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Heavy Metal Pollution of Natural Waters in Abakaliki, Ebonyi State, Nigeria

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Abstract: ***Abakaliki is one of the fast growing cities of South Eastern Nigeria. It depends mainly on surface water and limited groundwater supplies from a highly jointed and weathered shale-regolith aquifer. Since the aquifer is lithologically similar to a Nigerian rock formation that has been established as having groundwater - laden with heavy metals, the waters from the shale-regolith aquifer was tested for its heavy metal status. A few hand- dug wells and streams were also tested since they are hydraulically connected to the same aquifer. A total of 20 water samples were tested for their concentration levels with respect to iron (Fe); lead (Pb); copper(Cu); zinc (Zn); cadmium (Cd) and arsenic (As). Concentration levels for copper (Cu) and zinc (Zn) were below maximum contaminant levels (MCL) but iron(Fe) ranges from 0.2mg/l to 9.2mg/l. Its average value (5.44mg/l) exceeds the MCL by 18 times. The range for lead (Pb) is from BDL (below detection limits) to 13.8mg/l which exceeds the prescribed limits by 300 times. Cadmium (Cd) ranges from BDL to 0.67mg/l while arsenic levels vary from 0.1mg/l to 2.9mg/l. Their average values exceed prescribed limits by 50 and 159 times respectively. Mobilization of these heavy metals into natural water seem to be enhanced by iron oxyhydroxide reduction and nitrate reduction in processes that are microbially-driven. Health risks of the continued exposure of the Abakaliki population to these heavy metals is potentially serious.***

Keyword: Abakaliki; Shale-regolith aquifer; Heavy Metals; Maximum Contaminant Levels

1. Introduction

Water is perhaps one of the most essential elements on earth today but its usefulness diminishes greatly when it is polluted. Pollution occurs when toxic or undesirable substances are introduced into surface water bodies or groundwater. The introduction of harmful substances into water may be by naturally occurring processes without human input – (i.e.geogenic) or as a result of human activities like mining, industrial processes, waste disposal etc. (i.e. anthropogenic). Regulatory bodies like World Health Organisation (WHO) or United States Environment Protection Agency (U.S.E.P.A) usually set maximum contaminant levels (MCL) for various elements. Whenever any element or substance has a concentration value exceeding the MCL set for it by these regulatory bodies, such a water is said to be polluted. In establishing MCL's these regulatory bodies took into consideration, the impacts of the presence or excess levels of such substances on the human body.

One group of pollutants known to be toxic to human health is the heavy metal group. Heavy metals are defined as those metals with atomic number equal to or greater than 20 but this usually does not include alkali and alkali earth metals like Ca, Mg, Na and K. Metals are introduced into aquifers and surface water bodies through rock weathering and erosion or by human activities. The global concern about the presence of heavy metals or their elevated concentration levels in water is because of their high level of toxicity. Several heavy metals are known to be toxic to human, animal and plant life and therefore need to be detected in and removed from water before it affects whole populations of people.

A major characteristic of heavy metals is that they usually have very low concentrations in natural water. In fact they typically have < 0. 1 mg/l in most cases and for this reason, most chemical analyses of water tend to focus on major elements which are considered to be major because they constitute the greater percentage of dissolved solids in water, but it has been found that even at very low concentrations, heavy metals can be extremely dangerous to human health.

Some years ago, the widespread pollution of natural waters in Bangladesh by geognic arsenic drew global attention. The Bangladeshi case in the late eighties and nineties was well documented [1, 2, 3]. Later on, it was discovered that arsenic poisoning of natural water systems was not limited to Bangladesh and West Bengal of India alone. At least 19 countries in the world had the same problem [4]. The outcry that arose due to the arsenic problem helped to fuel a lot of research into the factors leaching arsenic into natural systems. It was discovered that the arsenic pollution of natural water in Assam State in India was connected with high levels of iron in the water[5, 6]. The occurrence of arsenic and iron in groundwater was linked to the aquifer sedimentology. High levels of arsenic and iron were found in fine grained, sands and silts that had plenty of organic matter and in the United States, it was also discovered that arsenic commonly occurredin calcareous metasediments[7].

A comparison between the sedimentology of arsenic occurrence in Bangladesh and United States led to the need to check for the presence of arsenic and other heavy metals in Nigerian rocks with similar lithologic characteristics. It was discovered that the Awgu Formation which comprises mostly of carbonaceous shales andcalcareoussandstones had elevated concentration levels of arsenic, lead and cadmium[8]. The focus of this paper therefore is to check the heavy metal status of natural waters in Abakaliki in Ebonyi State because the underlying rocks also are lithological similar to the Awgu Formation, though they differ in age.

2. The Study Area

2.1 Location

The study area is located within latitudes $6^0$16' N and 6^0 21' N and longitudes $8^0$05'E and 8^0 10' E covering an area of about 83square Kilometres. It is a rapidly growing city because of its status as a state capital. The area lacks good aquifers because it is underlain by shales instead of sands or gravels[9].The shales however provide limited quantities of water due to its fractured and jointed nature. The flat – lying topography, high runoff and heavy rains at Abakaliki have created many ponds and ephemeral streams. Only the Ebonyi -River is perennial. Unfortunately some of these surface water bodies and the shale – regolith aquifers do not always survive the long, dry spells of the dry season. They tend to dry up during the dry season but get recharged during the rainy season periods. Water quality in Abakaliki is a big issue because the waters harbour pathogens that cause river blindness and elephantiasis.

2.2 Geohydrological Setting

The study area (figure1) is underlain by Asu River Group of sediments which are albian in age. The main formation in the area is Abakaliki Formation (albian) which comprises dark grey to black shales. The shales outcrop in parts of the city like the Water Works area and Onuebonyi. The dips of the rocks range from 55^0 to 57^0 in the SE direction. North of the town a few outcrops of sandstone lenses may be found. The sandstones are fine grained, greyish to yellowish in colour with dark brown iron stains. Ancient volcanic activity led to the pyroclastics exposed at the Juju hill which is the highest point (topographically) in the area. At the Juju hill area, there are exposures of baked shales. The shales of Abakaliki Formation are folded, lead/zinc mineralized shales with sandstone lenses and limestone bed. The limestone bed is up to 30m in thickness while the thickness of the formation is more than 500m[10]. The sandstones of the Abakaliki Formation are fine grained and have calcareous cement. It has a highly fractured and weathered zone. Depth to the static water table range from 6.5m to 25m in some locations. Average values of K (hydraulic conductivities) estimated from joint/fracture density characteristics of the area is 6.06×10^{-3}cm/s.

3. Materials and Methods

Field work for the heavy metals involved collecting water samples from 20 locations. The samples were collected with 500ml acid-rinsed polypropylene containers and acidified to pH less than 2 in order to stabilise them for laboratory analysis. The samples were then analysed with Atomic Absorption Spectrophotometer at the PRODA laboratories of Federal Ministry of Science and Technology, Enugu.

4. Results and Discussion

Results of selected physico-chemical tests on the natural waters are given in Table 1. The pH values range from 6.5 to 8.4 which indicates mildly acidic conditions to alkaline. Most of the waters had pH values slightly greater than 7.0(neutral). The pH values also indicate the possibility of a well- buffered system. Values of total dissolved solids (TDS) range from 827.8mg/l to 1206.4mg/l which shows significant solute concentrations. Values in excess of 1000mg/l of TDS are considered to be brackish water. Fifteen of the samples (75%) had nitrate concentrations which when compared with dissolved oxygen levels appear to be anomalous, particularly in the presence of iron but this likely indicates redox processes in virtually all the samples. It has been suggested that groundwater - based redox processes are common in marine sediments[11]. The Abakaliki Formation (albian) was deposited in a marine environment.

Results from heavy metal chemical analysis are given by table 2. Five heavy metals and one metalloid were tested for and they include iron (Fe), lead (Pb), copper (Cu), zinc(Zn), cadmium (Cd) and arsenic (As). Though it is customary to give the units in µg/L (or parts per billion), the units of table 2 are in milligrams per litre.Iron (Fe) ranges from 0.2mg/l at Ugbuloke to 9.2mg/l at Obiagu Central. The permitted limit for iron in groundwater is 0.3mg/l but the results show that apart from the Ugbuloke all the samples have very elevated concentrations of iron. The average value of iron for all the samples is 5.44mg/l (see table 3) which exceeds the MCL (ie maximum contaminant level) by 18 times. The leaching of iron into water is microbial driven in the presence of humic and fulvic acids.The Abakaliki Formation is also known to have carbonaceous shales and iron oxides which could be leaching into the water. The range for lead (Pb) is from BDL (below detection limits) to 13.8mg/l. The MCL for lead is 0.015mg/l and the average value for the study area is 4.5mg/l which exceeds the MCL by 300 times. Sulphides like pyrites and galena occur in the study area. It is clear that the excess lead in the water is of geogenic origin. It has been suggested that lead in water usually tends to have strong correlation with iron because lead (Pb) adsorbs on to iron oxhydroxides which exist as particulate matter and also because non-soluble particles of lead may be present as Pb – carbonates[14].

Values of Copper (Cu) and Zinc are not significant geochemically but arsenic (As) ranges from 0.1mg/l to 209mg/l. The average value (1.59mg/l) exceeds the MCL by 159 times. There are numerous studies on the mechanism of arsenic mobilisation into groundwater. It has already been established that pyrite and arsenopyrite occur in association with lead/zinc mineralization. Arsenite in the form of trivalent arsenite (As^{3+}) is leached into water through the reduction of iron oxyhydroxides through microbial breakdown of organic matter. For some of the hand-dug wells and surface waters, it has been demonstrated that nitrate reduction may promote the leaching of pentavalent arsenate (As^{5+}) and (Fe^{3+}) into the water[15].

Values for cadmium range from BDL to 0.67mg/l in the area. The average value 0.25mg/l exceeds the MCL (0.05mg/l) by 50 times. The occurrence of cadmium is closely associated with zinc availability. The lead/zinc mineralisation in the study area will therefore facilitate the release of cadmium into the waters.From the foregoing, it can now be established that the natural waters of Abakaliki have elevated concentrations with respect to iron, lead, arsenic and cadmium. The maximum contaminant levels for these heavy metals have all been exceeded.

5. Health Implications

The health implication for excess iron in water is fortunately not grave. The real problem with iron enrichment is that it stains laundry, bath tubs, sinks and even human teeth. It can clog well screen of boreholes. Excess lead is however potentially dangerous. Lead has been implicated is diseases like anaemia, liver damage, kidneydisease, reduced IQ, behavioural and learning problems in children and irreversible edema[16].

Arsenic is toxic to human health. It has also been implicated in cancers of the bladder, lungs skin, liver and in prostate problems. Non – life threatening effects of excess arsenic in water include stomach pains, nausea, diarrhoea and partial paralysis.[16]

The maximum contaminant level MCL for cadmium is 0.015mg/l but the average value is 0.25mg/l which is50 times more than the MCL. Cadmium (Cd) directly affects the human body in a negative way, particularly the arteries of the body. It is also known to cause stomach irritation, vomiting and diarrhoea and death. Exposure to cadmium over an extended period of time can cause kidney damage[16].

6. Conclusion

The natural waters of Abakaliki are polluted with respect to heavy metals like iron, lead, arsenic and cadmium. The mechanisms by which they are leached into groundwater and surface water bodies in Abakaliki are not yet fully understood. More detailed geochemical investigations need to be carried out to determine these mechanisms so that mitigation measures can be established for dealing with the heavy metal pollution of the waters. It will also be necessary to examine in greater detail the actual health status of the population in order to establish the extent of the problem.

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Table 1: Selected physico – chemical parameters from the sampled sites.

S/N	Location	Sample No	pH	Temp ^{0}C	TDS mg/l	NO_3 mg/l	Dissolved Oxygen Mg/l
1	Ntezi Abu	L2	7.4	26	985.7	1.2	1072.0
2	Prison Hospital	L4	7.1	25	911.5	0.2	996.4
3	Obiagu West	L6	7.5	27	1102.0	2.4	600.0
4	Obiagu Central	L8	7.4	28	1004.7	2.8	673.8
5	Igbagu	L9	7.8	24	827.8	BDL	1102.0
6	Abakaliki Borehole	L10	7.3	28	902.3	3.7	1048.0
7	Water Works	L11	7.1	29	846.0	BDL	1247.6
8	Ofeiyi Oku	L12	7.3	24	956.7	BDL	1126.2
9	Primary School well	L13	6.9	23	975.6	0.7	997.7
10	Rice farm well	L14	7.2	25	1159.8	5.7	709.8
11	R. Iyiokwu	L18	7.7	21	1108.5	3.5	750.2

12	Quarry (Hw)	L19	7.6	22	1334	BDL	720.3
13	Juju hill (well)	L20	7.6	26	1294	4.4	620.0
14	Ebonyi River	L21	7.8	27	1209	3.9	576.8
15	Limestone Quarry	L22	8.5	22	1001.6	BDL	794.0
16	AkaeruIyimagu	L24	7.9	25	904.6	0.3	1014.7
17	Military Cantonment	L25	6.5	22	960.1	2.7	605.0
18	Ugbuloke	L26	6.7	24	1001.2	2.5	1148.2
19	Achi Stream	L28	7.5	26	1206.4	3.9	680.4
20	Abia Stream	L30	7.7	24	1108.7	3.5	794.00

Table 2: Heavy metal concentration in the waters of the study areas (in mg/l)

S/N	Location	Sample No	Iron	Lead (pd)	Copper (Cu)	Zinc (Zn)	Arsenic (As)	Cadmium (Cd)
1	Ntezi Abu (BH)	L2	6.9	7.5	BDL	BDL	1.0	BDL
2	Prison Hospital (BH)	L4	7.9	BDL	0.3	0.35	0.1	BDL
3	Obiagu West (BH)	L6	7.8	0.5	0.5	0.44	2.3	BDL
4	Obiagu Central (BH)	L8	9.2	10.1	0.3	0.1	4.1	BDL
5	Igbagu , (BH)	L9	1.8	3.2	0.4	0.11	2.4	BDL
6	Abakaliki (BH)	L10	6.9	0.1	0.6	0.74	1.5	BDL
7	Water Work Area (BH)	L11	3.3	BDL	0.1	0.41	0.7	BDL
8	Ofeiyi Oku	L12	4.4	3.7	0.4	0.09	1.1	BDL
9	Primary School (BH)	L13	2.9	2.3	0.2	0.09	1.2	BDL
10	Rice farm (HW)	L14	7.8	8.3	BDL	0.70	BDL	0.48
11	R. Iyiokwu	L18	2.3	14.7	0.1	0.64	1.3	BDL
12	Quarry (Hw)	L19	7.6	BDL	BDL	1.12	2.6	0.24
13	Juju hill (well)	L20	4.4	9.6	0.1	0.33	2.9	0.52
14	Ebonyi River I	L21	3.7	13.8	BDL	0.27	BDL	BDL
15	Limestone Quarry (HW)	L22	4.11	0.8	0.4	0.78	0.7	0.27
16	AkaeruIyimagu (HW)	L24	5.3	0.2	0.2	BDL	1.7	0.07
17	Military Cantonment Abakaliki< BH	L25	9.0	0.6	0.1	0.81	2.7	BDL
18	Ugbuloke (HW)	L26	0.2	0.3	0.3	0.11	0.2	0.11
19	Achi Stream	L28	4.7	0.5	0.3	BDL	1.7	0.67
20	Abia Stream	L30	3.7	0.3	BDL	0.43	0.5	0.01

Table 3: Comparison of Heavy Metal concentrations in AbakalikiwithW.H.O.(2006)[12]& USEPA 2010 [13] standards

Heavy Metals	WHO Standards 2006	U.S.E.P.A. (2010)	Average value	Exceeds MCL by
	Health Based guideline	Maximum Contamination level		
Iron(Fe)	No guide line	0.3mg/l	5.44mg/l	18
Lead(Pb)	0.01mg/l	0.015mg/l	4.5mg/l	300
Cooper(Cu)	2mg/l	1.3mg/l	0.29mg/l	0.22 times
Zinc (Zn)	-	-	0.44mg/l	-
Arsenic (As)	0.01mg/l	0.01mg/l	1.59mg/l	159 times
Cadmium(Cd)	0.003mg/l	0.005mg/l	0.25mg/l	50 times

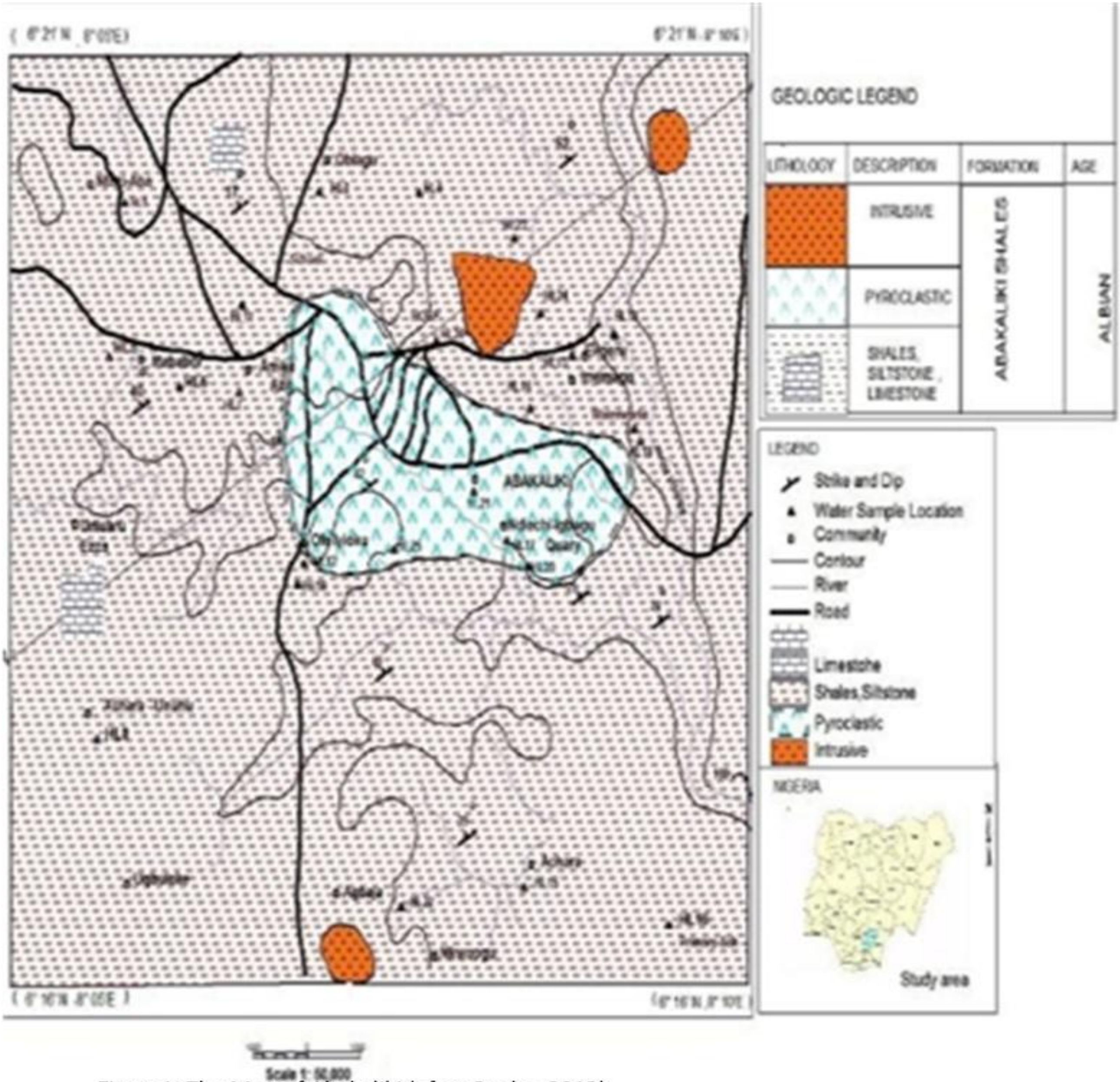

Figure1: The Map of Abakaliki (after Ozoko, 2012)