Elevated Concentration Levels of Heavy Metals in the Natural Waters of Awgu-Ndeabor Shales Aquifer, South-Eastern Nigeria

D. C. Ozoko

Department of Geology and Mining, Enugu State University Of Science and Technology, Enugu State, Nigeria

dan.ozoko@gmail.com

Abstract

The weathered horizon of Awgu-Ndeabor Shales is aquiferous. Lithologically the Awgu-Ndeabor Shales consist of grey shales, sandstones, siltones and occasional limestones. The weathered and fractured zone ranges from 30m-70m in thickness and supplies ground water to about 8(eight) boreholes and the Umara spring in the study area. Major element concentrations in the groundwater system are all well below WHO or USEPA limits. Heavy metals that exceed prescribed limits include Arsenic (As) , Cadmium (Cd) and Lead(Pb). The average concentration for arsenic (As) and Cadmium are 31.993mg/ ɭ and 5.55mg/ɭ which are more than 319 and 110times the Maximum Contaminant Levels (MCL) respectively. The lead (Pb) concentration has the average value of 128.44mg/ ɭ which is more than 8200 times the limit set by USEPA. These anomalous values pose serious health risks. The lead-zinc mineralization zone at Ishiagu which has a boundary with the study area and the host minerials in the Agwu-Ndeabor shales are probably responsible for this geogenic contamination of the water system.

Keywords: Geogenic, Awgu- Ndeabor, Arsenic, Cadmium and lead

1. Introduction

Access to potable water is limited in many parts of the world. The people of Awgu-Ndeabor area of Enugu State, south eastern Nigeria derive their water supply from a few shallow wells and springs but the potability of the water have not been properly evaluated.

Assessment of water potability involves the field and laboratory determination of physico –chemical parameters like pH, turbidity, total dissolved solids, major elements and heavy metals. Microbiological parameters include coliform bacteria, E. coli, protozoans and specific pathogens. Physical parameters like taste, odour, turbidity determine the aesthetics of the water while the chemical and microbiological aspects often pose health risks.

Most chemical analyses of water focus more on major element concentrations which are then compared with W.H.O. or some other national standards in order to check for contamination. The problem with this approach is that more often than not, major elements in groundwater rarely exceed the WHO or national drinking water standards. Yet this may not mean that such water that have been labeled potable are actually safe.

In Nigeria, the analyses for heavy metals do not form part of most chemical assessments for water potability. Although heavy metals occur in very trace quantities, the slightest elevation in their concentration levels can pose grave health risks. The presence of heavy metals in water may be due to anthropogenic activities or they may be occurring naturally (i.e geogenic). This paper assesses the general geochemical characteristics of ground water and surface water in Awgu-Ndeabor Shales aquifer in Enugu State, south eastern Nigeria but with a focus on occurrence of heavy metals in the natural water system. The study area is situated between latitudes 6˚00'N and 6˚05'N and longitudes 7˚30'E and 7˚35'E.

2. Geohydrologic Setting

Detailed lithologic studies of the rocks of the area revealed four lithologic facies, from oldest to the youngest they include grey shale and sandstone facies, dark grey shale facies and bluish-grey shale as shown in figure 1.The grey shale and sandstone facies comprises grey shales with intercalations of poorly laminated light grey colored siltstone and fine grained sandstone and fairly consolidated sandstone with occasional intercalations of siltstone as observed in locations L06,L07,L09 and L15. The dark grey facies consists of an alternating sequence of shale, sandy shale. siltstone and limestone (locations L01-L05,L10,L12, & L14) while the bluish-grey shale facies consists of a heterolithtic sequence of blue-black shale, mudstone, well laminated siltstones and limestones as observed in locations L11 and L13 along Ehu river (see figure 1). The weathered and fracture zone of the unit is about 40m thick..The beds of this unit trends NE with dip values ranging from $18^0 – 32^0$ W. The weathered and fractured zone forms an unconfined aquifer system ranging from 30m to 70m in depth. Below the weathered and fractured aquiferous zone, there are impermeable and well compacted grey Shales. This can be seen from the borehole logs in figure 2. The aquiferous condition of the Shales are made possible because they are highly jointed and fractured. The average linear ground water and hydraulic conductivity are 2.5×10^{-9} m/s and 1.5×10^{-2} m/s respectively. They were calculated from analysis of joint and fractures dimensions in the area. Ezeh (2012) determined the average field hydraulic conductivity of Awgu-Ndeabor Shales to be about 2.35×10^{-3} m/s on the basis of geoelectrical properties of the rocks. This has good agreement with the results of the present study.

The general flow direction is in the north eastern-southwest direction (figure 3.). The implication is that the Umara Spring could be receiving significant base flow from the unconfined aquifer system.

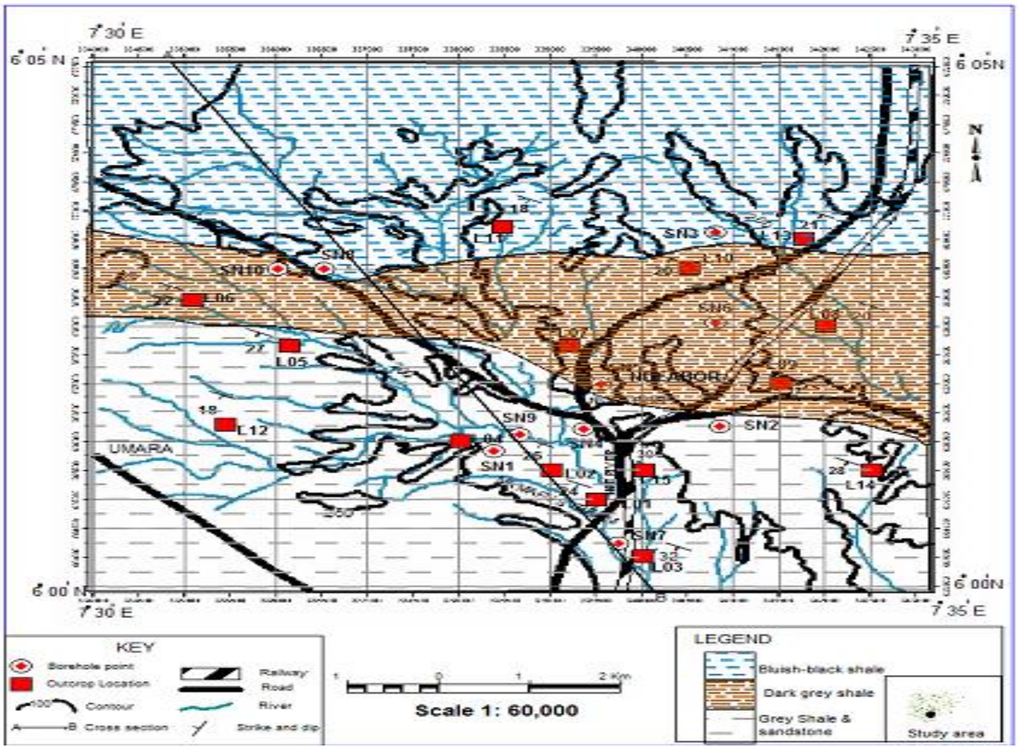

Figure 1: The Geologic Map of the Study Area

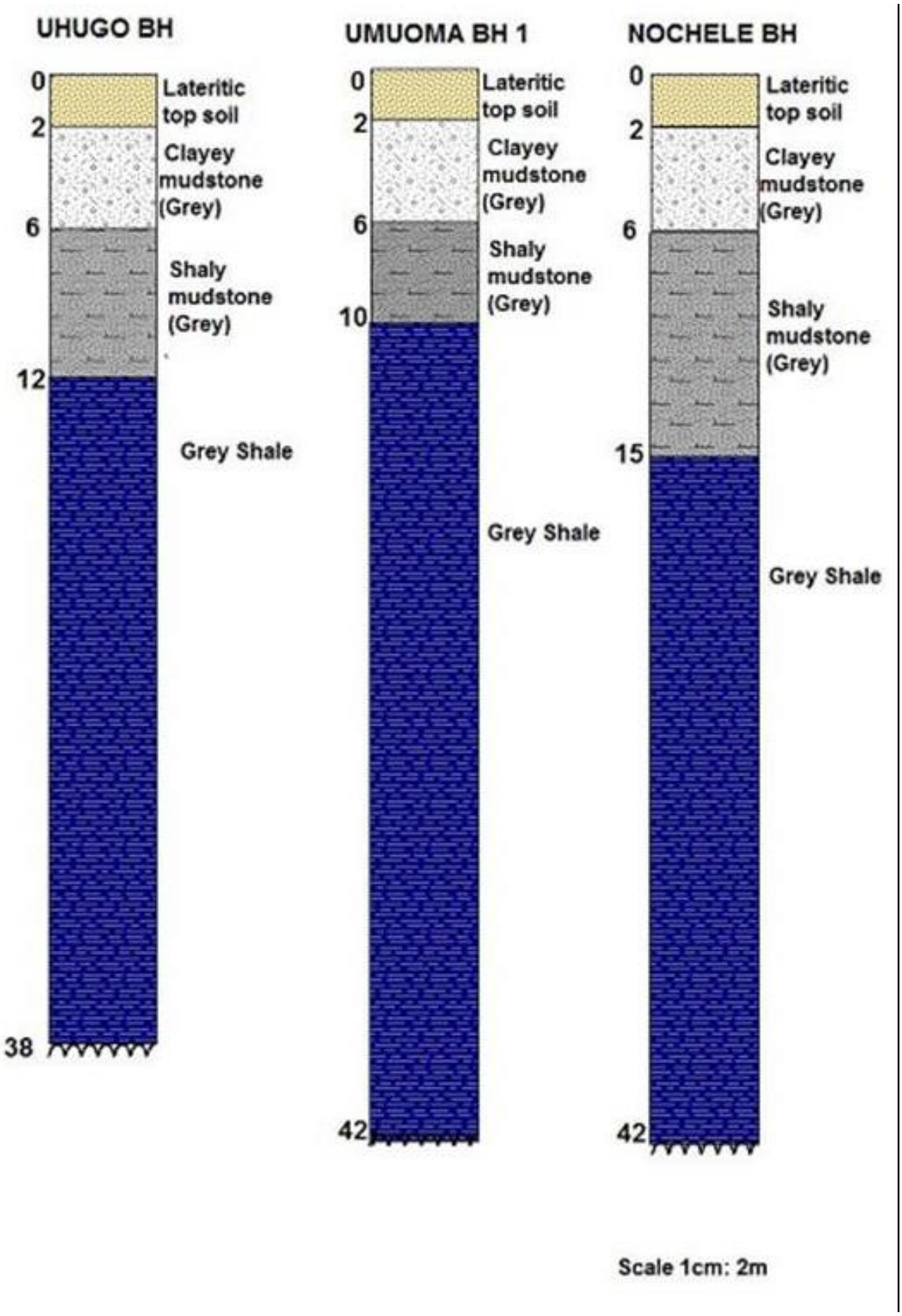

Figure 2: Borehole logs of some boreholes in Awgu –Ndeabor area.

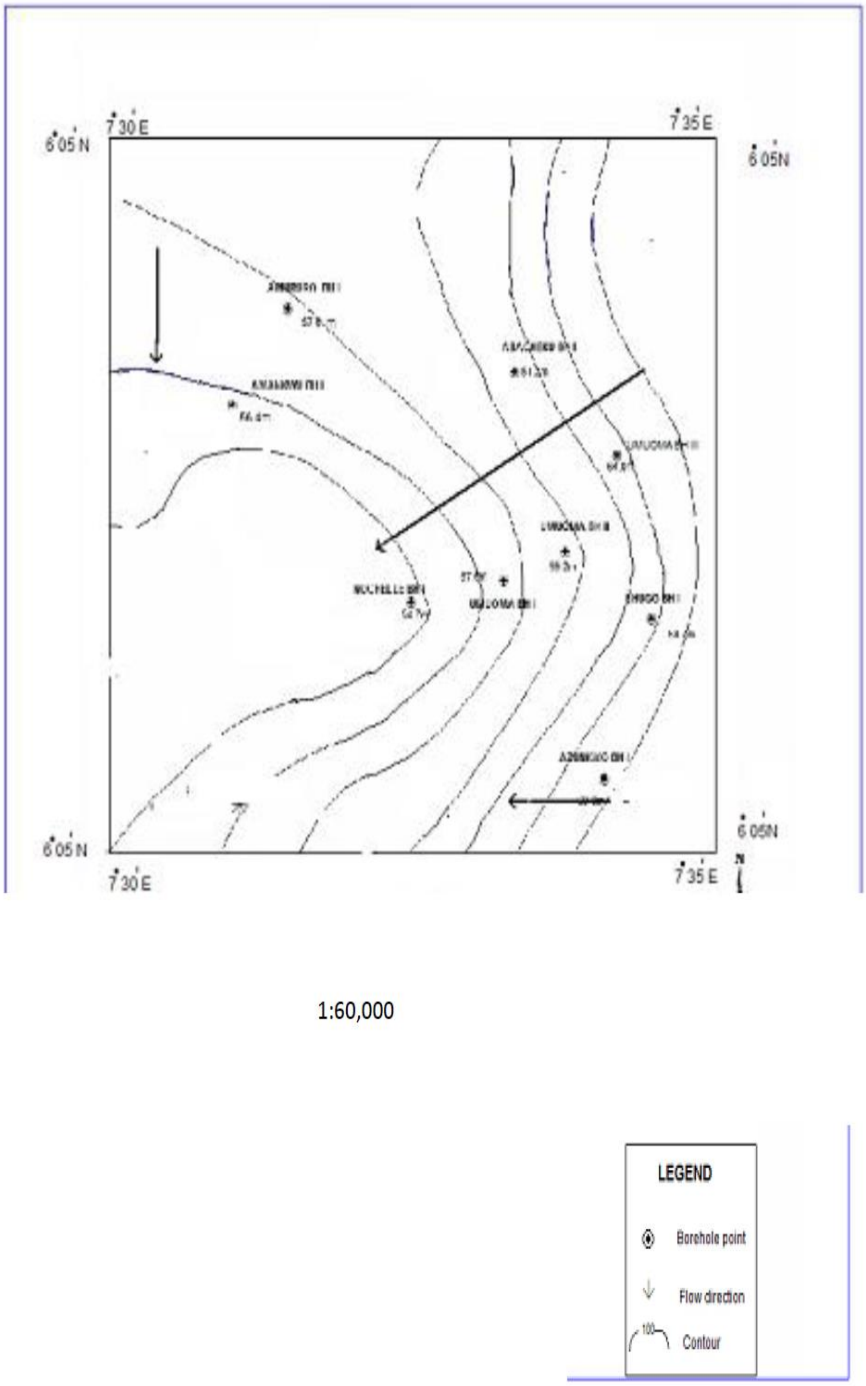

Figure 3: Groundwater flow direction in the study area.

3. Methodology

Geological field work was combined with the sampling of all the natural waters found in the unconfined shale aquifer and streams in the area. Parameters like temperature, electric conductivity, pH, TDS and Total Hardness were determined in the field using portable multi parameter water quality meter (sanxin, s×75.1). Carbonate species were stabilized before the removal of the samples to the laboratory. Major ions like Mg^{2+}, Ca^{2+} Na^{+}, HCO_3^- SO_4^{-2} and Cl^- were tested for in the laboratory using the methods of the America Water Works Association while heavy metals and minor elements like lead, Pb^+; arsenic, As ;Cadmium ,Cd; and iron, Fe^{total} ; were determined with Atomic Absorption Spectrometer .

4. General Physico-Chemistry

The physico-chemical parameters are shown in table1. The analyses show that the water samples have an average colour of 5.26 units. The total alkalinity of the water sample ranges from 494mg/l at Umara Spring water to 560mg/l Amururo borehole. The average total alkalinity of the water samples is 418.2mg/l. The pH values ranges from 6.7 at Umuoma III borehole, Amankwu borehole, Umara Spring water to 7.0 Azunkwo borehole, Amururo borehole. The Umara Spring has the least temperature value of 29^{o}C while the Abacheku borehole and Umuoma borehole I (see SN4 in figure 3) have the highest temperature value of 31^{o}C each. The total hardness of the water samples range from 350 to 450. Both Abacheku and Azunkwo boreholes have the highest value for total hardness of 450. Conductivity values range from 700 µs/m in Amururo borehole to 1250 µs/m in Umara Spring water. The average value for electric conductivity value is 929.5 µs/m. The values for TDS range from 1352.7mg/l at Umuoma borehole 1 to 1492.3mg/l at Azunkwo borehole.

Table 1:Physico-Chemical Parameters of the Awgu-Ndeabor Water Samples

Sample Number	Location	Condutivity µs/m	Temp. 0^C	Color (hazen)	Total Hardness	Total Alkalinity	pH	TDS mg/l
SN1	Umara spring	1250	29	7	350	494	6.7	1371
	Water							
SN2	Uhugo BH	900	30	5	425	530	6.9	1488.2
SN3	Abacheku BH	1200	31	7	380	519	6.9	148.1
SN4	Umuoma BH I	1000	31	5	450	540	6.9	1352.7
SN5	Umuoma BH II	760	30	5	416	520	6.8	1439.2
SN6	Umuoma BH III	715	30	4.5	473	537	6.7	1411.8
SN7	Azunkwo BH	1000	30	5	450	510	7	1492.3
SN8	Amururo BH	700	30	5	440	560	7	1384.5
SN9	Nochelle BH	850	30	5	382	542	6.8	1316.3
SN10	Amankwu BH	920	30	4.1	416	524	6.7	1446.1

The concentration of major elements are shown in Table 2.

These major ions include Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-}, CO_3^{-}, and NO_2^{-}.

Table 2: Major ion chemistry of natural waters in the Awgu-Ndeabor waters.

Sample Number	Location	Ca^{2+} mg/l	Mg^{2+} mg/l	Na^{+} mg/l	K^{+} mg/l	Cl^{-} mg/l	SO_4^{-2} mg/l	HCO_3^{-} mg/l	CO_3^{2-} mg/l	NO_2^{-} mg/l
SN1	Umara spring Water	114.8	31.4	7.3	5.2	145	281.4	638	217.3	0.2
SN2	Uhugo BH	95.3	29.8	5.8	4.8	150.2	228.6	610	229.8	0.1
SN3	Abacheku BH	182	158	4.5	3.8	42	262	710	122.1	0.3
SN4	Umuoma BH I	89.3	25.1	4.5	3.2	139.8	250.2	620	220.4	0.2
SN5	Umuoma BH II	128.4	27.2	3.5	2.1	123.2	231.7	671	252.1	0.1
SN6	Umuoma BH III	125.1	25.8	5.2	2.9	138.2	212.3	682	151.1	0.1
SN7	Azunkwo BH	215	170	2.8	3.4	22	315	675	91.1	0.1
SN8	Amururo BH	70.3	28.1	6.1	5.1	135.1	254.7	640	208.9	0.2
SN9	Nochelle BH	92.5	23.8	4.7	1.8	128	362.4	664	174.8	0.1
SN10	Amankwu BH	118.8	24.1	8.5	6.4	147	340	653	18.2	0.1

Calcium (Ca^{2+}) is one of the dominant constituents of the groundwater and its value ranges from 70.3 mg/l Amururo borehole to 215mg/l in Azunkwo borehole. The source of calcium in the area is dissolution of gypsum and calcite in the host rock. Azunkwo borehole which is situated close to the Pb – Zn mineralization area has the highest concentration of 215 mg/l. for calcium Magnesium (Mg^{2+}) has its highest value of 170mg/l at Azunkwo borehole and its least value at Nochelle BH borehole (23.8mg/l). The average value is 54.33mg/l. The source of magnesium (Mg^{2+}) is aragonite associated with the Awgu Shales.

Sodium (Na^{+}) is very high at Amankwu borehole with value of 8.5mg/l and average value of 5.29mg/l in the water samples analyzed. The primary sources of sodium in the area are weathering and dissolution of clay minerals, halite and industrial waste from mines at Ishiagu. The values of sulphate ($SO_4^{\ 2-}$) range from 212.3mg/l to 362.4 mg/l at Umuoma borehole and Nochele borehole respectively. The average value of sulphate ($SO_4^{\ 2-}$) in the area is 273.83mg/l. The source of sulphate ($SO_4^{\ 2-}$) in the study area is dissolution of gypsum, anhydrite and oxidation of galena.

Bicarbonate HCO_3^{-} is dominant anion in the water sample. Its values range from 610 mg/l to 710mg/l. The minimum value is at Uhugo borehole (see SN2 in figure 3) and maximum concentration occurs at Abacheku borehole (see SN3 in figure 1). The average value of bicarbonate ($HCO_3^{-)}$ in the water samples is 656.3mg/l. The high concentration of bicarbonates in the water samples is probably due to dissolution of limestone and calcite.

The range of Chloride (Cl^{-}) concentration in the water sample is 22mg/l to 150.2mg/l. The maximum concentration of chloride (Cl^{-}) is in Uhugo borehole (150.2mg/l) while the lowest concentration occurs at Azunkwo BH (22mg/l). The average value of chloride is 117.05mg/l. The chloride concentration is probably as a result of dissolution of habits trapped in the Shales.

Table 4: Comparison of Awgu-Ndeabor hydrochemistry with USEPA(2010) and WHO (2006) standards

	United State Environmental Protection Agency Standard (2010)	WHO's drinking water standards (2006)	Hydrochemical values for Awgu-Ndeabor water
Elements/substances	Maximum Contaminant Level (MCL)	Health based guideline by the WHO	Mg/l
Arsenic	0.01mg/l	0.01 mg/l	31.993mg/l
Cadmium	0.005 mg/L	0.003 mg/l	5.551 mg/l
Copper	1.3mg/L	2 mg/l	0.193 mg/l
Lead	0.015 mg/L	0,01 mg/l	128.44 mg/l
Chloride	250 mg/L	250 mg/l	117.05 mg/l
Color	15 (color units)	Not mentioned	5.26 mg/l
Iron	0.3 mg/L	No guideline	0.260 mg/l
Manganese	0.05 mg/L	0,5 mg/l	0.0013 mg/l
pH	6.5-8.5	No guideline	6.84
Total Dissolved Solids	500 mg/L	No guideline	1285 mg/l
Sulphate	250 mg/L	240 mg/l	273.83 mg/l
Chloride	250 mg/L	250 mg/l	117.05 mg/l
Sodium	No guideline	200mg/l	5.29mg/l

5. Heavy Metal Hydrochemistry

The following heavy metals like lead(Pb), cadmium(cd), copper(cu), arsenic(as), manganese(mn) and iron(fe) were selected for analysis because Reyment (1965) and Kogbe (1976) mentioned the occurrence of minerals like arseno-pyrite, pyrite, etc in Awgu-Ndeabor Shales.

Results of the heavy metal hydro chemistry are given in table 3. Again, the proximity of the study area to the lead zinc mineralization zone of Ishiagu was another factor in selecting which heavy metals to analyse for.

The concentration of lead (Pb) ranges from 36.3mg/l to 407.4mg/l. The lead concentration is highest at Umara Spring water and lowest in Abacheku borehole. Azunkwo borehole and Nochele borehole have concentration relatively higher than the rest probably because of their nearness to the lead – zinc mineralization in Ishiagu. The values of Pb decreases away from the Pb – Zn mineralization site at Ishiagu areas as shown in figure 4.

Table 3 :Concentration of heavy metals in the natural waters at Awgu-Ndeabor (in mg/l and µg/l)

Sample Number	Location	Cd^{2+}		Fe^{2+}		Pb^{2+}		Cu^{2+}		Mn^{2+}		As^{2+}	
		mg/l	µg/l	mg/l	µg/l	mg/l	µg/l	mg/l	µg/l	mg/l	µg/l	mg/l	µg/l
SN1	Umara Spring	8.432	843.2	0.182	18.2	407.4	40740	0.045	4.5	0.001	0.1	27.68	2768
SN2	Uhugo BH	4.216	421.6	0.5	50	67.52	6752	0.3	30	0.001	0.1	39.59	3959
SN3	Abacheku BH	2.572	257.2	0.263	26.3	36.37	3637	0.1	10	0.001	0.1	42.5	4250
SN4	Umuoma BH I	4.748	474.8	0.214	21.4	58.95	5895	0.1	10	0.001	0.1	35.18	3518
SN7	Azunkwo BH	5.123	512.3	0.2	20	81.64	8164	0.1	10	0.003	0.3	31.67	3167
SN8	Amururo BH	5.824	582.4	0.31	31	42.39	4239	0.621	62.1	0.001	0.1	21.91	2191
SN9	Nochele BH	7.945	794.5	0.149	14.9	204.8	20480	0.085	8.5	0.001	0.1	25.42	2542

The concentration of cadmium (Cd) in all the samples ranges from 2.572mg/l to 8.43 mg/l. Like lead, cadmium (Cd) concentration is highest at Umara Spring water and lowest in Abacheku borehole. There is a general reduction in the concentration of Cd away from the mining site execpt for Umuoma BH I and Amururo BH.

The concentration of Arsenic (As) in all the water samples ranges from 25.42 mg/l at Nochele borehole to 42.35 mg/l at Abacheku borehole . Arsenic (As) concentration is relatively high at Azunkwo borehole (31.67mg/l) and Umara Spring water (27.68mg/l) which are close to the Pb/Zn deposit in Ishiagu and its highest concentration is at Abacheku borehole which is far from the source point. The source of Arsenic (As) is dissolution of arsenopyrite which are in association with pyrite, sphalerite and minerals in the host rock.

The average value for copper (Cu^{2+})in the study area is 0.1963mg/l. Copper values range from 0.042 mg/l to 0.62 mg/l with its peak value at Amururo borehole and lowest value at Nochele borehole.

Iron(Fe^{3+}) concentration ranges from 0.149 mg/l to 0.500 mg/l with the highest value at Uhugo borehole and lowest value at Nochele borehole. The concentration of manganese ranges from 0.001 mg/l to 0.003 mg/l. The peak value occurs at Azunkwo borehole. Pyrite is found in association with Arsenopyrite and serves as the source of iron.

The concentration of manganese ranges from 0.001 mg/l to 0.003 mg/l. The peak value occurs at Azunkwo borehole.

The pie charts in figures 4-10 represent the distribution of these heavy metals in various boreholes. The results of the physical properties, average values of the six principal ions and heavy metals are compared with World Health Organization WHO (2006) standards and United States Environmental Protection Agency Standard (USEPA,2010) in table 4.

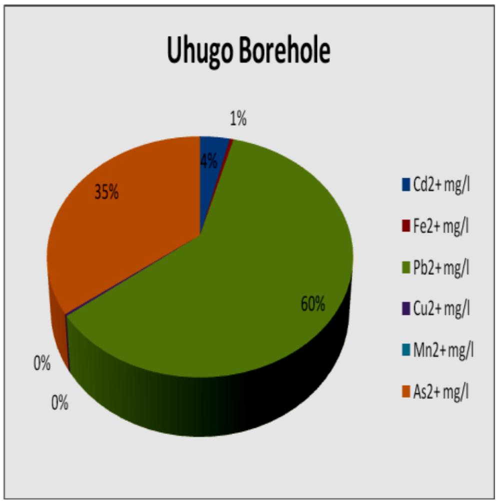

Figure 4: Pie chart showing variation of heavy metals in Uhugo bore hole

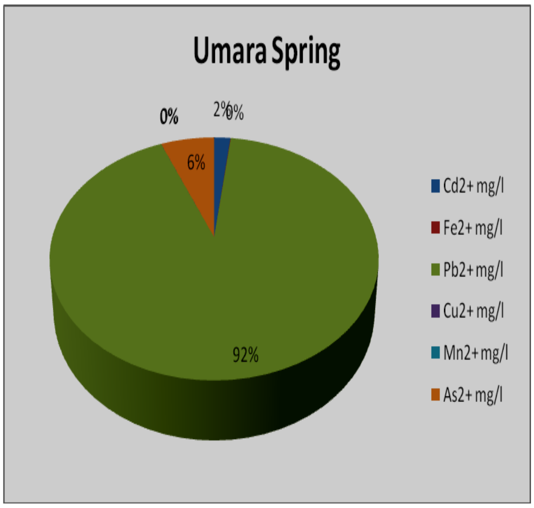

Figure5: Pie chart showing variation of heavy metals in Umara Spring water

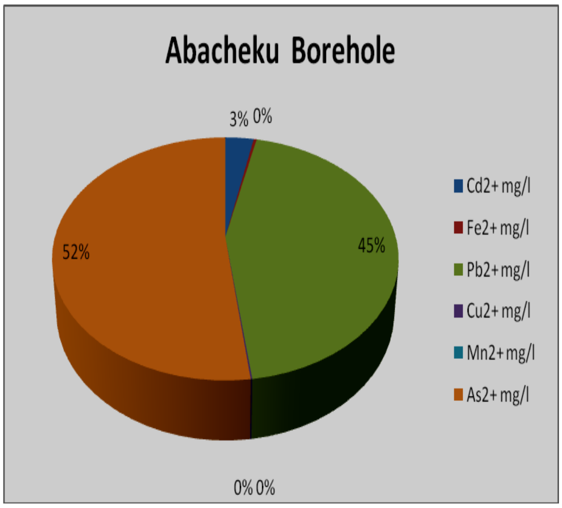

Figure 6: Pie chart showing variation of heavy metals in Abacheku borehole

HEALTH IMPLICATIONS

Although the human body needs trace elements or heavy metals. There are some of them that could be poisonous when allowed to accumulate in the body. These potentially dangerous heavy metals like lead ,mercury, aluminum ,arsenic ,cadmium and nickel could interfere with enzyme metabolic systems of the human body. Even very minute concentration levels of these heavy metals in the body could have serious negative health consequences because some of them like cadmium have considerably long biological half –lives.

The maximum contaminant level (MCL) for arsenic in drinking water is 0.01mg/l (USEPA,2010) but the average value for arsenic in the area is 31.993mg/l which is more than 319 times the Maximum Contaminant Level. The highest value for arsenic occurs in the Abacheku borehole (42.5mg/l) while the lowest value is 21.91mg/l (Amururo borehole. One of the ways of receiving arsenic poisoning is by drinking contaminated water or water from soils that are rich in arsenic.

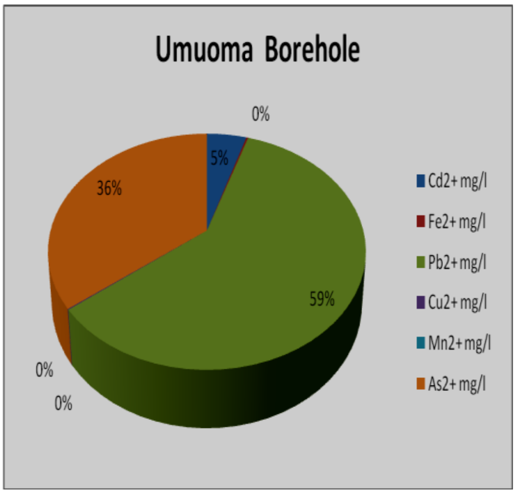

Figure 7: Pie chart showing variation of the Umuoma borehole I

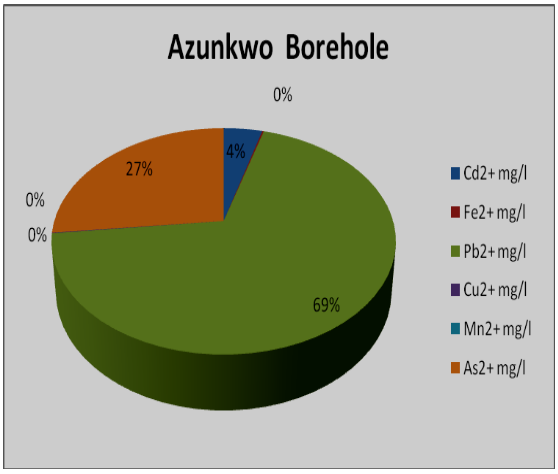

Figure8: Pie chart showing variation of the heavy metals in heavy metals in Azunkwo borehole

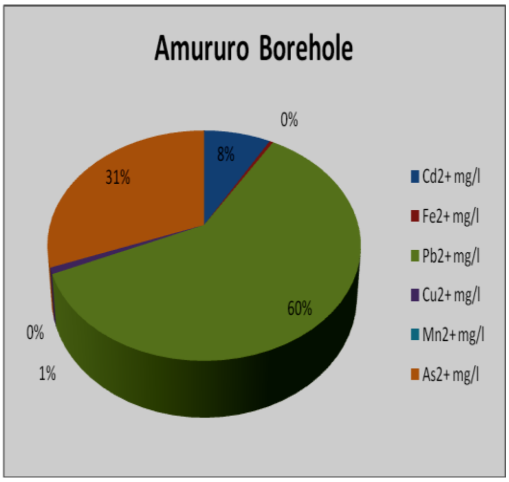

Figure 9: Pie chart showing variation of the Variation of the heavy metals in Amururo borehole

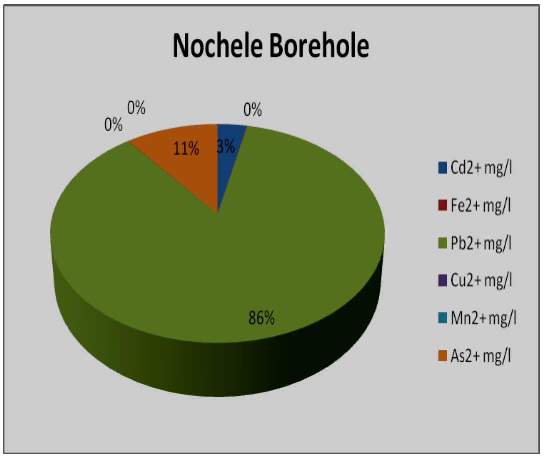

Figure10: Pie chart showing heavy metals in Nochele borehole

When a water sample has up to 60ppm of arsenic, it is considered very dangerous to human health. Arsenic can damage nerves, stomach, intestines and skin according (ASTRD,2007). Nerve damage due to arsenic include peripheral polyneuropathy and axonal degeneration. Even at lower concentrations, inorganic arsenic such as the one found in the Awgu-Ndeabor area may cause decreased production of red white blood cells, blood vessel damage, nausea, vomiting, diarrhea, 'a pins and needles' sensation in hands and feet, inflammation and ulceration of mucous membranes, kidney damage and ultimately, death (ASTRD,2007). Direct skin contact with arsenic may cause redness and swelling. Prolonged exposure might lead to chronic toxic effects like fatigue, loss of energy, ulceration in folds of skin, increased pigmentation of skin, appearance of corns or warts on the palm and soles, exfoliative dermatitis and sensory problems. Georing et al (1999) consider organic arsenic is to be a high priority hazard particularly because of its potential to be a human carcinogen.
The maximum contaminant level (MCL) for cadmium is 5ppb (ie 0.005mg/l) according to U.S.E.P.A. In the study area, the average value (5.551mg/l) exceeds the MCL by 110 times which clearly shows it to be a very high risk area . The lowest value for cadmium occurs at Abacheku borehole(SN3)(2.572mg/l) which incidentally is the same location for the maximum arsenic concentration of 42.5mg/l while the highest cadmium concentration is found in the Umara Spring(SN1) water. This spring water exceeds the allowed Maximum Contaminant Level of cadmium by 1686 times.

Cadmium has a direct adverse effect on cells in the arteries of the human body. The main problem with cadmium in that it has a very long biological half life and thus can take years to build up gradually. U.S.E.P.A prescribes a drinking water limit of 5ppb(five parts per billion or 0.0005mg /l) and this extremely low limit is an indication of how potentially dangerous cadmium could be to the human health. ATSDR (1999) notes that eating food or drinking water with very high cadmium levels severely irritates the stomach, leading to vomiting and diarrhoea, and sometimes death. The ATSDR report also found that when a person is exposed to lower levels of cadmium over a long period, the effect could be kidney disease.

The United States Environment Protection Agency (U.S.E.P.A) sets a limit of 15mg/l for lead (Pb) in drinking water but its range in Awgu-Ndeabor is between 36.37 mg/l and 407.4mg/l. The average value is 128.44mg/l which is more than 8200 times the limit set by U.S.E.P.A. In other words, the waters in Awgu-Ndeabor area could be a serious source of lead poisoning for residents living in the area. Excess lead can negatively impact red blood cells thereby causing anemia and have been known to cause damage to body organs like the liver, kidneys, hearts and the male gonad. Popcock et al, (1983) however suggests that symptoms of these lead-induced diseases are often precipitated by alcohol or exercise.

The ATSDR, (2007) report shares that in the Central Nervous System (C.N.S) excess lead could cause irreversible edema. The effects of lead concentration on children are many and dangerous even at low blood levels. The report also found that at such low blood lead concentration reduced I Q, learning and behavioral problems have been reported but at high blood lead levels, encephalopathy is likely to occur. Excess lead in the human body also affects reproductive health because it is gonadotoxic. It damages the male reproductive system. In women, it poses a grave danger to their unborn children leading to premature births. Even after birth, children from mothers with excess lead in their bodies could be much smaller than normal, might have decreased mental abilities, learning problems and reduced growth (ATSDR ,2007).

The chemical analysis for copper, iron and manganese did not indicate any excess levels in Awgu-Ndeabor area

It is very important observe here that the heavy metals contamination of the natural waters of Awgu-Ndeabor is geogenic. There are no known anthropogenic activities in the area to account for the occurrence of elevated concentrations of heavy metals in the water.

6. CONCLUSION/RECOMMENDATION

While the major elements in the Awgu- Ndeabor aquifer waters are within the recommended limits set by World Health Organization and U.S.E.P.A, there is clear evidence of serious pollution arising from elevated concentrations of arsenic, cadmium and lead. The levels of pollution are very high indeed and exceed the set limits by several hundreds or thousands. These excesses pose very grave health risks to the residents in the study area. Some of these health risks have been outlined but there is still need for health authorities to actually investigate the occurrence of some of these health risks in the area with a view to establishing a link between these diseases to the problem of heavy metal pollution. To alleviate the pollution arising from the area, detoxicification of the water is recommended.

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