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Advances in Applied Science Research, 2012, 3 (1): 312-318

ISSN: 0976-8610
CODEN (USA): AASRFC

Trace metals in ground and surface waters of the Oban Massif area, SE Nigeria

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ABSTRACT

Concentration levels of selected potentially toxic trace elements (Fe, Mn, Pb, Ni, Cd, Cr) were determined for surface waters and ground waters of deep and shallow aquifers within the Precambrian basement of Oban massif (south-eastern Nigeria). The aim of this was to determine the source of the elements and assess indications of possible pollution. Statistical analysis (mean, range and standard deviation) indicates no significant variations across sampling seasons and concentration levels are within common ranges. Correlations, factor analysis and metal load classification indicates geogenic processes of weathering and leaching of basement rocks as major source of these elements.

Keywords: trace elements, groundwater, factor analysis, correlation, Oban massif, Nigeria.

INTRODUCTION

Comprehensive hydrochemical studies have not been a routine part of groundwater supply schemes in most parts of Africa. However, in recent times, water quality studies have received tremendous interest in most developing countries. This has been so primarily due to increased awareness for the protection and management as well as the declining levels of availability of the resource.

The chemistry of ground and surface waters depends on a number of factors such as, general geology, degree of chemical weathering of various rock types, quality of recharge water and inputs resulting from human activities. These factors and their interactions results to a complex ground and surface water quality reflected in concentrations of major, minor and trace constituents. The trace elements are usually the major concern due to their potential toxicity and attendant deleterious impacts on plants, animal and human populations.

Though effective techniques have been devised for groundwater assessment in the Precambrian basement terrains of much of sub-Saharan Africa, underlying geology has not been given top priority [1].

This study attempts to ascertain the trace element chemistry of surface and ground waters of the water bearing units of the Precambrian Oban basement complex relative to underlying geology.

Description of study area

Location

The study area, Oban crystalline basement complex, lies between Longitudes $8^0 00'$E and $8^0 55'$E and Latitudes $5^0 00'$N and $5^0 45'$N (Fig. 1). The massif spans an area of about 8,740 sq. km [2], with elevations of about 150m (a.m.s.l) and a number of isolated hills with maximum height at 1,200m above sea level [3].

The massif is well drained, controlled by weathered zones, fractured and jointed areas, coursing in two directions: southwards and seaward; and northward to join the upper course of the Cross River in the Ikom depression.

Climate

The Oban massif area belongs to the tropical climate with two distinct seasons viz wet and dry. The wet season spans a period of about six months (May to October) and the dry season lasts from November to April. General temperature trend for the study area is high with negligible diurnal and annual variations. The average monthly temperatures in the area ranged from 26 – 34^0 C during the period of study. Mean annual rainfall of about 2,300mm have been reported for the area, with annual mean daily relative humidity and evaporation of 86 % and 3.85mm/day respectively (Petters et al., 1989). Regional run-off coefficient of the study area, are in the order of 0.21-0.61 and are due to topography and evaporation, [4].

Geology and hydrogeology

The massif is dominantly of two major sectors; the western sector (topographically sub-dued with higher human population density) and the eastern sector (topographically rugged country with peaks forested up to summits and sparse human settlements). These sectors also vary in terms of geology. The western sector is dominantly of gneisses, granites, quartzites, schists, dolerites, granodiorites and pegmatites [5], while the east is of Migmatites, biotite-hornblende-gneisses, granites and amphibolites [6]. [7] summarises the Oban massif as being underlain by highly deformed Precambrian crystalline rocks, mainly granites, gneisses and schists. Theses rocks exhibit varying degrees of weathering across the massif. They are intruded by pegmatites, granodiorites, diorites, tonolites, monzonites, charnokites and dolerites.

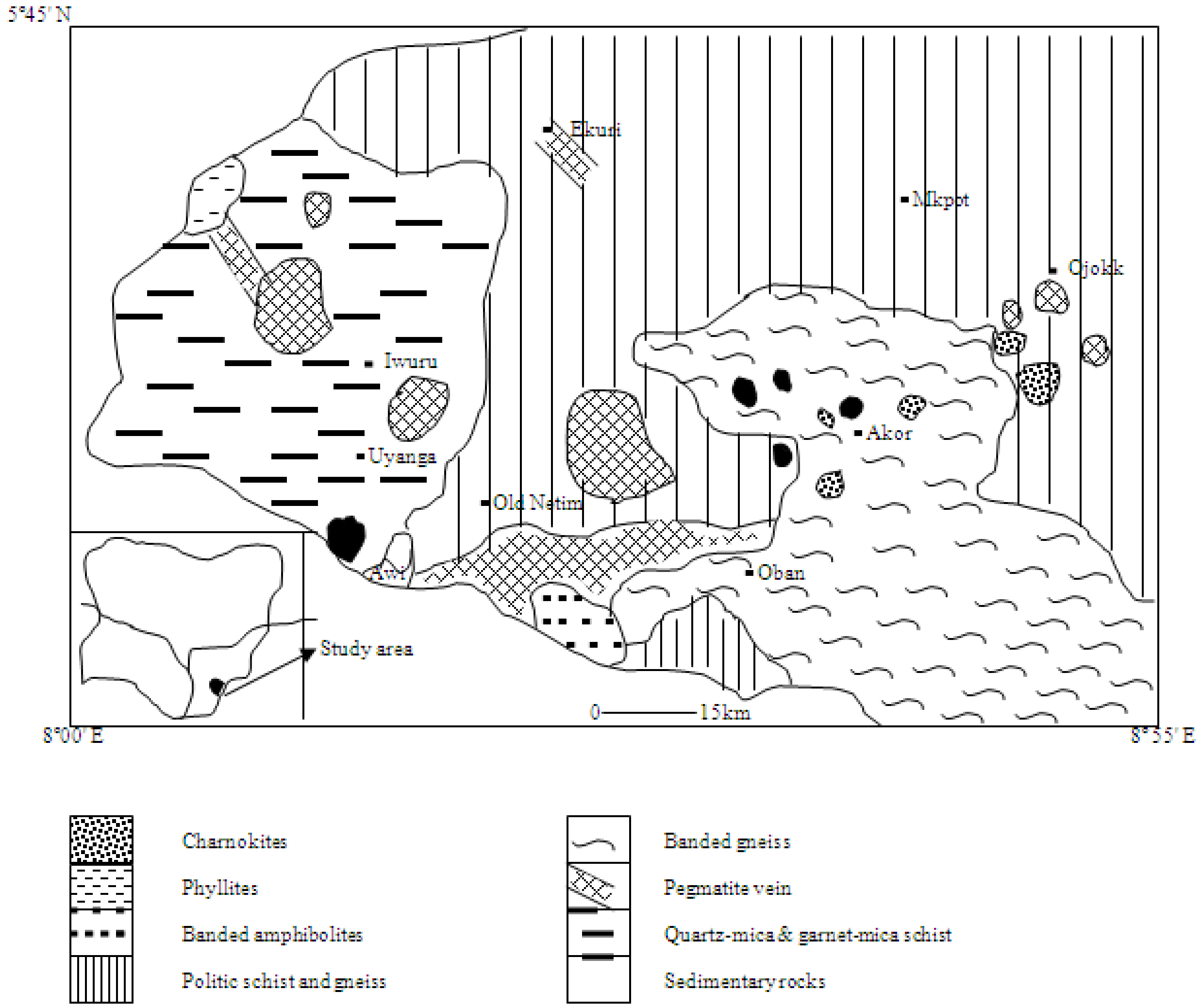

Fig. 1 Geologic map of the study area (Oban massif): insert map of Nigeria [7].

Economic minerals that have been identified within this basement complex include feldspars, galena, gemstones, graphite, gold, ilmenite, kaolin, manganese, mica, quartz, rutile, tin and uranium [8]. However current mining activities within the massif are limited to those of aggregates for the building and construction industries.

Groundwater within the Oban massif is controlled by structural discontinuities such as fractures, joints, fissures and regolith, [9] and [10]. Rates and levels of recharge to porous aquiferous media in the study area, suffer impedance due to the top lateritic cover characteristic of the area. This is consequent of the high clay contents of the top lateritic soils, hence their low permeability.

Depth extent of aquiferous layers as revealed from drilled sections varies across the western and eastern sectors of the study area. Three basic aquiferous units have been identified and wells penetrate these aquifers at different levels across the massif [11]. The aquifers are classified as deep and shallow aquifers. The shallow aquifer wells exhibit a maximum drill depth of less than 15m and are usually hand dug and open. The deep aquifer wells are those of drilled depth greater than 15m, extending up to 30m, mechanically drilled and usually pump fitted. This scenario hence entails the transfer of groundwater between these seemingly successive layers of different degrees of cross-cutting and depth of weathering. The fractures and lineaments act as conduits of groundwater from shallow aquifers to deeper levels.

MATERIALS AND METHODS

Methodology

Seventy six water samples were collected from wells (shallow and deep aquifers) and surface water bodies within the Oban massif area. These included samples from both the wet and dry seasons across the geologically varied massif. In-situ measurements included temperature, electrical conductivity, total dissolved solids, pH and Eh, using standard field equipment (PHT-027 multi-parameter water quality probe). Two samples were collected from each location in 75cl polyethylene bottles. The sample bottles were soaked in 10% HNO_3 for 24 hours and rinsed several times with de-ionized water prior to use. At the sampling locations, the bottles were thoroughly rinsed with aliquots of the sampled waters, prior to collection. One sample from each location was preserved by acidifying to pH ca.2 with 0.5ml of concentrated HNO_3 acid for trace metals analysis.

Major and trace elements contents where determined by atomic absorption spectrometry (AAS) model, UNICAM 939. The anion contents of samples were determined by colorimetric method using UNICAM UV2 spectrophotometer. All instrumental analyses were carried out in the laboratories of the Aluminium Smelter Company of Nigeria (ALSCON), Ikot Abasi, Nigeria.

RESULTS AND DISCUSSION

Statistical summary of physical parameters and trace elements of the waters are given in Tables 1(a) & 1(b). The temperature means of the waters were 27.06ºC, 27.83ºC and 27.0ºC for the shallow & deep aquifers, and surface waters in the dry season respectively. During the wet season, values were 28.0ºC, 28.07ºC and 26.9ºC respectively. The pH ranges were; 5.12-6.86, 5.08-6.34 and 6.15-6.77 in the dry season and 5.88-7.69, 6.27-8.65 and 5.63-8.10 in the wet season for shallow, deep and surface waters respectively. The waters tended to be less acidic to alkaline from dry to wet season, showing variations related to soil CO_2 and bicarbonate concentration (Ekwere, 2010). Electrical conductivity (EC) which expresses ionic strength of solution, recorded mean values of 300.65, 96.44 and 32.11µs/cm in the dry season and 258.88, 200 and 566.67µs/cm in the wet season for shallow, deep and surface waters respectively. Total dissolved solid (TDS) recorded average values of 180.2, 61.83 and 2058ppm (dry season) and 285.88, 200 and 566.67ppm (wet season) for the shallow, deep and surface waters respectively. Generally EC and TDS concentration values were lower in the dry compared to the wet seasons. Results of major ions are documented in [11].

Table. 1(a) Descriptive statistics of parameters as measured in the dry season

Source	Statistics	Temp(^{0}c)	pH	EC(µs/cm)	TDS(ppm)	Fe	Mn	Ni	Cr	Cd	Pb
Shallow aquifer	Min	26	5.12	24.8	15.9	0.003	0.008	0.001	0.001	0.001	0.001
	Max	28	6.86	622	398.7	0.334	0.428	0.039	0.021	0.003	0.008
	Mean	27.06	6.02	300.65	180.2	0.063	0.175	0.010	0.007	0.001	0.002
	SD	0.79	0.46	255.62	169.72	0.092	0.159	0.015	0.005	0.001	0.002
Deep aquifer	Min	26	5.08	34.6	22.18	0.002	0.043	0.001	0.001	0.001	0.001
	Max	32	6.34	250	209	0.134	0.368	0.009	0.009	0.002	0.004
	Mean	27.83	5.72	96.44	61.83	0.043	0.128	0.002	0.003	0.001	0.001
	SD	1.75	0.37	92.31	59.17	0.06	0.12	0.003	0.003	0.001	0.001
Surface water	Min	26	6.15	20.9	13.40	0.009	0.002	0.005	0.001	0.001	0.001
	Max	29	6.77	47.4	30.38	2.984	0.184	0.027	0.007	0.007	0.005
	Mean	27	6.51	32.11	20.58	0.347	0.068	0.01	0.003	0.003	0.003
	SD	1.05	0.27	7.28	4.66	0.88	0.06	0.01	0.00	0.00	0.00

Table. 1(b) Descriptive statistics of parameters as measured in the wet season

Source	Statistics	Temp(^{0}c)	pH	EC(µs/cm)	TDS(ppm)	Fe	Mn	Ni	Cr	Cd	Pb
Shallow aquifer	Min	27	5.88	80	60	0.001	0.007	0.003	0.003	0.001	0.001
	Max	30	7.69	580	890	9.80	0.201	0.061	0.036	0.021	0.021
	Mean	28	6.84	285.88	333.75	2.51	0.077	0.017	0.010	0.004	0.004
	SD	0.92	0.54	176.27	262.57	3.57	0.054	0.015	0.013	0.006	0.006
Deep aquifer	Min	26	6.27	60	40	0.046	0.005	0.003	0.003	0.001	0.001
	Max	30.4	8.65	430	570	1.759	0.224	0.041	0.034	0.015	0.017
	Mean	28.07	7.17	200	196.15	0.72	0.087	0.014	0.015	0.005	0.004
	SD	1.08	0.72	124	149.64	0.642	0.064	0.012	0.009	0.005	0.005
Surface water	Min	26	5.63	210	140	0.128	0.008	0.003	0.002	0.001	0.001
	Max	28	8.10	800	790	1.108	0.165	0.036	0.015	0.025	0.041
	Mean	26.9	7.18	566.67	462.22	0.547	0.075	0.011	0.008	0.006	0.01
	SD	0.73	0.69	165.53	184.84	0.31	0.04	0.01	0.00	0.01	0.01

Trace metal concentration

Descriptive statistics of trace elements in comparison with maximum admissible concentrations (MAC) and [12] standards for drinking water are presented in Table 2. Concentration levels of Fe, Mn, Ni, Cr, Cd and Pb were below the maximum admissible concentration for drinking water.

Table 2. Mean concentration of trace elements (mg/l) across seasons

Source	Season	Fe	Mn	Ni	Cr	Cd	Pb
Deep aquifer	Dry	0.043	0.128	0.002	0.003	0.001	0.001
	Wet	0.72	0.087	0.014	0.015	0.005	0.004
Shallow aquifer	Dry	0.063	0.175	0.010	0.007	0.001	0.002
	Wet	2.51	0.077	0.017	0.010	0.004	0.004
Surface water	Dry	0.347	0.068	0.010	0.003	0.003	0.003
	Wet	0.547	0.075	0.011	0.008	0.006	0.010
Common range^a		0.04-6200	0.01-110	0.001-0.7	0.032-5	0.18-1.0	10-5600
MAC^a		200.00	50.00	20.00	50.00	3.00	1.50
WHO		0.3	0.1			0.005	0.050

Common range^a in µg/l (adapted from [13])
MAC^a maximum admissible concentration (adapted from [14])
WHO (2001)

The mean abundance of these trace elements are in the order of Fe > Mn > Ni > Cr > Cd > Pb. This indicates that the probable source of these elements is mainly the rocks of the Precambrian basement. All the major host rocks and possible host minerals for these elements are present in the area [11].

Iron (Fe) has highest mean concentration for surface water in the dry season, higher than the recommended value by [12]. Mean concentration of Fe^{2+} is higher in the shallow aquifers than the deep aquifers in the dry season. This trend is also evident in the wet season, but the mean value is least for surface waters. Iron (Fe^{2+}) is largely mobilized and redistributed during the chemical weathering of igneous and metamorphic rocks. Relatively higher values in the wet season are attributed to leaching of iron (Fe^{2+}) from soil material into the water table as water level increases alongside increase in precipitation. Depreciation in contents for surface waters is related to dilution by surface run-off.

Manganese records values higher than the [12] standard (0.1mg/l) in some locations for the shallow and deep aquifers in the dry season. Similar trend is noticed in some locations in the wet season for all water types. However the average values across the study area, for both sampling seasons, are below the standard value. Cadmium (Cd) exhibited values below MAC and WHO safety standards across seasons, except for one location. Surface water from one location had Cd at 0.007mg/l which is higher than [12] standard at 0.005mg/l. Nickel, chromium and lead had all values for shallow and deep aquifers and surface waters below the MAC limits.

Table 3 shows the mean concentration levels of the trace elements across the western and eastern sectors of the massif relative to geology. Fe, Mn, Ni and Cr have mean values that are higher on the western than the eastern sector. Cadmium and lead have values higher on the eastern flank. The higher level of metals on the western flank is adjudged to biodegradation of organic wastes with release of metal loads eventually leached into sub-surface waters.

Correlation matrices

Pearson's correlation matrix is normally used to find relationships between two or more variables. Correlation at 5% level of significance ($P < 0.05$), show significant correlation between the following pairs Fe and Ni; Cd and Ni, Cr and Pb and Ni, Cr, Cd (Table 4). Values of $r > 0.3$ were considered as significant from correlation results. The source of these elements is the Precambrian basement complex. This is supported by the mean elemental concentration of these elements in rocks and water [13].

Table 3. Mean variation of parameters across sectors of the massif (Values in mg/l)

Element	Western sector	Eastern sector
Fe	7.13	1.63
Mn	0.13	0.07
Ni	0.011	0.010
Cr	0.010	0.009
Cd	0.002	0.004
Pb	0.002	0.005
Lithology	Gneiss, quartzite, schist, granodiorite, pegmatite, gneissic-granite.	Migmatites, schists, amphibolites, quartzite, syenites.

Table. 4 Correlation coefficients of trace elements in the waters of the study area

	Fe	**Mn**	**Ni**	**Cr**	**Cd**	**Pb**
Fe	1					
Mn	-0.138	1				
Ni	**0.343**	-0.187	1			
Cr	0.127	0.011	0.297	1		
Cd	0.263	0.063	**0.396**	**0.742**	1	
Pb	0.244	-0.115	**0.417**	**0.608**	**0.649**	1

Factor analysis

Factor analysis is a multivariate statistical technique that is widely used to aid interpretation of geochemical data and enhances subtle but significant single-element anomalies [15]. In other words, factor analysis has the simple objective of revealing an underlying relation that is presumed to exist within a set of multivariate observation, [16]. By so doing the structure of the underlying system that produced the data is well understood. Factor analyses were employed in this study to process data and determine the sources of trace elements relative to physical parameters as well as factors controlling such. Results of R- mode factor analyses for average concentrations of trace elements in the waters are shown in factor matrix Tables 5.

Due to the uniform geology of the area two distinct factors were recognized and these account for about 60% of total data variance.

Factor 1 accounts for 37% of the data variance and consists of Pb, Cd, Cr, Ni and Fe as significant components. The factor is interpreted to be related to geogenic process of rock weathering and mineral dissolution. The principal components are major constituents of the varied mineral species of varied saturation states, contained in the rocks of the study area [11]. Factor 2 with principal components as electrical conductivity (EC), total dissolved solids (TDS) and Mn constitute about 22% of data variance. It is interpreted as reflective of processes of weathering, infiltration, dissolution and water mixing [11].

Classification of sampled water

An attempt to classify these waters was carried out. This was based on the method of [17] and modified by [18], which uses the water pH and metal load. The metal load as expressed in this study was computed as Mn+Ni+Cr+Cd+Pb. Figure 2 shows that all the waters except for three locations fall within the near-neutral low metal field of the plot. This indicates the natural process of weathering of the Precambrian rocks in the area as the major source of these elements [11]. The three locations within the acid low metal field could reflect effects of leaching by acidic rainwater of altered rocks giving rise to the acidic nature of the groundwater. However studies have shown that metal concentrations in groundwater are diminished by influx of unpolluted waters and by adsorption and precipitation processes [19] and [20]. Hence amounts of metal input from anthropogenic and weathering process may have been removed by the aforementioned processes.

Assessment through speciation modelling reveals that, concentration levels of these metals and their presence within limiting mineral phases (carbonates and sulphates) reduce the risk of their contamination to groundwater within the study area [11].

Table 5. Factor loading for sampled water.

Parameter	Factor 1	Factor 2
Temp	-0.0190	-0.0872
pH	-0.0144	-0.1693
EC	-0.0634	**0.9592**
TDS	-0.0321	**0.9398**
Pb	**0.8941**	-0.0756
Cd	**0.7534**	-0.2819
Cr	**0.7328**	0.3967
Ni	**0.8881**	0.1446
Fe	**0.6805**	-0.0240
Mn	-0.2940	**0.5636**
Eigen value	4.0367	2.4439
% total variance	36.70	22.23
Eigen value cumul.	4.0367	6.4806
Cumul. % variance	36.70	58.92

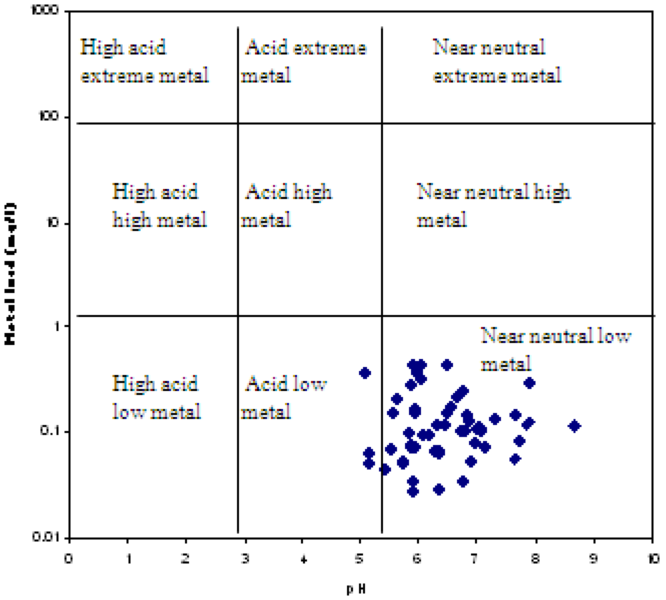

Fig. 2 Classification of water samples based on the plot of metal load and pH

CONCLUSION

The concentrations of the elements are generally below common ranges indicating no contamination with respect to these elements. Correlation matrices, R- mode factor analysis and metal loads indicate the sources of these elements as natural mainly from the leaching of the Precambrian basement rocks. Their concentration levels are controlled by prevailing pH conditions, degree of weathering as well as minimal human activities across the massif. The deduced data set will serve as a reference background for future monitoring and vulnerability of the aquifers to pollution due to an expected increase in urbanization and industrial activities.

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