

Baseline concentration and sources of trace elements in groundwater of Cross River State, Nigeria

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To cite this article:

Aniekan Edet, Aniediobong Ukpong, Therese Nganje. Baseline Concentration and Sources of Trace Elements in Groundwater of Cross River State, Nigeria. *International Journal of Environmental Monitoring and Analysis*. Vol. 2, No. 1, 2014, pp. 1-13.

doi: 10.11648/j.ijema.20140201.11

Abstract: Groundwater samples were collected from wells in Cross River State (Nigeria) and analysed for trace elements including Ba, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Rb, Sr and Zn. The primary aim of the study was to determine the baseline concentrations of these metals, while the secondary aim was to assess the present level of pollution, as a basis for future impact of human and industrial activities on the groundwater quality. Multivariate statistical methods were applied to determine the relationships between the different trace elements and also infer their different sources. The results showed that the contents of Ba, Fe, and Pb in groundwater from some locations were higher than the World Health Organisation, WHO maximum admissible concentration (MAC) of 700µg/l, 300µg/l and 100µg/l respectively. The contents of Cd, Co, Cu, Fe, Mn, Ni, Pb, Rb and Zn were lower than the concentrations in freshwater, while the contents of Ba, Cr, Li, Mo and Sr in some of the locations exceeded the values in typical freshwater. Correlation and cluster analyses indicated common sources for some elements, while factor analysis suggested dissolution of brine, dissolution of barite mineral, weathering of the bedrock and prevailing oxidation-reduction potential of the environment as the main factors responsible for the occurrence of these trace elements in groundwater. The present data therefore is expected to serve as a good guide for future groundwater management of the area.

Keywords: Trace Metals, Background Values, Multivariate Analysis, Pollution, Nigeria

1. Introduction

Groundwater can be polluted with trace elements from a variety of sources, such as weathering, decomposed vegetative and animal matter, fallout from air particulate and industrial activities [1]. Though some trace metals such as copper, cadmium, chromium, zinc etc are essential to humans, however when the concentration is high, it may cause some physiological disorder [1, 2]. Therefore, there is the need to document the present levels of trace metals in groundwater, especially in an industrially virgin area such as the present study area. Few studies have been conducted with respect to the content of trace elements in water of the study area. For example, [3, 4] documented the distribution of Fe and Mn in surface waters of Akpabuyo and Odukpani in the southern parts of the study area. Reference [5], reported on the use of different indices for monitoring heavy metal contamination in southern parts of Cross River State. Analysis of groundwater from Calabar area in the south indicated that most trace elements in groundwater

were below normal averages and do not pose any risk to the aquifer [6, 7]. References [8] and [9], noted that the concentrations of Fe and Mn in groundwater of northern parts of the Cross River State were within the normal averages when compared to global waters

A large number of workers have also researched on trace elements contents of groundwater in Nigeria. However, majority of these works were tailored to the contents of Fe and Mn. Reference [10] revealed that the concentrations of Fe and Mn in groundwater of Nigeria are due to natural sources. They also reported that, the maximum values observed for Fe and Mn in groundwater of Nigeria were well over the WHO [11] guideline values of 0.30mg/l and 0.10mg/l for Fe and Mn, respectively.

To date no baseline or comprehensive study has been done to determine the trace element content in the groundwater of the study area. In this study, therefore the concentration of various trace elements and their sources were carried out as a prelude to future industrial development and attendant pollution in the study area.

2. The Cross River State Area

The study area, Cross River State is situated in southeastern corner of Nigeria (Fig. 1). The mean annual rainfall for the area varied from more than 3000 mm in the

south through about 2000 mm in the central parts to less than 1800 mm in the north. The rainfall patterns consist of alternating wet (April-October) and dry (November-March) periods. Mean annual air temperature for the area ranged from 30.1°C in the north to 22.4°C in the south [12].

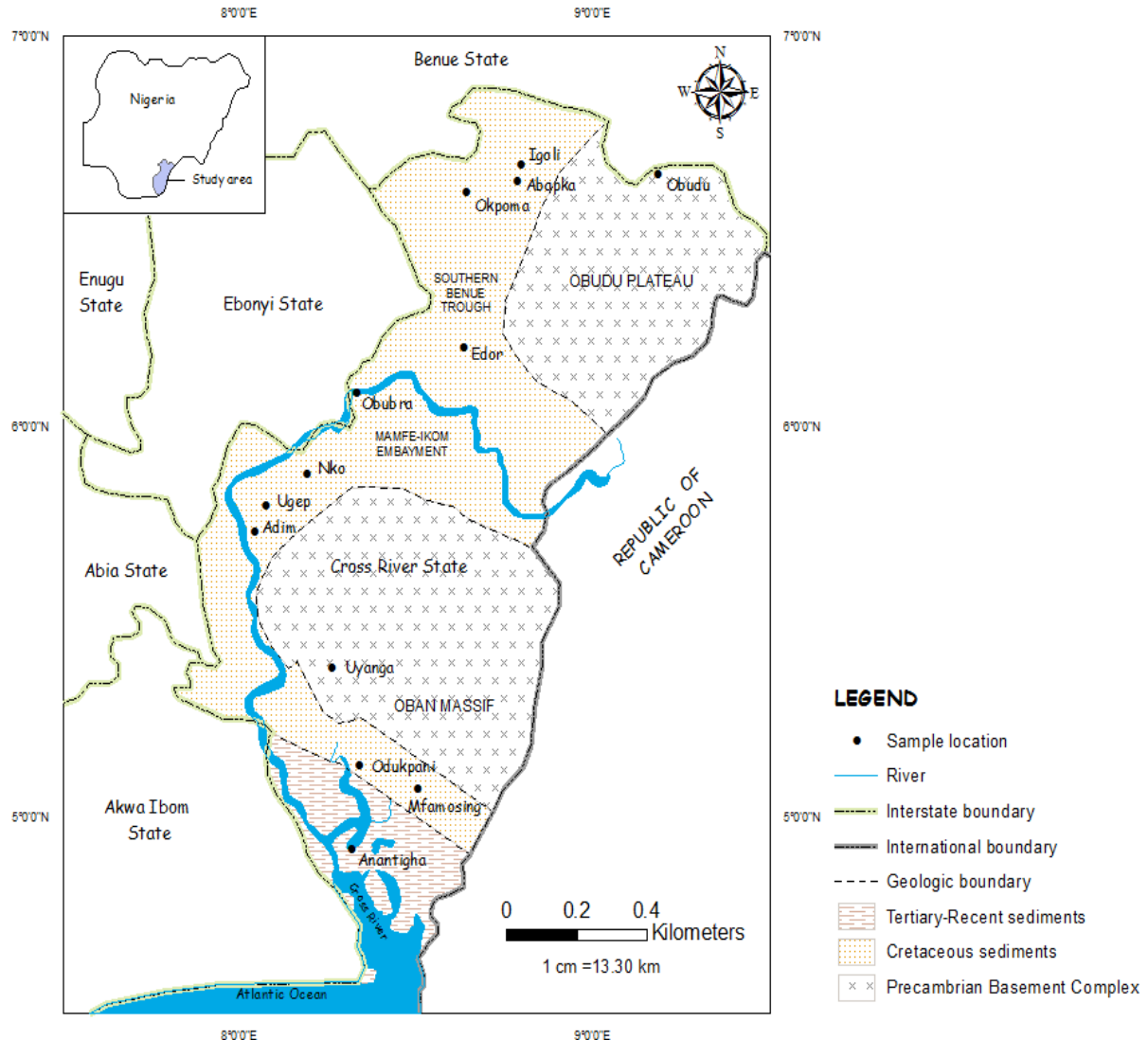


Figure 1. Map of study area, Cross River State including sampled locations

The main physical features of Cross River State include highlands with elevations in excess of 400 m above sea level. By contrast, the low lands have elevations of up to 350 m decreasing southwards to a few meters near the coast in the south. In terms of geology, the area is underlain by Precambrian Crystalline Basement. Cretaceous to Tertiary age sedimentary rocks overlies the basement rocks. The basement areas consist predominantly of gneisses, schists, amphibolites, pegmatites, granites, granodiorites, diorites, tonalities etc, while the sedimentary formations consists of conglomerates, sandstones, shale, limestones, marls, clays, sands and silts. The hydrogeology is largely dependent on the lithology of the area. The major hydrogeological units of the area are the crystalline basement; sandstone-siltstone-limestone-intrusive; shale-intrusive; shale; coastal

plain sand and alluvium [13, 14].

3. Materials and Methods

3.1. Sampling and Analyses

Sixteen groundwater samples were collected from 13 locations within the study area (Figure 1). Sampling, preservation and analyses of the groundwater samples were based on standard procedures as described in Reference [15]. The groundwater temperature, pH/Eh, electrical conductivity (EC)/total dissolved solids (TDS) and dissolved oxygen (DO) were conducted insitu using potable kits. The analyses for trace elements were performed using a Parkin Elmer ELAN 6000 inductively coupled plasma

B

Location Name	Ba	Cd	Co	Cr	Cu	Fe	Li	Mn	Mo	Ni	Pb	Rb	Sr	Zn
								µg/L						
Anantigha	71	<0.10	0.41	2.0	1.2	<1.0	<1	36	<0.10	1.0	10	7.2	21	12
Odukpani	28	<0.10	<0.10	4.6	0.25	<1.0	<1	<1.0	1.8	<1.0	<0.10	19	96	5.0
Uyanga	42	<0.10	0.40	4.4	0.23	<1.0	1.5	15	0.40	<1.0	1.4	3.7	27	3.0
Adim	94	<0.10	0.34	3.3	0.79	1600	<1	3.4	0.57	1.2	1.5	8.1	55	4.1
Ugep	106	<0.10	0.12	<1.0	0.13	<1.0	<1	15	<0.10	<1.0	<0.10	10	31	9.0
Obubra	46	<0.10	0.11	3.8	0.30	320	<1	1.7	<0.10	<1.0	2.9	3.3	49	1.5
Okpoma	78	<0.10	<0.10	6.5	0.18	<1.0	7.2	<1.0	0.16	<1.0	<0.10	1.1	608	<0.10
Igoli	48	<0.10	<0.10	26	4.3	<1.0	83	37	0.40	<1.0	<0.10	4.3	1180	152
Abakpa	802	<0.10	5.5	3.4	2.8	<1.0	4.7	207	<0.10	6.7	13	53	284	16
Edor	111	<0.10	<0.10	<1.0	<0.10	<1.0	<1	<1.0	<0.10	<1.0	<0.10	8.7	22	3.4
Nko	176	<0.10	0.59	7.1	1.5	<1.0	<1	<1.0	1.9	<1.0	<0.10	109	399	12
Obudu	89	<0.10	<0.10	2.9	0.40	89	<1	<1.0	0.47	1.2	<0.10	19	58	<0.10
Mbarakom	812	<0.10	<0.10	<1.0	0.27	<1.0	2.4	2.3	<0.10	<1.0	<0.10	34	110	1.7

^aSee Fig. 1

The chloride values ranged between 0.98 and 139.02mg/l with an average of 26.97mg/l. The nitrate contents ranged from 0.07 to 187.04mg/l with an average of 32.7mg/l. Three samples from Anantigha, Nko and Abakpa exceeded the MAV of 10 mg/l. Sulphate contents ranged from 0.38 to 626.05 mg/l with average of 58.93mg/l with one sample from Igoli exceeding the MAV of 400mg/l. The concentration of bicarbonate varied between 6.91 and 80.0 mg/l with an average of 23.27mg/l.

The sodium contents ranged from 2.88 to 676.27mg/l (average of 76.66mg/l) with one sample (10%) exceeding the MAV of 200mg/l and 11 samples (90 %) have concentrations lower than the MAV. The potassium values ranged from 0.64 to 108.93mg/l with an average of 15.51 mg/l with two samples from Abakpa (45.4 mg/l) and Nko (108.93 mg/l) exceeding the MAV of 12 mg/l. The calcium contents varied from 4.2 to 68.79mg/l (average of 15.65 mg/l). The contents of magnesium ranged from 0.38 to 8.74 mg/l (average 2.56 mg/l).

4.2. Concentration of Trace Metal in Groundwater

Barium (Ba)

The average content of barium in the groundwater is 192.54µg/l. The Ba concentration in two samples exceeded the MAV (700µg/l). However, the contents of Ba in all the groundwater samples exceeded typical value in freshwater of 3µg/l [27]. More than 75% of barium contents in groundwater are in the ionic form Ba^{2+} . The relatively high concentration of barium was attributed to barite mineralization in the study area [23, 24, 25, 26].

Cadmium (Cd)

Cd contents in the groundwater of the study area were below the detection limit (BDL) of the equipment (<

0.10µg/l) from all the locations within the study area. This was attributed to low cadmium related activity and /or non-geologic source.

Cobalt (Co)

The contents of Co in six samples were BDL. All the samples had Co concentrations below the values for typical freshwater (10 -18µg/l), [27]. Co is non-toxic and more than 70% occurred in the ionic form as $Co(OH)_2$, while less than 10% occurred in the form Co^{2+} .

Chromium (Cr)

Chromium is a low mobility element especially, under moderately oxidizing and reducing conditions and near neutral pH (Machender et al., 2011). Cr values ranged between < 0.10 and 26.0µg/l with three samples having concentrations BDL. The concentrations of Cr in 10 samples were lower than the MAV (50µg/L), but higher than typical value in freshwater of 0.18 µg/l [27]. Cr occurred in the ionic form, $CrOH^+$ in groundwater of the study area.

Copper (Cu)

The contents of Cu in all samples considered were lower than the MAV of 1000 µg/l and typical values in freshwater (10-2800µg/L). The ionic form, $Cu(OH)_2$ was the main species, which constituted more than 60% of the total copper in groundwater of Cross River State.

Iron (Fe)

Eighty five per cent of the groundwater samples complied with the MAV (300 µg/l) for drinking and domestic purposes in terms of Fe content. Samples from two locations at Obubra and Adim exceeded the MAV.. However, the content of Fe in all the groundwater samples

fell within the range documented for freshwater (0.04 - 6200 µg/l).

High iron concentration in groundwater in some locations probably resulted from interaction of oxidized iron minerals and organic matter and subsequent dissolution of Fe_2CO_3 at a comparatively lower pH [2]. Another probable source of the high iron content was attributed to the removal of dissolved oxygen by organic matter, which resulted in reduced conditions. Under reducing conditions, the solubility of iron bearing minerals increases leading to enrichment of dissolved iron content in groundwater [28, 29].

Lithium (Li)

The content of Li in the groundwater of the study area were below the MAV of 50µg/l. One sample (Igoli), however had Li content of 83µg/l. The concentrations of Li in groundwater samples from four locations (Igoli, Abakpa, Uyanga, Mbarakom) exceeded typical Li content in freshwater (1.1 µg/l). The relatively high contents of lithium at Igoli and Abakpa were related to the saline groundwater in these locations.

Manganese (Mn)

The average value is 24.8µg/L, which is lower than the MAV (500µg/l) and within the average range in freshwater (0.1-110 µg/L).

Molybdenum (Mo)

Molybdenum contents were below the MAV of 70µg/l. The concentrations in groundwater from five locations (Odukpani, Adim, Nko, Uyanga, Obudu) exceeded typical level in freshwater of 0.3 µg/L. The dominant dissolved molybdenum species in the groundwater of the study area is MoO_4 comprising between 73.6 and 96.6% in groundwater of the area.

Nickel (Ni)

The values of Ni are below the MAV of 70µg/L. In all the locations sampled, the concentrations of Ni were lower than the level of Ni in a typical freshwater (10 µg/l). The dominant species of nickel in the groundwater include Ni (OH)₂ comprising 45 to 63%; Ni^{2+} with 11 to 20%; NiCO_3 , 10 to 17% and Ni (OH)⁺, 10 to 16%.

Lead (Pb)

More than 90% of the groundwater samples had Pb values below the MAV of 10 µg/L and typical values in freshwater of 10-5600µg/l. The dominant lead species in groundwater of the study area include Pb (OH)₂ comprising 15-55% and Pb (CO₃)₂ varying between 10 and 55%. The other lead species in the groundwater were Pb (OH), PbCO₃ and Pb (OH)₃ respectively, in the range 12-33%, 12-16% and 10-16%.

Rubidium (Rb)

The concentration of Rb exceeded concentration in typical freshwater (1.0 µg/L).

Strontium (Sr)

The concentrations of Sr in groundwater of the study area exceeded typical concentration in freshwater (50.0 µg/l) at seven locations. The main source of strontium is attributable to the saline groundwater at Abakpa, Igoli, Nko and Okpoma [30, 31, 32, 33].

Zinc (Zn)

The concentrations of zinc in groundwater of the area are lower than the MAV of 5000 µg/l and average concentration in typical freshwater (0.1-240 µg/L). In all the groundwater samples considered, Zn (OH) constituted the major ionic species ranging between 91.5% and 96.0%.

Table 2. Statistical summary of physicochemical parameters and trace elements contents in groundwater samples, Cross River State, Nigeria.

Type	Parameter	Units	Mean	Med	Min	Max	SD	MAV ^a	Freshwater ^b	Background value ^c	Threshold value ^c
Physical	Temp	°C	29.19	29.00	28.40	30.10	0.58				
	EC	µS/cm	458.72	101.90	70.80	2416.00	716.50	1400			
	TDS	ppm	229.24	51.00	35.40	1213.00	359.16	1000			
	pH		6.20	6.01	5.32	7.85	0.79	6.5-8.5			
	Na ⁺		76.66	8.72	2.88	676.27	190.87	200			
Chemical	K ⁺		15.51	2.78	0.64	108.93	31.93	12			
	Ca ²⁺		15.65	10.20	4.20	68.79	18.62				
	Mg ²⁺	mg/l	2.56	1.30	0.38	8.74	2.99	100			
	Cl ⁻		26.97	7.76	0.98	139.02	44.44	250			
	HCO ₃ ⁻		23.27	10.20	6.91	80.00	24.13				
	SO ₄ ²⁻		58.39	2.05	0.00	626.05	179.44	400			
	NO ₃ ⁻		32.71	12.30	0.07	187.04	51.87	50			
	Ba		192.54	89.00	28.00	812.00	275.38	700	3	800	800.00
	Cd		0.10	0.10	0.10	0.10	0.00	5	0	0.1	0.10
	Co		0.62	0.11	0.10	5.50	1.48	1000 ^d	10.0 - 18.0	0.43	0.47

Type	Parameter	Units	Mean	Med	Min	Max	SD	MAV ^a	Freshwater ^b	Background value ^c	Threshold value ^c
Heavy metal	Cr		5.15	3.40	1.00	26.00	6.56	50	0.18	4.2	4.20
	Cu		0.96	0.30	0.10	4.30	1.27	1000	10.0-2800.0	0.44	1.72
	Fe		155.31	1.00	1.00	1600.00	443.17	300	40.0-6200000	4.1	4.10
	Li	µg/l	8.22	1.00	1.00	83.00	22.55	50	1.1	4.2	4.60
	Mn		24.80	2.30	1.00	207.00	56.27	50	100.0-110000.0	0.43	0.72
	Mo		0.48	0.16	0.10	1.90	0.63	70	0.3	3.5	3.50
	Ni		1.47	1.00	1.00	6.70	1.57	70	10	0.43	1.72
	Pb		2.28	0.10	0.10	13.00	4.23	100	10.0-5600.0	4.4	4.40
	Rb		21.57	8.70	1.10	109.00	30.08		1	43	46.50
	Sr		226.15	58.00	21.00	1180.00	337.85		50	4.3	4.65
	Zn		16.92	4.10	0.10	152.00	40.90	5000	0.1-240	3.5	3.50

^aWHO (1993, 2004, 2008); ^bPais and Jones Jr; ^cCoestsiers et al., 2009; ^dSiegel, 2002(MAV-Maximum Admissible Value; Med-Median; Min-Minimum; Max-Maximum; SD-Standard Deviation; MCL-maximum Admissible value; RV-Reference value)

4.3. Trace Elements and Lithology

The range of contents of different elements in groundwater samples within different lithologic units are presented in table 3. The data showed that the highest concentrations were obtained from the sandstone terrain, while the lowest concentrations were from the basement, which consist of igneous and metamorphic rocks. The low concentrations were attributed to the fact that, when the basement rocks are weathered, the weathered materials tend to be transported to sedimentary terrain in the lower elevations along with the dissolved elements. The high concentrations in the sandstone were attributed to the salt deposits associated with them [30, 31, 32, 33].

4.4. Natural Background Level (NBL) and Threshold Values (TV)

Natural background levels (NBL) and threshold values (TV) for the trace metals were established following the method of reference [34]. For the determination of NBL,

the method utilized a value defined as the 90 or 97.7 percentile of a chosen dataset to approach the natural composition of the media when no national method exist for derivation of NBL. The selection of 90 or 97.9 percentile depends on the amount of data. When large amount of data (≥ 60 sampling points) are available, the 97.7 percentile is preferred; while for smaller data set (< 60 sampling points), the 90 percentile is suggested. The sample points in the present study were less than 60, hence the 90 percentile was applied. For the determination of threshold values (TV), two cases were suggested as follows [34]:

Case 1: $NBL < REF$: $TV = (NBL + REF)/2$

Case 2: $NBL \geq REF$: $TV = NBL$

where REF is the baseline concentration in natural or unpolluted groundwater or guideline or maximum admissible concentration. The natural background level and threshold values for the trace metals are presented in Table 2.

Table 3. Classification of metals in groundwater samples from different geologic terrain

Element	Sand	Shale	Sandstone	Basement
Ba	71	28 - 78	48 - 802	42 - 812
Cd	<0.10	<0.10	<0.10	<0.10
Co	0.41	<0.10 - 0.11	<0.10 - 5.5	<0.10 - 0.10
Cr	2.0	3.8 - 6.5	<1.00 - 26.0	<1.00 - 4.4
Cu	1.2	0.18 - 0.30	<0.10 - 4.3	0.23 - 0.40
Fe	<1.0	<1.00 - 320	<1.00 - 1600	<1.00 - 89.0
Li	<1.0	<1.00 - 7.2	<1.00 - 83.0	<1.00 - 2.4
Mn	36	<1.00 - 1.7	<1.00 - 207	<1.00 - 15.0
Mo	<0.10	<0.10 - 1.8	<0.10 - 1.9	<0.10 - 0.47
Ni	1.0	<1.0	<1.00 - 6.7	<1.00 - 1.2
Pb	10	<0.10 - 2.9	<0.10 - 13.0	<0.10 - 1.4
Rb	7.2	1.10 - 3.30	4.30 - 109	3.7 - 34.0
Sr	21	49 - 608	22 - 1180	27 - 110
Zn	12	<0.10 - 5.0	3.40 - 152	<0.10 - 3.0

Table 4. Classification of groundwater samples from Cross River State based on metal load

Metal Load	pH	Classification	Studied sample
mg/l			
< 1	< 3	High acid Low metal	
1 - 100		High acid High metal	
> 100		High acid Extreme metal	
< 1	3. - 5	Acid Low metal	
1 - 100		Acid High metal	
> 100		Acid Extreme metal	
< 1	> 5	Near Neutral Low metal	Anantigha, Edor, Mbarakom, Nko, Obubra, Obudu, Odukpani, Okpoma, Ugep, Uyanga
1 - 100		Near Neutral High metal	Abakpa, Adim, Igoli
> 100		Near Neutral Extreme metal	

Table 5. Calculated index of geo-accumulation (I-geo)

S/N	Sample ID	Location name	Ba	Cd	Co	Cr	Cu	Fe	Li	Mn	Mo	Ni	Pb	Rb	Sr	Zn
1	CR 12	Anantigha	-4.08	-0.58	-0.65	-1.66	0.86	-2.62	-2.66	5.80	-5.71	0.63	0.60	-3.16	1.70	1.19
2	CR 13	Odukpani Qua Town	-5.42	-0.58	-2.69	-0.45	-1.40	-2.62	-2.66	0.63	-1.54	0.63	-6.04	-1.76	3.90	-0.07
3	CR 15	Uyanga	-4.84	-0.58	-0.69	-0.52	-1.52	-2.62	-2.07	4.54	-3.71	0.63	-2.24	-4.12	2.07	-0.81
4	CR 18	Adim	-3.67	-0.58	-0.92	-0.93	0.26	8.02	-2.66	2.40	-3.20	0.90	-2.14	-2.99	3.09	-0.36
5	CR 19	Ugep	-3.50	-0.58	-2.43	-2.66	-2.34	-2.62	-2.66	4.54	-5.71	0.63	-6.04	-2.69	2.26	0.78
6	CR 23	Obubra	-4.71	-0.58	-2.55	-0.73	-1.14	5.70	-2.66	1.40	-5.71	0.63	-1.19	-4.29	2.93	-1.81
7	CR 23	Okpoma	-3.94	-0.58	-2.69	0.05	-1.87	-2.62	0.19	0.63	-5.04	0.63	-6.04	-5.87	6.56	-5.71
8	CR 26	Igoli-Ogoja	-4.64	-0.58	-2.69	2.05	2.70	-2.62	3.72	5.84	-3.71	0.63	-6.04	-3.91	7.52	4.86
9	CR 28	Abakpa-Ogoja	-0.58	-0.58	3.09	-0.89	2.08	-2.62	-0.42	8.33	-5.71	3.38	0.98	-0.28	5.46	1.61
10	CR 32	Edor	-3.43	-0.58	-2.69	-2.66	-2.72	-2.62	-2.66	0.63	-5.71	0.63	-6.04	-2.89	1.77	-0.63
11	CR 35	Nko	-2.77	-0.58	-0.13	0.17	1.18	-2.62	-2.66	0.63	-1.47	0.63	-6.04	0.76	5.95	1.19
12	CR 38	Obudu-Udigie	-3.75	-0.58	-2.69	-1.12	-0.72	3.86	-2.66	0.63	-1.67	0.90	-5.49	-1.76	3.17	-5.71
13	CR 47	Mbarakom	-0.56	-0.58	-2.69	-2.66	-1.29	-2.62	-1.39	1.83	-5.71	0.63	-6.04	-0.92	4.09	-1.63
		Mean	-3.53	-0.58	-1.57	-0.92	-0.46	-0.66	-1.63	2.91	-4.20	0.88	-3.98	-2.61	3.88	-0.55
	Statistics	Minimum	-5.42	-0.58	-2.69	-2.66	-2.72	-2.62	-2.66	0.63	-5.71	0.63	-6.04	-5.87	1.70	-5.71
		Maximum	-0.56	-0.58	3.09	2.05	2.70	8.02	3.72	8.33	-1.47	3.38	0.98	0.76	7.52	4.86
		Std.Dev.	1.49	0.00	1.71	1.32	1.72	3.82	1.87	2.60	1.75	0.76	2.77	1.80	1.92	2.86

Table 6. Classification of groundwater based on index of geo-accumulation (I-geo)

Index of geo-accumulation	Designation of groundwater quality	Trace metal
>5.00	extremely contaminated	Fe, Mn, Sr
4.0-5.0	strongly-extremely contaminated	Mn, Sr, Zn
3.0-4.0	strongly contaminated	Co, Fe, Li, Sr
2.0-3.0	moderately-strongly contaminated	Cr, Cu, Mn, Sr
1.0-2.0	moderately contaminated	Cu, Fe, Mn, Sr, Zn
0.0-1.0	uncontaminated-moderately contaminated	Cr, Cu, Li, Mn, Ni, Pb, Rb, Sr, Zn
<0.0	uncontaminated	Ba, Cd, Cr, Cu, Fe, Li, Mo, Pb, Rb, Sr, Zn

4.5. Metal Load

Metal load classification of the groundwater samples was based on the methods of references 35 and 36. The method used pH and the total concentration of all the metals under consideration. The total metal concentration here was computed as:

$Ba + Cd + Co + Cr + Cu + Fe + Li + Mn + Mo + Ni + Pb + Rb + Sr + Zn$.

For the metals with contents below detectable limit, the detection value of the equipment for that metal was used as the concentration level as follows: These included Cd (0.1 µg/l), Co (0.1 µg/l), Cr (1.0 µg/l), Cu (0.1 µg/l), Fe (1.0 µg/l), Li (1.0 µg/l), Mn (1.0 µg/l), Mo (0.1 µg/l), Ni (1.0 µg/l), Pb (0.1 µg/l) and Zn (0.1 µg/l). The data from Table 4 showed that the groundwater samples from Anantigha, Edor, Mbarakom, Nko, Obubra, Obudu, Odukpani, Okpoma, Ugep and Uyanga, which constituted 70% of all the samples, were classified as near neutral to low metal. The remaining 30% of the samples from Abakpa, Adim, and Igoli were classified as near neutral and high metal.

4.6. Trace Metal Pollution

4.6.1. Index of geoaccumulation

The index of geoaccumulation [37] evaluation method was used to determine the level of contamination. This index required the measured value of each parameter and the given evaluation criteria (background) value. The index of geoaccumulation (I-geo) was determined as follows: $I_{geo} = \log_2[C_n / (1.5 \times B_n)]$, where C_n is the measured concentration of element n in the pelitic fraction of sediment ($< 2\mu m$) and B_n is the geochemical background for the element n . B_n is either directly measured or obtained from the literature (average shale value). The factor 1.5 was introduced to include possible variations of the background values that are due to lithologic variations. In this study, the I-geo was modified for the assessment of the level of trace metal contamination in the groundwater of Cross River State. In the modification, C_n was the measured concentration of element n in the groundwater sample and B_n the background concentration for the trace element n in groundwater obtained from the literature (Table 2).

According to the I-geo scheme, groundwater samples are classified as follows: $I_{geo} < 0$ uncontaminated; $0 < I_{geo} < 1$ uncontaminated to moderately contaminated; $1 < I_{geo} < 2$ moderately contaminated; $2 < I_{geo} < 3$ moderately to strongly contaminated; $3 < I_{geo} < 4$ strongly contaminated; $4 < I_{geo} < 5$ strongly to extremely contaminated; $I_{geo} > 5$ extremely contaminated (Mueller, 1969). The calculated index of geoaccumulation and levels of contamination by each element are listed in Tables 5 and 6. Table 5 shows that the groundwater samples from all the sampled sites were uncontaminated with respect to barium, cadmium, chromium, copper, iron, lithium, molybdenum, lead, rubidium, strontium and zinc. However, the groundwater is

extremely contaminated by iron (Adim), manganese (Anantigha, Abakpa-Ogoja) and strontium (Okpoma, Igoli-Ogoja, Abakpa-Ogoja, Nko). Most of the trace elements showed various degree of contamination as presented in Table 6.

4.6.2. Enrichment Factor

The methods of determining pollution index or enrichment factor (EF) proposed by references 38, 39 and 40 were used to assess the level of groundwater pollution in the study area. The enrichment factor was computed by averaging the ratios of the concentration to maximum admissible value (MAV) values (Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Zn) and background value (Rb, Sr) of all the trace elements considered as follows: $(Ba/700 + Cd/5 + Co/1000 + Cr/50 + Cu/100 + Fe/300 + Li/50 + Mn/50 + Mo/70 + Ni/70 + Pb/100 + Rb/43 + Sr/4.3 + Zn/500) / 14$. An enrichment factor greater than 1 indicates that the element concentrations were above tolerable limits which can be from anthropogenic or natural geological sources [41, 42]. High EF values > 2.0 were recorded for groundwater at Abakpa-Ogoja, Igoli-Ogoja, Okpoma and Nko (Table 7). EF values in the range 1.00 - 2.0 were recorded for Adim, Obubra, Odukpani and Mbarakom, while low EF (< 1.00) values were recorded for five locations (Anantigha, Uyanga, Ugep, Obubra, Edor). The values of EF are related mainly to the levels of Cr, Cu, Li and Zn in groundwater. Generally, enhanced concentration of trace elements in groundwater is related to geological sources as source of contamination since the area is devoid of any major industry and characterised by low level mining activities by means of physical methods.

Table 7. Enrichment factor for different sample locations

S/N	Name	Enrichment Factor
1	Anantigha	0.43
2	Odukpani	1.64
3	Uyanga	0.49
4	Adim	1.33
5	Ugep	0.57
6	Obubra	0.91
7	Okpoma	10.13
8	Igoli-Ogoja	19.83
9	Abakpa-Ogoja	5.21
10	Edor	0.40
11	Nko	6.84
12	Obudu	1.04
13	Mbarakom	1.98

4.7. Multivariate Analysis

4.7.1. Correlation

The correlation coefficients between physicochemical parameters and trace elements and between different trace elements are reported in table 8. High correlations among elements indicated common source [43]. Barium and Co show high correlation with Mg^{2+} , Cl^- and NO_3^- . Chromium, Cu, Li, Sr and Zn is correlated with EC/TDS, pH/Eh, Na^+ , HCO_3^- and SO_4^{2-} , while Mn, Ni and Pb correlated with Cl^- and NO_3^- . Potassium correlated with Mo and Rb, while pH/Eh correlated with Mo and Pb. Rb is highly correlated with Ca^{2+} , Mg^{2+} and Cl^- . Correlation of some trace elements (Ba, Co, Mn, Ni, Pb) with nitrate may be related to local anthropogenic activities. Barium, cobalt, manganese and nickel had high positive correlation between them: Ba-Co

($r = 0.65$, $p < 0.01$), Ba-Mn ($r = 0.61$, $p < 0.01$) and Ba-Ni ($r = 0.66$, $p < 0.01$), which indicated same sources for these elements. Strong correlations were found for Co-Mn ($r = 0.97$, $p < 0.01$), Co-Ni ($r = 0.99$, $p < 0.01$) and Co-Pb ($r = 0.79$, $p < 0.01$) and were attributed to similar sources. Chromium had strong positive correlation with Cu ($r = 0.79$, $p < 0.01$), Li ($r = 0.96$, $p < 0.01$), Sr ($r = 0.92$, $p < 0.01$) and Zn ($r = 0.95$, $p < 0.01$), which indicated common origin. Moreover, the following pairs of significant correlation were observed; Li-Sr ($r = 0.88$, $p < 0.01$), Li-Zn ($r = 0.99$, $p < 0.01$), Mn-Ni ($r = 0.97$, $p < 0.01$) and Mn-Pb ($r = 0.83$, $p < 0.01$). Finally, Mo-Rb ($r = 0.59$, $p < 0.01$), Ni-Pb ($r = 0.76$, $p < 0.01$) and Sr-Zn ($r = 0.85$, $p < 0.01$). These correlations indicated several geogenic sources for these elements and limited/local anthropogenic activities.

Table 8. Pearson Correlation between physicochemical parameters and different elements

A Physicochemical parameters and trace elements

	EC	TDS	pH	Eh	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	SO_4^{2-}	NO_3^-
Ba	0.142	0.141	-0.296	0.299	-0.027	0.416	0.382	0.524	0.860	0.236	-0.145	0.947
Co	0.144	0.144	-0.328	0.326	-0.010	0.353	0.335	0.500	0.835	0.227	-0.131	0.953
Cr	0.941	0.942	0.706	-0.758	0.971	0.107	0.067	0.535	-0.018	0.824	0.981	-0.157
Cu	0.930	0.930	0.416	-0.467	0.868	0.316	0.239	0.738	0.462	0.892	0.806	0.389
Fe	-0.218	-0.218	-0.082	0.092	-0.167	-0.187	-0.137	-0.255	-0.243	-0.285	-0.139	-0.266
Li	0.915	0.918	0.546	-0.610	0.993	-0.053	-0.121	0.416	-0.087	0.752	0.995	-0.146
Mn	0.266	0.266	-0.346	0.326	0.155	0.234	0.194	0.476	0.763	0.304	0.031	0.923
Mo	0.117	0.112	0.647	-0.601	-0.055	0.566	0.713	0.374	0.185	0.302	-0.011	-0.054
Ni	0.134	0.134	-0.359	0.354	0.002	0.277	0.264	0.451	0.783	0.190	-0.118	0.930
Pb	-0.015	-0.014	-0.579	0.564	-0.092	0.092	0.038	0.198	0.614	0.065	-0.209	0.809
Rb	0.222	0.216	0.466	-0.421	-0.077	0.980	0.980	0.767	0.798	0.490	-0.110	0.486
Sr	0.993	0.994	0.697	-0.745	0.968	0.279	0.215	0.689	0.198	0.919	0.956	0.039
Zn	0.937	0.939	0.549	-0.612	0.998	0.003	-0.073	0.460	-0.028	0.794	0.993	-0.096

B Trace elements

	Ba	Co	Cr	Cu	Fe	Li	Mn	Mo	Ni	Pb	Rb	Sr	Zn
Ba	1.000												
Co	0.651	1.000											
Cr	-0.228	-0.088	1.000										
Cu	0.192	0.447	0.793	1.000									
Fe	-0.146	-0.084	-0.103	-0.078	1.000								
Li	-0.128	-0.072	0.961	0.802	-0.121	1.000							
Mn	0.609	0.971	0.045	0.567	-0.146	0.098	1.000						
Mo	-0.235	-0.136	0.141	0.024	0.004	-0.064	-0.242	1.000					
Ni	0.660	0.993	-0.087	0.433	-0.072	-0.054	0.969	-0.183	1.000				
Pb	0.424	0.785	-0.184	0.361	-0.055	-0.136	0.825	-0.308	0.759	1.000			
Rb	0.417	0.374	-0.045	0.225	-0.172	-0.174	0.242	0.590	0.310	0.111	1.000		
Sr	-0.046	0.038	0.924	0.767	-0.192	0.881	0.144	0.077	0.041	-0.133	0.073	1.000	
Zn	-0.117	-0.023	0.948	0.850	-0.124	0.989	0.150	-0.019	-0.014	-0.067	-0.103	0.848	1.000

Values in bold represent significant correlation at $p < 0.05$.

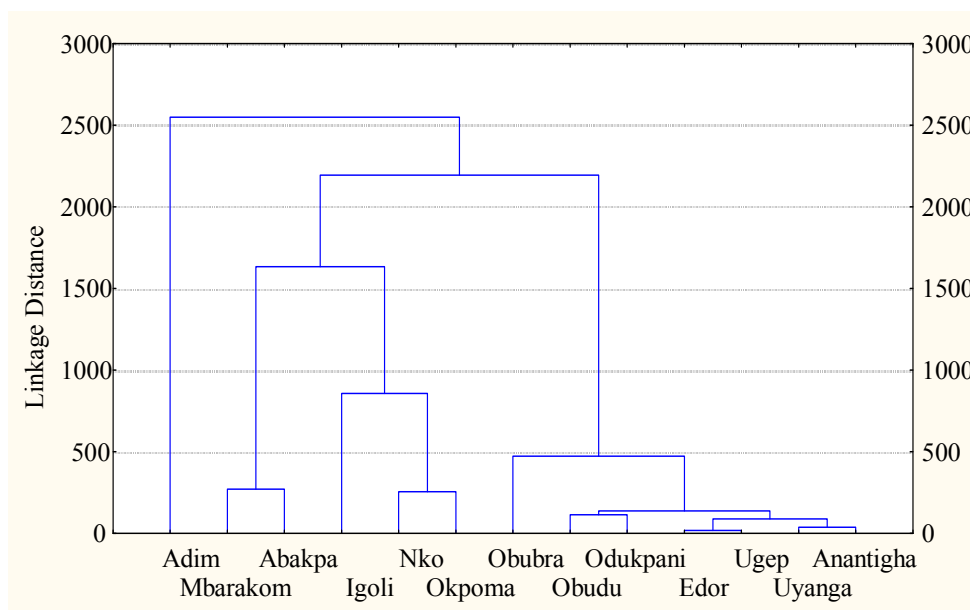


Figure 2. Dendrogram of cluster analysis based on the minor and trace elements for the different sampling sites.

Table 9. Factor loading values and explained variance

Parameter	Factor			
	1	2	3	4
Temp	0.24	0.39	-0.20	-0.71
EC	0.95	0.12	0.21	0.01
TDS	0.95	0.12	0.20	0.01
pH	0.59	-0.44	0.64	-0.01
Eh	-0.65	0.43	-0.58	0.01
Na ⁺	0.98	0.00	-0.06	0.00
K ⁺	0.10	0.26	0.91	0.02
Ca ²⁺	0.03	0.20	0.96	0.04
Mg ²⁺	0.54	0.41	0.69	0.03
Cl ⁻	0.06	0.78	0.58	0.05
HCO ₃ ⁻	0.83	0.19	0.45	0.09
SO ₄ ²⁻	0.97	-0.13	-0.05	-0.01
NO ₃ ⁻	-0.04	0.93	0.23	0.11
Ba	-0.01	0.94	0.19	-0.12
Co	0.00	0.95	0.13	-0.07
Cr	0.96	-0.14	0.07	0.02
Cu	0.86	0.41	0.12	-0.05
Fe	-0.17	-0.17	-0.07	-0.84
Li	0.97	-0.08	-0.13	-0.02
Mn	0.16	0.96	-0.02	0.01
Mo	-0.02	-0.33	0.79	0.15
Ni	0.01	0.95	0.07	-0.09
Pb	-0.10	0.85	-0.16	0.15
Rb	-0.02	0.28	0.92	0.04
Sr	0.96	0.04	0.18	-0.02
Zn	0.97	-0.04	-0.09	0.00
Eigen value	10.90	7.33	4.30	1.25
% total variance	41.91	28.18	16.54	4.80
Cumul.	10.90	18.22	22.53	23.77
Cumul. % total variance	41.91	70.10	86.64	91.44

Values in bold represent marked loadings are > .700000

4.7.2. Cluster Analysis

Cluster analysis was applied to identify similar groups between the different sampling sites in the study area. The resultant dendrogram grouped the 13 sample locations into five significant clusters (Figure 2). Cluster 1 had Adim with Fe>Ba>Sr; Cluster 2 consisted of Abakpa and Mbarakom having Ba>Sr>Fe, while cluster 3 with Sr>Ba>Fe had Igoli, Nko and Okpoma. Cluster 4 with Fe>Sr>Ba had Obubra, Obudu, Odukpani and Anantigha. Three locations (Edor, Ugep and Uyanga) had Ba>Sr>Fe, which constituted cluster 5. The concentrations of Ba, Sr, and Fe in cluster 5 are lower compared to the concentrations of the same elements in cluster 2. Thus generally, with low concentration of the trace elements, and with lack of major industrial or mining activity in Cross River State, the source of these elements cannot be attributed to any anthropogenic sources rather geogenic sources.

4.7.3. Factor Analysis

Results obtained from the application of the principal component analysis (PCA) are listed in Table 9. The PCA revealed four factors with eigenvalues greater than 1 and which explained 91.44% of the total variability of the elements were considered. EC/TDS, Na⁺, HCO₃⁻, SO₄²⁻, chromium, copper, lithium, strontium and zinc were associated with the first factor, being the most important components and explained 41.91% of the variability. On the other hand, chloride, nitrate, barium, cobalt, manganese, nickel and lead were associated with the second factor, which represented 28.18% of the variability, while potassium, calcium, magnesium, molybdenum and rubidium were associated with the third factor, which explained 16.54% of the variability. Finally, factor four with variability of 4.80% contained only iron. As stated earlier, under cluster analysis, the low concentration of elements indicated that since the area is devoid of any

major industrial and mining activities, the source of elements in the groundwater is mainly from weathering, minor geochemical processes including dissolution, adsorption and precipitation and local anthropogenic activities to an extent.

Factor 1 which contained EC/TDS, Na^+ , HCO_3^- , SO_4^{2-} , Cr, Cu, Li, Sr and Zn was attributed to the dissolution of brine and to an extent to the dissolution of minerals. Dissolution of brine with high concentration of Sr has been reported in some parts of the study area by references 30, 31, 32, and 33. Factor 2 had Cl^- , NO_3^- , Ba, Co, Mn, Ni and Pb. This was attributed to dissolution of barite mineral and limited anthropogenic activities. The occurrence of barite mineral had been reported in the study area by references 23, 24, 25 and 26. Factor 3 with K^+ , Ca^{2+} , Mg^{2+} , Mo and Rb was partly attributed to weathering of the bedrock and to an extent to dissolution of brine, while Factor 4 had only Fe and was attributed to the prevailing oxidation-reduction potential of the environment.

5. Summary and Conclusions

The data from this study showed that groundwater samples from Nko, Igoli and Abakpa had enhanced total dissolved solids values due to dissolution of salt beds. The pH of the groundwater samples showed acidic to alkaline groundwater. The concentrations of chloride, sulphate and bicarbonate were below the maximum admissible value (MAV). However, the concentration of nitrate from some locations exceeded the MAV due to poor waste management. The concentrations of sodium, calcium and magnesium in all the groundwater samples were within the permissible limit. However, potassium contents in some locations were higher than the MAV.

The trace elements considered in this study in most of the locations sampled had concentrations below MAV and typical values in fresh water. The contents of barium, iron and lead in some locations were higher than the WHO maximum admissible concentration (MAC), while the contents of cadmium, cobalt, copper, iron, manganese, nickel, lead, rubidium and zinc were within the ranges in freshwater. The concentrations of barium, chromium, lithium, molybdenum and strontium at some locations were higher than the ranges documented for freshwater. Groundwater of the study area is uncontaminated with respect to cadmium, cobalt, and copper in all locations. Most of the elements, especially Fe, Mn, Sr and Zn showed various degree of contamination. In addition, the values of enrichment factor (EF) for most elements and locations were greater than 1. This indicated contamination from geogenic sources as the area lacks major industrial and mining activities.

Multivariate analyses showed high correlations among different elements indicated common source for these elements. Cluster analysis showed that the concentrations of three elements (Fe, Sr, Ba) were responsible for the major clusters. Thus generally, with low concentration of

the trace elements, and with lack of major industrial or mining activity in Cross River State, the source of these elements cannot be attributed to any anthropogenic source rather geogenic sources. The principal component analysis (PCA) revealed four factors that were attributed to dissolution of brine; dissolution of barite mineral and limited anthropogenic activities; weathering of the bedrock, and the prevailing oxidation-reduction potential of the environment, respectively for factors 1, 2, 3 and 4. In conclusion, with no major industry in the area, low concentration of elements, the groundwater in Cross River State is pristine with respect to the elements considered. Hence this study will serve as a good guide for future groundwater monitoring, pollution and management.

Acknowledgement

The first author is grateful to Alexander von Humboldt for providing fellowship to the University of Tuebingen (Germany). Prof Peter Grathwohl, my host at the University of Tuebingen and putting the facilities of the institute at my disposal. Prof Dr K-D Balke and Mr. Matthias Flegr for their hospitality during the period of this work in Tuebingen. Many thanks to Mr. Joern Breuer of Institute of Agricultural Chemistry, University of Hohenheim, Germany for analyses of the trace elements

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