the Littoral province of Cameroon approximately 50 km from the Gulf of Guinea (Fig 1). The hydrographical network (Fig. 1) is such that springs flow into streams which in turn flow into minor rivers like the Tongo Bassa, Ngoua, that feed major rivers of Wouri and Dibamba, which eventually empty in the Atlantic Ocean (Olivry, 1984). The area experiences the humid equatorial climate modified by the relief of Mt Cameroon and has two seasons, a rainy (April to October) and a dry season (November to March). Peak rainfall occurs within the months of June and September with an average annual precipitation of 4000 mm per year. Temperature ranges between 23° C to 33° C with January and February identified as the hottest months of the year. The soils vary from yellow through brown to black freely drained sandy, ferralitic

soils sandy at the base and sandy-clayey at the top soils (Asaah *et al.*, 2006). This area is part of the Douala lagoon system which forms part of the coastal low lands of Cameroon. The Douala coastal environment describes a barrier island lagoon formation. A number of such old barrier island were colonised by districts (Akwa, Deido, Bepanda, Bassa, Bonamoussadi) which today supports the high population density metropolitan area of Douala (Asangwe, 2007). The lagoon system is about 50 km away and has a broad embayment as it opens in to the Atlantic Ocean, which greatly enhances tidal movement, often leading to the inflow of saline waters. The area is characterised by low-lying geomorphic features with faint slopes almost at sea level. The gentle topography generally drops from East to West towards the Wouri River and leads to flooding of the area. The altitude is about 57m in the East, passing on to 23m in the Centre and dropping to 3m in the West towards the Wouri River (Fig 1). The high magnitude of run-off from the River Wouri estuarine system in to the land-water interface leads to a high water table which leads to flooding of the area.

The study area is part of the Phanerozoic Cretaceous-Quaternary Douala Sedimentary Basin covering an area of about 7000km<sup>2</sup> with a maximum width of 60 km (Dumort, 1968; Regnault, 1986). This Basin is one of the several divergent margin basins along the South West African Coast whose origin and structure are associated with the opening of the South Atlantic Ocean during the break - up of the Gondwanaland (Tamfu and Batupe, 1995). The geology of this basin has been described by several workers (Dumort 1968, Regnault, 1986; Tamfu and Batupe, 1995). The main lithologies in the basin include conglomerate, sandstone, limestone, shale, and alluvium. The stratigraphy of the Douala sedimentary basin according to Tamfu and Batupe (1995) consists of Precambrian basement, unconformably overlain by a sedimentary sequence ranging in age from Cretaceous to Recent (Fig. 2). Both shallow and deep aquifers occur in the Douala basin. The deep aquifer principally constitutes the basal sandstones of the Moundeck Formation and the Palaeocene sands of the Matanda Formation which is highly exploited by bore-wells of SNEC (The National Water Cooperation) and industries Douala. The shallow aquifer system consists of the Quaternary alluvium and the Mio-Pliocene alluvium that constitute the Wouri Formation (Fig. 2). The entire study area is dominated by this formation. It generally consists of unconsolidated fine to coarse grained sands and gravels mixed with silts and clays in various proportions (Mafani, 1999). The general thickness ranges between 50 and 60m.

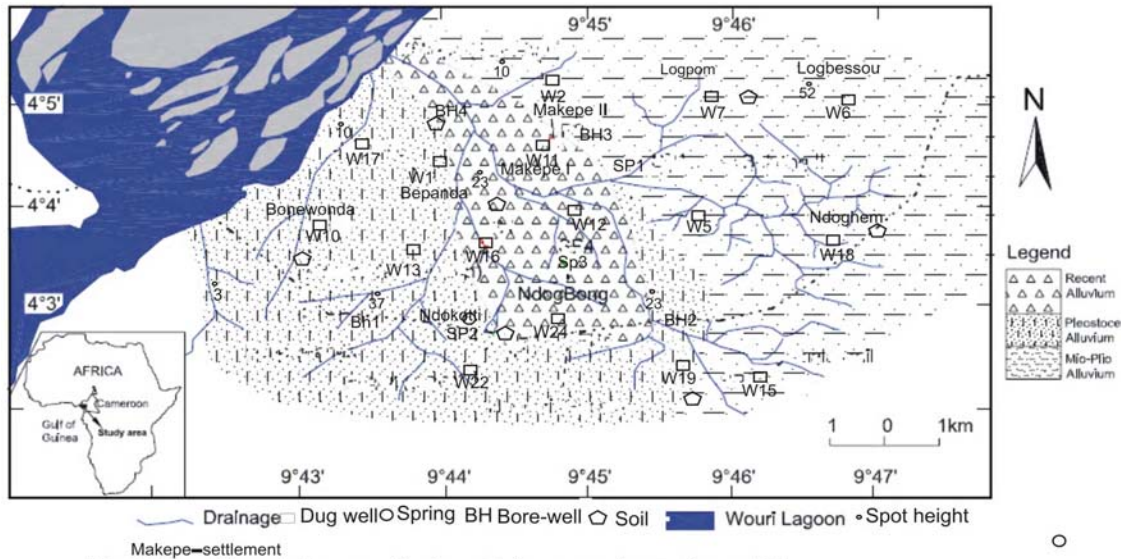


Fig.1. Map of the study area: Geology, drainage and sampling points

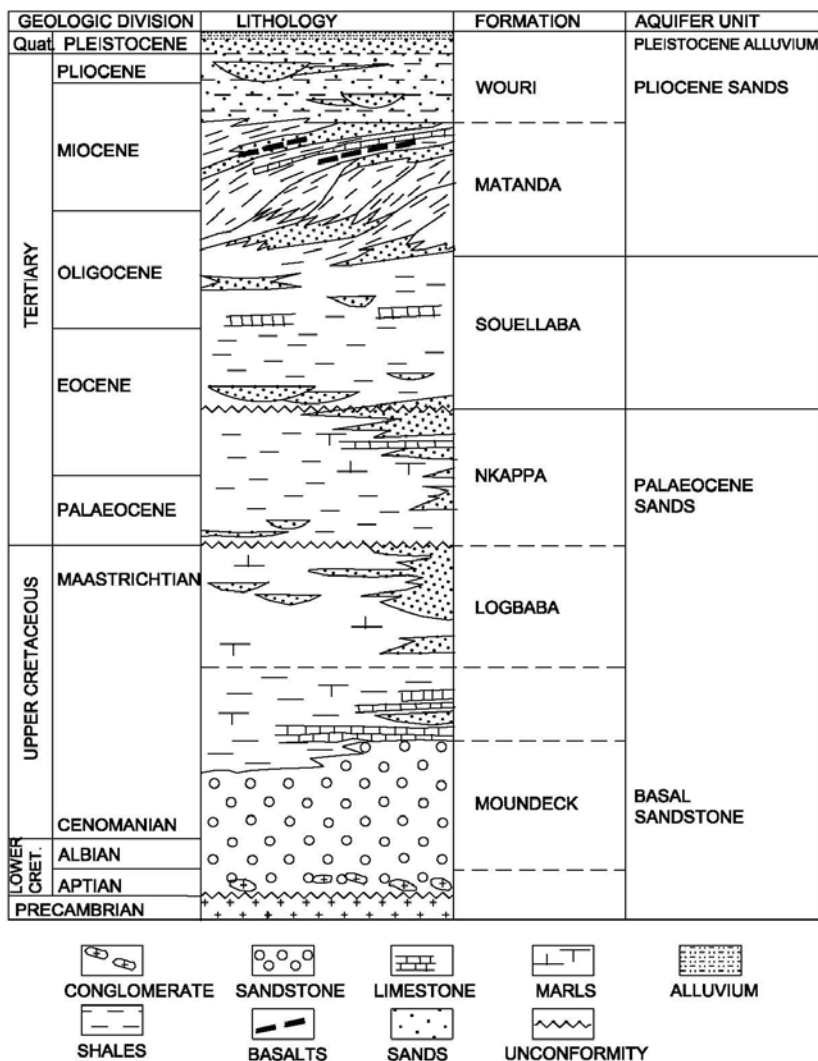


Fig. 2. Chronostratigraphic column of the douala basin showing the four major aquofer units (modified from mafany 1999; regnoul 1986)

The shallow aquifer is made up of the Mio-Pliocene sands at the base and the Quaternary alluvium lying on top (Fig. 2) which together forms the Wouri Formation. It consists of fine to coarse grain sands and gravels mixed with silts and clays, and lies on top of Miocene shale of Matanda Formation which serves as the aquiclude. According to Djeuda et al. (2001), the aquifer has a thickness which range between 50 and 60m meanwhile many perched aquifers occur where lentils of channel filled sands are hosted in clay layers, leading to considerable lateral and vertical variations. The water table is generally less than 10 meters below the surface (Mafany, 1999). Bore-well discharges of 80m<sup>3</sup>/hour/well have also been reported (Djeuda et al., 2001). The aquifer is mainly recharged by precipitation. Waste water from drainage channels also infiltrates this aquifer. Several streams drain the area and may also recharge the aquifer depending on the seasons and the water levels. Average groundwater level fluctuations range between 0.3 and 2.1m between the dry and wet season. The aquifer is highly exploited by hand dug wells which show water levels of approximately 1-15m. The general direction of groundwater flow is from the East to West towards the Wouri Lagoon and the salt water creeks (Crique Docteur) (Mafany, 1999). According to Mafany (1999) the shallow aquifer is in direct continuity with the brackish waters of the Wouri estuary and the network of coastal creeks, which allows the direct penetration of saline water especially during the dry season when the water table levels drop. The deep aquifer unit consists of the Basal sandstones of the Moundek Formation, underlain by the Precambrian granites in turn overlain by shale and marls of the Logbaba Formation, and the Palaeocene sands of the Nkappa Formation (Fig. 2). Palaeocene sand is exploited by bore-wells towards the north-eastern part of the study area with thickness of about 200m and discharges of 250 m<sup>3</sup>/hour/well (Djeuda et al., 2001). Information for depth of bore-wells is not available however; according to Djeuda et al. (2001) most of the wells owned by private individuals tap the Mio-Pliocene alluvium meanwhile those owned by industries tap the Palaeocene (deep aquifer).

## MATERIALS & METHODS

Water samples were collected from three springs, four bored-wells, eighteen hand-dug wells, three rain samples. Sampling was planned to coincide with the peak of the rainy season and dry season using July 2007, October 2007, February 2008, and July 2008, October 2008 and January 2009. Samples were collected from both natural undeveloped areas with little settlements and in the highly urbanised areas of the catchments (Fig. 1). The results obtained from the undeveloped

natural areas were to serve two purposes (1) to identify the natural processes controlling groundwater chemistry; (2) to compare with the results of the highly urbanised areas so as to identify the impact of urbanisation on the groundwater chemistry. Field measurements were carried out for electrical conductivity, pH and temperature using properly calibrated equipments. Samples were collected in 250ml acid rinsed plastic bottles. Two set of samples were collected at each site for chemical analysis. The samples were then filtered through a 0.45µm millipore filter paper and nitric acid was added into one of these bottles. This bottle was kept for analysis of cations. Samples were stored and transported in a cool flask 4°C with ice blocks to the laboratory where they were stored in a refrigerator pending analysis.

Chemical analysis of water samples were carried out in Hydro geochemistry laboratory of the Indian Institute of Technology Bombay- India and the Water analysis laboratory of the Hydrologic Research Centre-Cameroon. HCO<sub>3</sub><sup>-</sup> was determined as total alkalinity by titration with H<sub>2</sub>SO<sub>4</sub> (0.02 N) and methyl orange as indicator, as outlined in APHA/AWWA (1998). Cations (Na, K) and SiO<sub>2</sub> were analysed by inductively coupled plasma atomic emission spectrometry (ICP-AES) and (Ca, Mg and Total Hardness) by EDTA titrimetric method with 0.01M EDTA titrant, Murexide and Erychrome Black T dye as indicators for calcium and total hardness respectively, procedures as outlined by APHA (1998). A UV-Visible light spectrophotometer was used to analyse SO<sub>4</sub><sup>2-</sup> (by turbidimetry) using standard sulphate solution and barium chloride crystals with conditioning reagent (APHA/AWWA, 1998). Chloride was analysed by Ion selective Electrode meter (ORION). Nitrate was analysed by Ion chromatography with an instrument model DX-120 (Dionex). Seven sediment samples were collected from small cliffs in the study area for chemical and mineralogical analysis (Fig. 1). Powder samples were prepared from the sediments and both XRD (Siemens D-5000 diffract meter using CuKα radiation, Ni filter and automatic divergence slit) and XRF (Philips PW 1404/10 XRF spectrometer) analytical techniques were used to determine the mineralogical and chemical composition of the samples. Simple statistical analysis was performed with the aid of Microsoft excel 2003. Pearson correlation matrices and ratio of ions were used to find the relationship between variables. Saturation indices (SI) with respect to siliceous minerals (quartz, chalcedony and amorphous silica), carbonates (calcite, aragonite and dolomite) and sulphates minerals (gypsum and anhydrite) together with the equilibrium partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) were determined for the samples using PHREEQC program contained in AQUACHEM software version 3.70.

**RESULTS & DISCUSSION**

Results of XRD analysis of all seven sediment samples show a similar mineralogical composition which consists mainly of quartz, clay minerals (predominantly kaolinite) and feldspars. An important mineralogical characteristic is the high peak for quartz and the absence of calcite and dolomite. XRF data (Table 1) also shows that  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  content of the samples generally make up more than 70%.  $\text{Fe}_2\text{O}_3$  content is also important with some samples SL4, SL6 and SL7 having above 6%. The rest of the oxides of the major elements have values less than 2% (Table1).

Results of rainwater and groundwater samples collected from both the natural areas with little settlements and the highly developed- urbanized areas are given in Table 2a. The concentrations of the chemical constituents in groundwater are significantly higher than those in rainwater (Table 2b). This indicates that the dissolution of salts and other processes have considerably modified the chemical composition of rainwater during its infiltration in to the subsurface. Groundwater is generally acidic with pH range of 4.3-6.9. Electrical conductivity varies from  $48.5\mu\text{s}/\text{cm}$  (W7) to  $1021\mu\text{s}/\text{cm}$  (W13). Such large variation could be ascribed to many factors including heterogeneities in the geology (Fig.2), variation in the chemical

composition of wet and dry atmospheric sea salts deposition and anthropogenic activities. The chemistry of groundwater changes in different parts of the flow system. In the natural upstream hill areas (little residential areas), groundwater is slightly acidic (average pH ranging from 4.2 to 6.2) (Table 2) with low concentrations of the various dissolved ions and eventual low values of electrical conductivity generally within  $100\mu\text{s}/\text{cm}$  except for W15. This may reflects the short residence time and low degree of both water rock interaction and anthropogenic inputs.

Groundwater in this area also contains low levels of organic pollutants. The mean nitrate concentration is 2.2 mg/L and 3.3 mg/L in the wet and dry seasons respectively except for W15, (Table 2). Average sulfate concentrations range from 9.2mg/L -14.4 mg/L except for W15, average chloride concentration range from 3.0mg/L - 4.3mg/L for the dry season except W15 and silica concentrations also range from 2.8mg/L – 10.1mg/L in the rainy season (Table 2). Ca and  $\text{HCO}_3$  are the dominant ions for groundwater in the natural-upstream areas meanwhile three hydro chemical facies ( $\text{Ca-HCO}_3$ ,  $\text{Ca-Na-HCO}_3$  and  $\text{Na-Ca-HCO}_3\text{-Cl}$ ) are observed for the water samples in the rainy season. Almost the same pattern of hydrochemical facies ( $\text{Ca-HCO}_3$ ,  $\text{Ca-Na-HCO}_3$ , and  $\text{Ca-Na-SO}_4\text{-HCO}_3$ ) is observed in the dry

**Table 1. Chemical composition of the alluvial sediments (%)**

Sample No	$\text{SiO}_2$ %	$\text{Al}_2\text{O}_3$ %	$\text{Fe}_2\text{O}_3$ %	% MgO	% CaO	% $\text{Na}_2\text{O}$	% $\text{K}_2\text{O}$
SL 1	62.00	14.70	5.52	0.15	0.11	0.09	0.32
SL 2	69.73	12.01	4.06	0.15	0.12	0.09	0.38
SL 3	51.86	24.09	6.71	0.16	0.33	0.06	0.41
SL 4	60.10	19.93	4.82	0.15	0.08	0.09	0.37
SL 5	67.799	12.41	4.02	0.599	0.459	0.138	0.109
SL 6	59.183	15.826	6.198	0.758	1.014	0.104	0.342
SL 7	63.418	14.446	6.71	0.666	0.047	0.126	0.236

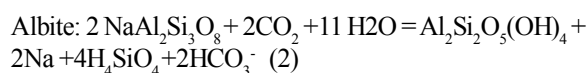
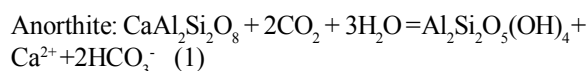
  

Sample No	$\text{TiO}_2$ %	% MnO	$\text{P}_2\text{O}_5$ %	SrO %	LOI%	OM%	Total Wt %
SL 1	1.95	0.03	0.131	0.01	12.4	1.9	99.3
SL 2	1.1	0.03	0.122	0.004	11.5	0.39	99.7
SL 3	1.89	0.02	0.17	0.02	13	1.13	99.8
SL 4	1.76	0.02	0.08	0.003	10.9	1.26	99.6
SL 5	1.925	0.053	0.129	0.004	10.96	1.26	99.9
SL 6	1.891	0.059	0.122	0.012	12.3	1.77	99.6
SL 7	1.194	0.054	0.131	0.008	11.73	1.19	100.0

Table 2a: Summary of physico-chemical parameters and Na/Cl ratio of groundwater and rainwater for the rainy season

Sample ID	pH	Cond (us/cm)	Na(mg/l)	K(mg/l)	Ca(mg/l)	Mg(mg/l)	HCO <sub>3</sub> (mg/l)	Cl(mg/l)	SO <sub>4</sub> (mg/l)	NO <sub>3</sub> (mg/l)	SiO <sub>2</sub> (mg/l)	Na/Cl
Natural upstream area with little settlement n=4												
W6	6.3	101.0	4.9	1.8	16.0	2.4	55.0	3.5	10.2	1.7	6.5	1.39
W7	6.3	85.1	3.4	2.1	17.0	3.6	62.5	3.1	12.8	2.2	3.3	1.08
W15	6.3	239.8	15.5	6.5	14.0	2.4	46.3	21.6	13.1	7.3	5.2	0.72
W18	4.3	78.0	5.6	1.6	8.0	1.2	18.8	4.1	15.2	2.2	3.0	1.36
Developed urbanized area n=4												
W1	6.0	757.8	68.1	27.8	34.1	3.6	60.0	107.3	30.1	128.2	8.2	0.63
W2	5.2	254.0	13.1	15.6	17.0	3.0	25.0	29.5	16.5	19.3	3.9	0.45
W5	6.9	316.0	10.4	4.9	28.1	3.6	61.3	16.4	24.4	13.6	8.0	0.63
W10	5.8	505.8	45.4	21.0	19.0	3.0	43.8	62.7	23.3	144.6	7.8	0.72
W11	5.9	527.5	43.3	17.5	26.0	3.0	45.0	60.2	33.7	136.5	5.4	0.72
W12	4.8	492.0	40.5	19.6	26.1	2.4	27.5	54.4	38.8	43.1	5.1	0.74
W13	4.6	657.5	47.6	26.5	16.0	1.8	21.3	70.5	27.2	100.2	6.9	0.68
W15	6.3	239.8	15.5	6.5	14.0	2.4	46.3	21.6	13.1	7.3	5.2	0.72
W16	6.3	540.0	29.6	17.8	52.1	3.6	115.0	40.8	32.0	95.9	17.0	0.73
W17	6.4	571.3	39.3	20.2	27.1	4.2	52.5	57.7	34.0	20.1	6.5	0.68
W19	5.3	203.4	15.8	4.6	10.0	3.0	23.8	20.7	20.9	90.5	2.5	0.76
W22	6.3	483.0	19.2	10.5	31.1	3.6	56.3	31.2	23.9	46.9	4.7	0.62
W24	5.7	528.8	42.2	18.2	18.0	4.2	43.8	58.8	31.9	113.7	2.5	0.72
SP1	4.4	193.8	21.2	7.4	7.0	2.4	13.8	17.9	28.7	52.4	3.8	1.19
SP2	4.0	215.5	14.5	5.3	11.0	3.0	12.5	14.8	21.3	49.5	4.4	0.98
SP3	5.8	325.5	42.3	5.4	8.9	2.8	20.7	36.9	22.8	41.0	3.8	1.15
B1	4.5	34.3	0.6	1.1	7.0	1.8	10.0	2.1	14.1	1.0	10.7	0.30
B2	5.0	34.4	1.0	1.8	9.0	0.6	20.0	4.1	11.2	1.0	12.7	0.24
B3	4.4	41.0	3.2	0.6	10.0	0.0	8.8	2.5	13.1	10.1	5.0	1.25
B4	4.5	361.0	40.3	12.5	9.0	1.2	16.3	41.6	21.2	21.1	6.3	0.97
Rain water n=1												
R1	5.8	20.4	0.7	0.9	0.9	0.1	0.7	0.9	1.4	1.3	nd	0.78
R2	5.9	17.8	1.1	1.6	1.2	0.0	0.9	1.4	1.9	1.0	nd	0.79
R3	5.6	4.6	0.6	0.4	0.7	0.1	0.4	0.5	0.8	1.1	nd	1.2

season. Generally more sites exhibit higher conductivity and higher levels of the various ions in the wet seasons than the dry season in both the natural undeveloped areas with little settlements and in the urbanized areas (Table 2). This could be due to the fact that more salts are leached out due to the high water table during the wet season. The source of dissolved ions in groundwater in these undeveloped areas may be contributed from the dissolution of aerosols, particulates or dust in rain water before it falls to the ground for infiltration in to the groundwater table. Weathering of minerals such as feldspars present in the alluvial sediments, may also contribute ions to groundwater. Plagioclase is the most common rock forming mineral involved in hydrolysis. It comprises a solid solution between Na and Ca end-members, in which the Ca-end member is preferentially weathered relative to sodium and therefore the concentration of Ca in groundwater increases. The dissolution of anorthite and albite, the two end members, leads to the introduction of cations ( $\text{Ca}^{2+}$  and  $\text{Na}^+$ ), bicarbonate and the production of kaolinite which is consistent with the presence of this mineral phase in the alluvial sediments as revealed from the XRD analysis. This dissolution can be written as follows (Herczeg, 2001):



In the study area, the natural undeveloped area is located upstream (North East, Logpom Ndoghem and Logbessou) meanwhile the urbanized area is located downstream (Fig 1). Major ion concentrations generally increase down stream with an associated increase in electrical conductivity (Table 2), towards the urbanized areas. Groundwater of electrical conductivity above 400 $\mu\text{S}/\text{cm}$  is dominantly distributed in the Bepanda, Ndokotti, Ndogbong- Makepe (Fig 1) which underlies the old valley settlements and equally the urbanized high density areas. The content of organic pollution also increases downstream with nitrate concentrations reaching a maximum of 161mg/L (W10) in the rainy season. Average nitrate concentration is 144mg/L and 140mg/L (Table 2) for the wet and dry seasons respectively which is far higher than that of the natural upstream areas with little settlements. The high nitrate concentration is a characteristic of shallow groundwater in urban areas in many developing countries (Barret *et al.*, 1999; Zingoni *et al.*, 2005; Takem *et al.*, 2009), and reflects a significant degradation of groundwater due to anthropogenic pollution. The concentration of chloride range from 14.8mg/L-

107.3mg/L and 15.8mg/L - 85.9mg/L, for the wet and dry season respectively, sodium ranged from 14.5 - 68.1mg/L and 12.6-57.6mg/L for the wet and dry season respectively. Average calcium concentrations for all sampling periods ranged from 7.0mg/L - 34.1mg/L except for W16 (54mg/L), for the wet season and 6.0mg/L-32.1mg/L except for W16 (72.2) for the dry season. Silica concentrations in groundwater ranged from 2.5-17.0 with the maximum value occurring in W16 (Table 2).

Unlike the hydro chemical facies observed in the natural areas, samples in the urbanized area are generally dominated by Na-Ca-Cl water types. The ionic content of groundwater in the developed urbanized area is highly variable, however the dominant cations are  $\text{Na}^+$  and  $\text{Ca}^{2+}$  meanwhile the dominant anions are  $\text{Cl}^-$  and  $\text{HCO}_3^-$ . The dominance of Na and Cl ions in many water samples (Table 2) indicates the possible effect of seawater via direct mixing (Lalraj *et al.*, 2007), marine spraying, and fall-out of airborne marine salts (Edmunds *et al.*, 2003). On the other hand, the significant amount of Ca and  $\text{HCO}_3^-$  in some samples like W16 and W22 reflect the contribution from water rock interactions- principally hydrolysis of feldspars (Shrinivasamoorthy *et al.*, 2001). The main elements contributing to groundwater salinity are Na, Cl, K, and  $\text{NO}_3^-$  that shows strong positive correlation ( $r > 0.7$ ) with EC (Table 3) (this is discussed later). Ionic concentrations of water samples have been plotted on piper diagram (Fig 3) to evaluate the geochemical characteristics of the sampled waters. Groundwater samples in the upstream undeveloped areas mostly plot in the Ca- $\text{HCO}_3^-$  field and partly as Ca- Na-( $\text{SO}_4 + \text{HCO}_3^-$ ) type, meanwhile six major water types (Na-Cl, Na-Ca-Cl, Na-Ca-Cl- $\text{SO}_4$ , Na-Ca-Cl- $\text{HCO}_3^-$ , Ca-Na-Cl- $\text{HCO}_3^-$ , and Ca-Na- $\text{SO}_4$ - $\text{HCO}_3^-$ ) occur for hand dug well and Ca- $\text{SO}_4$ , Ca- $\text{SO}_4$ - $\text{HCO}_3^-$  water types occur for bore-wells in the urbanized area (Table 4).

Groundwater is dominated by the cations,  $\text{Na}^+$  and  $\text{Ca}^{2+}$  which reflects the geochemical nature predominantly of quartz, feldspars and clay minerals. XRD analysis show that these minerals are mainly found in the aquifer sediments. As shown in equations 1 and 2 above, the dissolution of feldspars will release  $\text{Na}^+$  and  $\text{Ca}^{2+}$  in to the groundwater. Another possible source of these ions is the dissolution of gypsum and halite (Barker *et al.*, 1998; Shanyengana *et al.*, 2004) however there are no such sources of minerals, regarding the geology of the area. Furthermore if gypsum is the source of  $\text{Ca}^{2+}$  there should be a positive correlation with  $\text{SO}_4^{2-}$  which is however absent (Table 3). The high concentration of sodium can be attributed, besides rock weathering to sea salt atmospheric deposition and possible marine intrusion

Table 2b: Summary of physico-chemical parameters and Na/Cl ratio of groundwater and rainwater for the dry season

Sample ID	pH	Cond( $\mu$ s/cm)	Na(mg/l)	K (mg/l)	Ca(mg/l)	Mg(mg/l)	HCO <sub>3</sub> (mg/l)	Cl(mg/l)	SO <sub>4</sub> (mg/l)	NO <sub>3</sub> (mg/l)	SiO <sub>2</sub> (mg/l)	Na/Cl
Natural upstream area little settlements n=2												
W6	6.2	107.9	2.6	1.8	20.0	0.0	47.5	4.3	9.2	2.9	10.1	0.60
W7	5.7	59.1	4.9	2.0	12.0	2.4	35.0	3.0	10.6	3.2	4.0	1.64
W15	5.8	218.2	13.6	6.3	20.0	4.9	40.0	20.7	26.6	6.3	2.8	0.66
W18	4.2	73.5	3.6	2.2	10.0	1.2	12.5	4.3	14.4	3.3	3.0	0.84
Developed area n=2												
W1	5.4	740.5	57.6	26.7	30.1	2.4	60.0	85.9	36.7	126.5	5.2	0.67
W2	5.2	232.0	14.9	7.0	8.0	3.6	20.0	33.1	20.5	18.5	3.5	0.45
W5	6.8	332.0	15.0	5.2	28.1	2.4	105.0	21.9	32.3	15.9	7.8	0.69
W10	5.3	526.5	47.0	16.6	22.0	4.8	25.0	77.1	23.6	140.4	7.8	0.61
W11	5.5	510.0	39.4	15.1	26.1	4.8	32.5	61.2	27.4	97.9	2.8	0.64
W12	5.0	488.5	47.9	15.6	24.0	3.6	25.0	64.5	39.7	43.7	2.6	0.74
W13	6.2	899.0	50.7	20.8	18.0	2.4	115.0	83.8	33.4	96.0	1.6	0.61
W15	5.8	218.2	13.6	6.3	20.0	4.9	40.0	20.7	26.6	6.3	2.8	0.66
W16	6.8	619.5	31.1	18.3	72.2	3.6	150.0	45.1	26.2	109.4	18.2	0.69
W17	6.8	509.0	40.7	18.7	22.0	4.8	50.0	61.9	37.5	17.3	6.5	0.66
W19	4.5	183.7	12.8	4.6	12.0	2.4	15.0	20.7	21.0	76.9	2.5	0.62
W22	6.2	443.5	24.4	11.1	32.1	3.6	57.5	33.8	45.3	42.8	4.7	0.72
W24	5.7	528.0	42.1	15.6	24.0	4.8	37.5	66.5	62.4	121.1	2.5	0.63
SP1	5.1	202.7	15.1	4.5	6.0	2.4	7.5	18.5	23.2	50.2	3.8	0.82
SP2	3.9	193.5	12.6	4.6	6.0	2.4	5.0	15.0	22.0	54.5	4.4	0.84
SP3	4.8	225.0	28.5	2.5	6.0	3.6	7.5	30.7	23.9	41.7	3.8	0.93
B1	4.4	27.8	0.5	1.6	6.0	0.0	7.5	2.7	16.5	2.0	10.7	0.19
B2	4.6	34.1	0.7	2.2	6.0	2.4	7.5	5.0	15.0	2.5	12.7	0.14
B3	4.2	37.7	3.8	1.5	4.0	0.0	5.0	4.0	17.6	10.8	5.0	0.97
B4	4.3	348.0	34.2	6.9	4.0	1.2	10.0	42.5	18.6	20.5	6.3	0.80
Rain water n=1												
R1	5.2	13.3	0.5	0.7	0.9	0.1	0.7	0.8	1.4	1.2	nd	0.64
R2	5.4	12.0	1.0	1.7	1.2	0.1	0.8	1.3	1.7	0.8	nd	0.76
R3	5.0	7.2	0.3	0.3	0.8	0.0	0.6	0.4	0.7	1.0	nd	0.77



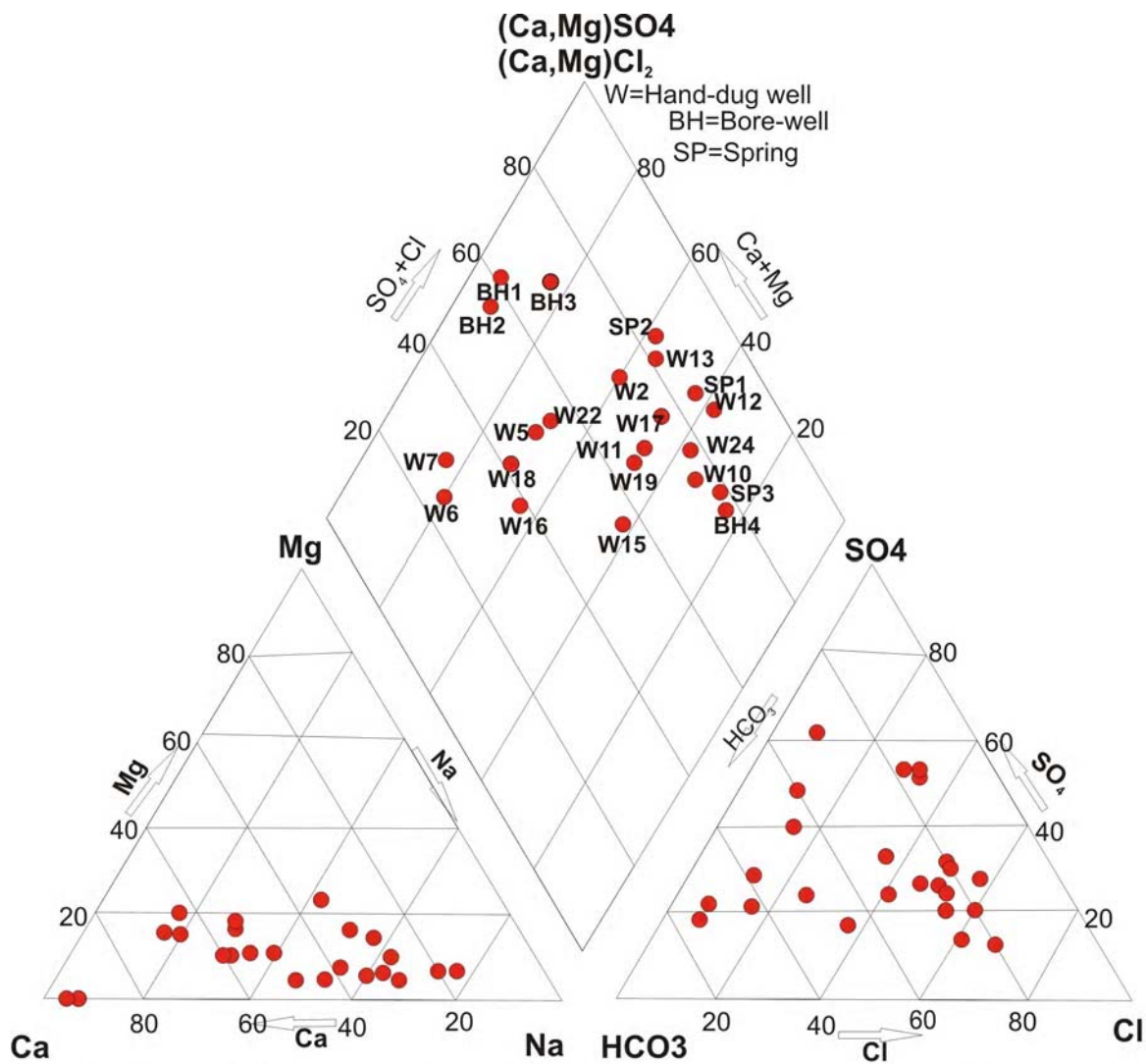


Fig. 3. Piper plot for major ion data for rain season July 2007 sampling

Table 3. Pearson's correlation matrix for groundwater samples for the natural and developed (urbanized areas)

	EC	Na	K	Ca	Mg	HCO <sub>3</sub>	Cl	SO <sub>4</sub>	NO <sub>3</sub>
EC	1.0								
Na	0.91	1.00							
K	0.95	0.76	1.00						
Ca	0.59	0.41	0.61	1.00					
Mg	0.46	0.51	0.49	0.39	1.00				
HCO <sub>3</sub>	0.64	0.41	0.54	0.52	0.19	1.00			
Cl	0.94	0.98	0.74	0.42	0.53	0.39	1.00		
SO <sub>4</sub>	0.66	0.66	0.65	0.40	0.57	0.32	0.66	1.00	
NO <sub>3</sub>	0.76	0.75	0.76	0.48	0.41	0.34	0.78	0.51	1.00

**Table 4. Summary of hydrochemical facies of groundwater samples for the natural (low settlement) and developed (urbanized areas) in the unconfined aquifer of Douala**

Sample ID	Hydrochemical facies
Natural upstream area (little settlement)	Ca-HCO <sub>3</sub> Ca-Na-(SO <sub>4</sub> +HCO <sub>3</sub> ) Na-Ca-HCO <sub>3</sub> -Cl
Developed area (Urbanized area)	Na-Cl Na-Ca-Cl Ca-Na-Cl Na-C a-Cl-SO <sub>4</sub> Na-C a-Cl-HCO <sub>3</sub> Ca-Na-SO <sub>4</sub> -HCO <sub>3</sub> Ca-SO <sub>4</sub> Ca-SO <sub>4</sub> -HCO <sub>3</sub>

mixing. Sulfate in groundwater is obtained principally from gypsum and anhydrite (Sacks, 1996), which make up a significant part of many evaporate deposits. However from the geology of the area no evaporate rocks have been recorded. Sulfur is present in reduced form in igneous, sedimentary, and metamorphic rocks as metallic sulphides (Hem, 1985). This sulfur is oxidized to sulfate when weathered in contact with aerated water. This together with atmospheric sea salt deposition and seawater intrusion can be responsible for the SO<sub>4</sub> inputs in the groundwater. Meanwhile anthropogenic inputs from sewage and other industrial waste can be another possible source. The positive correlation between SO<sub>4</sub> and NO<sub>3</sub> (Table 3) corroborates this fact Chloride is the dominant anion (Table 2) with average concentrations of above 100mg/L in some sample points in the developed areas. This is far higher when compared to average concentration obtained from the natural undeveloped upstream samples (5mg/L). Chloride is a minor constituent of the earth's crust but a major dissolved constituent in groundwater. Natural sources of chloride in groundwater are from atmospheric sources, mixing of brine, sea water intrusion mixing, evaporites and marine shales (Hem, 1985; Barker *et al.*, 1998; Marlin *et al.*, 2000; Grobe and Machel, 2002). Based on the geology of the area, there is no evidence of the presence of neither brine nor evaporites. Sea spray is a possible source of chloride since the area is located close to the coast. Sea spray leads to the deposition of salts on ground both by precipitation and dry fallout. The high water table in this area results to flooding of the land especially during the rainy season. This will lead to the leaching of accumulated salts in to the ground water system. Sea water mixing in to shallow groundwater is also a possible source of chloride, especially so with those

wells which are close to the Wouri lagoon, B4 and W17. According to Mafani (1999) the unconfined aquifer is in hydraulic continuity with the brackish waters of the Wouri lagoon as such during high tides there is inland movement of brackish waters of the lagoon.

The concentration of bicarbonate is also very variable with average ranging from 5mg/L (B3) to 150mg/L (W16). According to Regnault (1986) the geology of the area is mainly composed of unconsolidated sands and gravels in a kaolinitic matrix. XRD results equally shows that mainly quartz, feldspars and clay minerals are present in the aquifer sediments. Silicate weathering is the probable source of bicarbonate in groundwater (equation 1 and 2). Silica concentrations in groundwater ranged from 2.5-17.0 with the maximum value occurring in W16. The low levels of silica could be related to the resistant nature of the sediments dominantly composed of quartz, and to the short residence time of groundwater.

To further identify possible source of ions in groundwater, ionic ratios (Table 2) and correlation matrices (Table 3) have been studied to define possible relationships between ions. A positive correlation is observed between Ca and HCO<sub>3</sub> (Table 3) which indicates that both ions are probably coming from the same source. The calcium and bicarbonate pair often comes from dissolution of carbonate minerals such as calcite and dolomite. These minerals are however absent in the aquifer sediments. The source of these ions could therefore be from dissolution of feldspars as indicated equation (1 and 2).

Na shows a strong positive correlation with Cl, R= 0.96 and 0.92 for the wet and dry season respectively (Table 3). Despite this strong correlation, variations are observed in their ionic ratios as shown in (Table 2). Average ionic ratios of Na<sup>+</sup>/Cl<sup>-</sup> for groundwater ranged from 0.5-1.4 and 0.5-1.6 (Table 2a and b), for the rainy and dry season respectively, however most of the samples fall around an ionic ratio between 0.6 and 0.8 (Table 2). Few samples fall close to the sea water ratio of 0.86 indicating the process of sea water mixing. Mafany (2006) has indicated the process of sea water intrusion in the unconfined aquifer of Douala. Few samples on the other hand have a ratio greater than 1 (Table 2). According to Vengosh and Rosenthal, (1994), the Na/Cl ratio during mixing between groundwater and sea water is 0.86, for fresh groundwater Na/Cl >1, meanwhile Na/Cl =1, indicates dissolution of halite (Vengosh and Rosenthal, 1994). None of the samples have Na/Cl =1, therefore halite dissolution is not a possible source for Na<sup>+</sup> and Cl<sup>-</sup> ions in groundwater. This can be confirmed from the geology of the area (Regnault, 1986; Mafany, 1999). However all the samples from the natural upstream areas have a Na/Cl ratio >1 indicating fresh water. Data on the Na/Cl ratio

for some samples for example (SP1, SP2, and B3) (Table 2), in the developed area, show excess of Na compared to the ratio of sea water (0.86). This probably indicates an additional source of  $\text{Na}^+$  probably from anthropogenic inputs and/or from ion exchange between groundwater and the aquifer sediments (El Yaouti *et al.*, 2009). Cation exchange is an important factor that modifies the chemical composition of groundwater. In coastal aquifers with complex interaction between sea water and fresh groundwater, cation exchange contributes significantly to the composition of groundwater (Djabri *et al.*, 2008; El Youti *et al.*, 2009).  $\text{Ca}^{2+}$  exchange for  $\text{Na}^+$  on the surfaces of clay minerals such as kaolinite which is abundant in the aquifer sediments, may lead to an increase in the concentration of  $\text{Na}^+$  in groundwater. According to Apello and Postma (1996), the occurrence of Ca-Cl water type in coastal aquifers indicates the active process of sea water mixing where,  $\text{Na}^+$  from sea water is exchanged for  $\text{Ca}^{2+}$  adsorbed on the clays. In the study area however, NaCl water types occur close to the Wouri lagoon meanwhile Ca-Cl water types have not developed (Table 4). The same situation occurs in the unconfined aquifer of Bou-Areg (NE Morocco) (El Youti *et al.*, 2009). According to the same author this suggests that the area is in the first state of salinization. If groundwater in this area is controlled by salt water mixing, the Na/Cl ratio should be close to 0.85, the ratio for sea water. However this is not the case for most samples in the area (Table 2). This therefore suggests that marine origin by sea water intrusion is not the main source of Cl<sup>-</sup>. Other possible sources of this element may be linked to atmospheric dry deposition and much likely to waste water (septic tanks) and other sources of domestic and industrial waste water contamination and fertilizers (Ahmed *et al.*, 2004; Hudak 2000). This supposition of groundwater contamination by sewage is supported by the elevated nitrate concentrations (12 out of 19 sample sites have average  $\text{NO}_3^-$  of above 40mg/L with a maximum reaching 144.6mg/L (W10) (Table 2) obtained for groundwater samples in the developed areas. The positive correlation between major ions (Cl and  $\text{SO}_4$ ) versus  $\text{NO}_3^-$  suggests that they probably come from the same source. The fact that other possible sources of nitrate such as agricultural fertilizers and nitrate bearing minerals are absent in the area, suggests the contribution from domestic sewage. This has already been observed by Takem *et al.* (2009). The high population density, poor sanitation facilities coupled with the uncontrolled disposal of both domestic and industrial waste in the area, (Guevart *et al.*, 2006; Ndjama *et al.*, 2008) supports this fact.

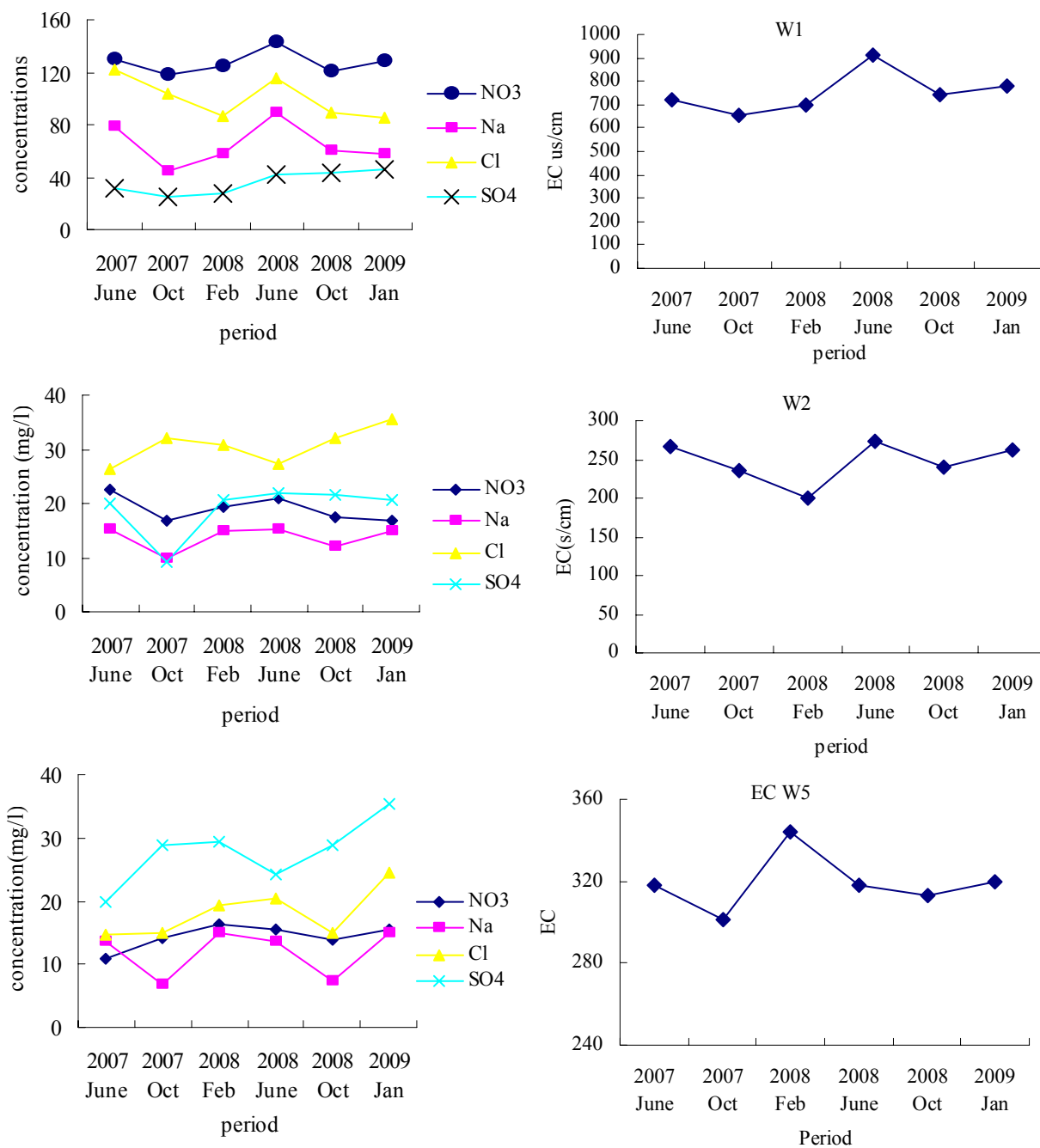
Saturation indices (SI) for water samples have been calculated with respect to selected siliceous, carbonate and sulfate minerals (Table 5) All groundwater samples

are under saturated (SI<0) with respect to calcite and dolomite which suggests that these mineral phases are absent in the aquifer sediments. This result supports that of the XRD analysis. However, some water samples show super saturation (SI>0) with respect to quartz, chalcedony and amorphous silica (Table 5) which suggests that these mineral phases are present in the aquifer sediments. Feldspar and quartz are possible sources of silica in groundwater; meanwhile weathering of feldspars is denoted in samples which are supersaturated with respect to quartz (W16). All the groundwater samples are under saturated with respect to gypsum and anhydrite (Table 5) which suggest that evaporate mineral phases are absent in the aquifer sediments.

Groundwater in the area is generally acidic with average pH ranging from 3.9 to 6.8 in the rainy season and 4.0 to 7.0 for the dry season (Table 2). The higher partial pressure of ( $\text{pCO}_2$ ) in groundwater (range  $10^{-1.78}$  to  $10^{-0.1}$  atm) (Table 5) compared to that of the atmosphere  $10^{-3.5}$  atm could suggest that the water has gained  $\text{CO}_2$  during infiltration probably from root respiration and decomposition of soil organic matter (Apello and Postma, 1996). Njitchoua *et al.*, (1997) in a study of the geochemistry and recharge mechanism of groundwater from the Garoua sandstone aquifer, Northern Cameroon indicates that high partial pressure of  $\text{CO}_2$  observed is due to root respiration of plant and the decomposition of soil organic matter. The high precipitation in the area (4000mm/year) would lead to leaching of much of the base forming cations (Ca, Na, Mg, K) from the soils (Table 1) which will lead to a drop in the acid neutralizing capacity of the infiltrating rain water. Soils in the area are generally acidic with an average pH of 4.6 and most sites have pH less than 5 (Table 1). The acidity in groundwater could therefore results from reduction in the acid buffering capacity (Chapman, 1996), caused by soil acidification. Moreover, the sandy nature of aquifer materials (dominantly clay- rich quartz sands) and short residence time provides low degree of water rock interaction (little capacity to attenuate the inputs of acidity) in which the groundwater water still retains most of its rainfall signatures (rainfall in the area is acidic). According to de Caritat (1999), cation exchange of sea salt  $\text{Na}^+$  with  $\text{H}^+$  and/or  $\text{Al}^{3+}$  held in the exchange sites of clays, will release  $\text{H}^+$  in the infiltrating groundwater thereby lowering the pH which in tend results in the acidification of groundwater. However it is not known if this process alone could lead to the observed acidification. The pH of rainwater evolves from 5.2 (R1) close to the Wouri lagoon, passing to 5.4(R2) in the center at Bepanda and increasing to 5.9(R3) inland at Logpom (Table 2). The acidic nature of rainwater is similar to the results of Sigha *et al.* (2003) for rainfall in the Southern part of Cameroon. The acidity of rainfall can be attributed to  $\text{SO}_2$  and nitrous

**Table 5. Summary of saturation indices (SI) and partial pressures of CO<sub>2</sub> (pCO<sub>2</sub>) for groundwater from the unconfined aquifer of Douala**

	Anhydrite	Aragonite	Calcite	Dolomite	Chalcedony	Gypsum	Quartz	Amorphous silica	pCO <sub>2</sub>
Min	-3.44	-5.17	-7.57	-10.17	-3.47	-3.18	-0.64	-1.9	10 <sup>-0.1</sup>
Max	-2.29	-1.07	-0.6	-2.4	0	-2.08	0.43	-0.83	10 <sup>-1.78</sup>
Mean	-2.88	-3.4	-3.27	-6.6	-0.73	-2.69	-0.155	-1.4	-
STD	0.375	1.29	1.61	2.3	-0.72	0.37	0.26	0.26	-



**fig. 4. Temporal variation in Electrical Conductivity (EC) and major ion concentrations in selected wells (Continues)**

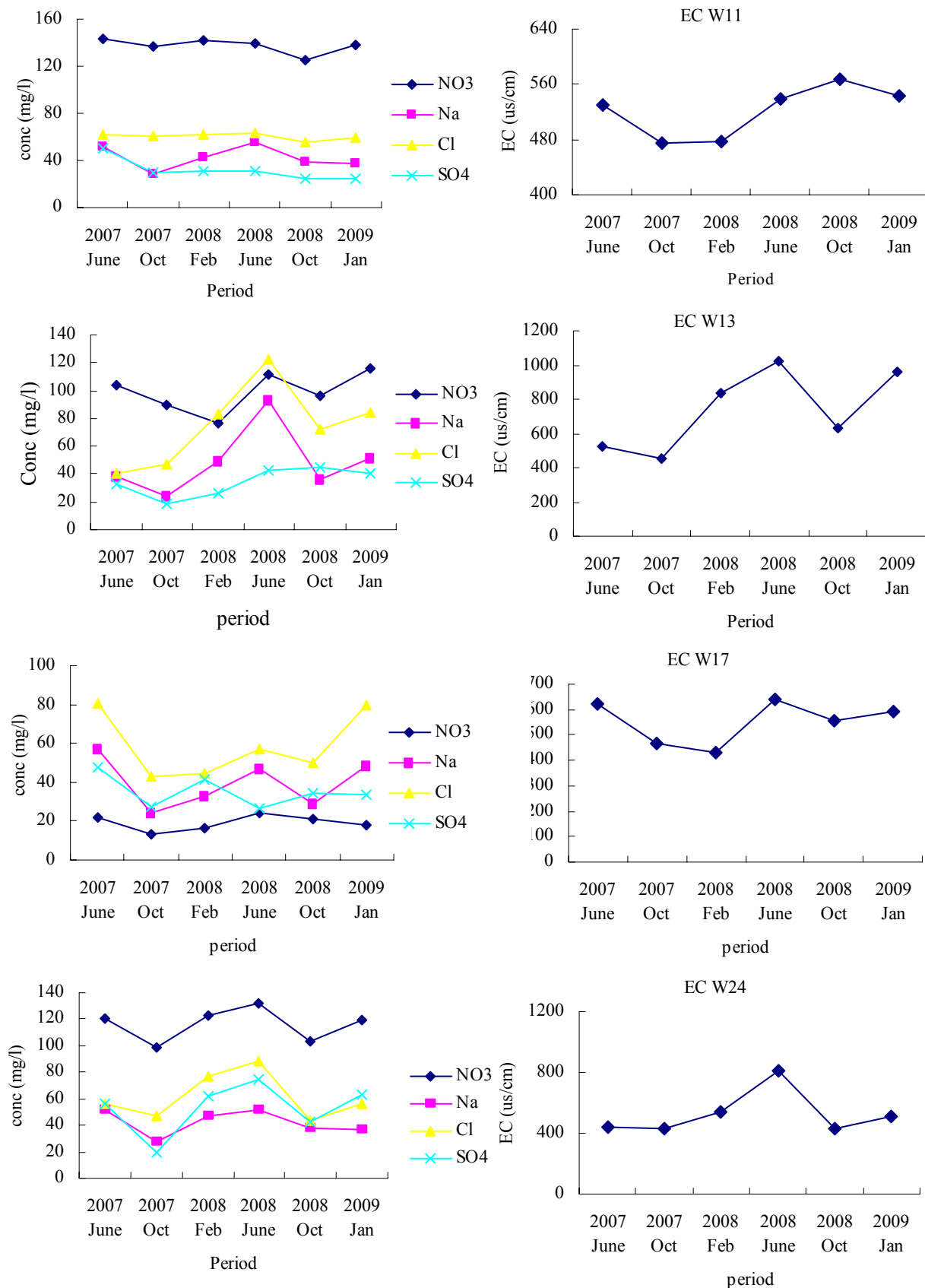


fig. 4. Temporal variation in Electrical Conductivity (EC) and major ion concentrations in selected wells (Continuation)

emissions considering the industrialized nature of the town (Chapman 1996). This is however in contrast with the results of Sigha et al. (2003) where acidity is related to biomass burning. It is possible that a contribution from the above factors and not just one is responsible for the acidic nature of groundwater in the area.

Physico-chemical parameters (EC, Cl, SO<sub>4</sub>, NO<sub>3</sub> and Na) have been used to access the spatial variation of groundwater chemistry. Groundwater in the upstream-inland areas with little settlements has low concentrations of major ions and electrical conductivity meanwhile downstream electrical conductivity increases giving a peak in the centre of the study area with informal settlements (Table 1). In the upstream inland areas, (NE section) (Fig. 1) of Logbessou and Logpom groundwater is dominantly composed of Ca- HCO<sub>3</sub> and Na-HCO<sub>3</sub> water types indicating hydrolysis of feldspars as mentioned above. This group of water is poor in Cl, NO<sub>3</sub> and SO<sub>4</sub> indicating the absence of anthropogenic inputs as there are very few sources of contamination in this area. Downstream in the central region, the levels of Cl, SO<sub>4</sub> and NO<sub>3</sub> increases with NO<sub>3</sub> concentrations, getting above the (WHO 1989) (45mg/L) standards in many samples. Since these groups of wells are situated in the central region which is characterized by informal settlements, high population density (Bepanda, Ndogbong and Bonewonda) (Fig. 1) and many sources of contamination, the nitrate reflects anthropogenic inputs possibly originating from domestic and industrial wastes and leaking sewage. A similar situation is indicated in the semi formal urban settlements of Epworth (Zimbabwe) (Zingoni *et al.*, 2005). As confirming factor are the occurrence of faecal indicator bacteria and the recurrent occurrence of water borne diseases (Guevart *et al.*, 2006; Ako *et al.*, 2009 Takem et al 2009). Na- Ca-Cl -SO<sub>4</sub> and Na-Ca-HCO<sub>3</sub>-SO<sub>4</sub> are the dominant water types (Table 4). The third group of water (W17 and B4) dominantly Na-Cl and Na-Ca-SO<sub>4</sub>-Cl, are mainly located downstream close to the Wouri lagoon (Fig. 1). These waters are rich in SO<sub>4</sub> and Cl but poor in NO<sub>3</sub> which suggests the possible effects of seawater mixing from the lagoon, and sea spray.

The temporal variation of physicochemical parameters (EC, Cl, SO<sub>4</sub>, NO<sub>3</sub> and Na) during the study period helps access the temporal evolution of groundwater chemistry. No clear cut trend is shown between the chemical composition of the samples with time either with the months or seasons; however some interesting features are observed for the temporal variation of the above constituents for some sample points (Fig. 4). A temporal pattern in the above constituents is observed where at the peak of the rainy season in June, there is a general rise in these constituents which drops in October, towards the end of the rainy season and peaks up again in January at the

peak of the dry season (Fig. 4). However maximum concentrations are observed in June (rainy season). Salts from dry deposition and sea spray accumulate on the soil during the dry season. With the beginning of the rainy season, the salts are washed in to the aquifer however maximum leaching occurs at the peak of the rainy season in June were most of the salts are leached to the system. Traore et al. (2006) have made a similar finding in the Bamako- Mali urban area. Equally during the peak of the rainy season, the water levels rises up to the ground surface as such ions are derived from anthropogenic sources especially ions washed from flooded pit latrines. This observation has also been made by Rajmohan and Elango (2006) in the Palar and Cheyyar river basins, Southern India. However continuous rains cause dilution and leads to a drop in concentrations during the end of rains in October. Meanwhile with the peak of the dry season in January, there is evaporation which further increases the concentration of ions (Fig. 4). This is however in contrast with results of Mafany (1999), where high concentrations of constituents were instead observed in the dry season.

## CONCLUSION

Through investigating the major ion chemistry of rain water groundwater and sediments collected from natural undeveloped areas and the highly urbanized settlements in the coastal unconfined aquifer of Douala, an attempt has been made to identify the major natural and anthropogenic processes controlling the chemistry of groundwater. In the natural undeveloped areas groundwater chemistry is mainly determined by weathering of feldspars and atmospheric deposition. However, the short groundwater residence time and the highly resistant nature of the sediments to weathering, ensures that weathering takes place only to a limited extent. This leads to the low levels of major ions and the associated low values of electrical conductivity. Downstream in the urbanized areas, EC increases with associated increases in the various dissolved constituents. The occurrence of significant amounts of nitrates in most sample points reflects a degradation of groundwater due to anthropogenic pollution meanwhile Na-Cl and Na-Ca-Cl are dominant water types. The chemistry of groundwater in the urban area may be controlled by many processes involving: (1) atmospheric deposition of sea salts; (2) anthropogenic inputs; (3) possible sea water mixing; (4) weathering of feldspars especially in some wells like W16 and W22; (5) cation exchange between groundwater and clay. Calcium ions in groundwater is being exchanged for Na<sup>+</sup> as seen for some samples like SP2 and SP1 which show an excess of Na<sup>+</sup> compared to the sea water ratio of Na/Cl. The chemistry of groundwater is mainly dominated by Na and Cl close to the Woruri lagoon downstream, indicating effects of sea spray and possible seawater intrusion.

Another characteristic fact which has been pointed out in this study is the vulnerability of the groundwater to acid deposition. Leaching of base forming cations from the soil due to high rainfall, leads to a drop in the acid buffering capacity of the system as a result of soil acidification. The short residence time of groundwater in the aquifer together with the resistant nature of the aquifer sediments equally provides very little buffer for acid inputs. Because of the consequences with regards to increased solubility and decrease sorption of trace metals, the causes of acidity should be investigated in more detail. There is a necessity to obtain significant time series data.

#### ACKNOWLEDGEMENT

This work was supported by a fellowship from the Third World Organisation for Women in Science (TWOWS) to G T. We thank IITB and the Institute of Geological and Mining Research (IRGM) for providing laboratory and infrastructure facilities.

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