HEAVY METALS CONCENTRATION IN GROUNDWATER OF EOCENE AMEKI FORMATION IN ONITSHA, ANAMBRA BASIN, SOUTH EASTERN NIGERIA

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ABSTRACT
The extensive use of metals and metalloids in most industrial operations in Onitsha and environs and the retrospective effects it is expected to have on the immediate environment (especially groundwater) informed this research. The research set out to determine the suitability of groundwater in the Eocene Ameki Formation for drinking and other domestic uses. This is because, the safety level of this fresh water supply source is in doubt judging the prevalence of numerous unmonitored anthropogenic activities in the study area. In order to deal with this doubt, groundwater samples were collected from selected boreholes that serve as sources of drinking water and domestic purposes in Onitsha. The samples were analyzed for the levels of concentration of some selected heavy metals including – Lead, Cadmium, Arsenic, Iron and Mercury using the atomic absorption spectrometer following the standard procedure of the American Public Health Association (APHA) for water and waste water quality analysis. The groundwater samples however presented problems with Lead and Iron besides the peculiar acid pH of southeastern Nigeria groundwater. Inter-parameter correlation using the Analysis of Variance (ANOVA), traced the parameters to a common source which is land use. Groundwater insurance for every land use remains a viable option to preventing pollution while the very sources of these metals in terms of activity should be traced and mitigated. The traces of some of the heavy metals found in some of the water samples analyzed may not be unconnected with the raw effluents discharged into the environment from both domestic and industrial activities. This will require efficient central sewer system to hold and treat effluents and secure landfills (since porous media is involved) for proper solid waste handling whatever the source.

Key words: Groundwater, heavy metals, Ameki Formation, anthropogenic activities, land use.

1. INTRODUCTION

Heavy metals are among the most common environmental pollutants, and their occurrence in waters and biota indicate the presence of natural or anthropogenic sources. The main natural sources of metals in water are chemical weathering of minerals and soil leaching. The anthropogenic sources are associated mainly with industrial and domestic effluents, urban storm, water runoff, landfill, mining of coal and metallic ores, atmospheric sources and inputs from rural areas (Krenkel, 1975). The existence of heavy metals in aquatic environments has led to serious concerns about their influence on plant and animal life. Metals and metalloids consists the bulk of pollutants released into the environment. It owes this record to its extensive use in human production industries. Heavy metals by definition refer to metals that have specific gravity five times greater than the specific gravity of water which is 1. Notable examples include Arsenic 5.7, Cadmium 8.68, Iron 7.8, Lead 11.34, and Mercury 13.546 (Bhatia, 1999). Heavy metals like other chemical compounds have the capacity to bio-accumulate in biological systems and sometimes they may accumulate to toxic levels in plants, animals and humans. Water being a universal solvent readily dissolve and circulate these metals through dispersion into the entire hydrologic cycle. By this circulatory means, it tends to touch the entire water regimes from the gaseous water vapor through infiltration to evaporation.

Through bioaccumulation, these metals enter the food chain as the by-products of their metabolism constitute health risks to other life forms other than the first contact in the web. These metals especially the non – nutritional ones such as lead, cadmium, mercury are said to be the most dangerous. While rock weathering influences the inorganic chemistry of water on the natural stance, human activities tend to contribute to the release of greater percentage of these pollutants into the environment. Increased use of metal base fertilizers in agriculture, improper disposal of industrial effluents and generally poor attitude to municipal waste management may produce leachates from landfills, incinerator ash and recycling of metal scraps consist human activities that may lead to increased heavy metals concentration in the environment. The water bearing formation feeding the boreholes is a porous sand member of the Ameki Formation intercepted at depths of 200-240 feet which enhances hydrologic interaction between the surface and subsurface (Anunobi, A.1998).

2. LITERATURE REVIEW

Metals entrance routes into the soils, air and water include (i) industrial effluents (ii) automobile wastes – engine oils and lubricants/metals scraps (iii) municipal wastes and (iv) acid rain that in turn induces rock weathering (Agarwal, 2009). The concept of waste to wealth is considered a concern as some experts believed that waste derived fuels contain heavy metals. Recall that water quality defines the physical, chemical and biological baseline characteristics of water. Good quality water used for drinking purposes should be free from pollutants, living and non-living organisms. It should not contain minerals and organic substances at concentrations that could produce adverse effects on any kind of use. It should be aesthetically acceptable, free from apparent turbidity, color, odor and taste (USEPA, 1999).

Other ways through which metals are introduced into the hydrologic cycle include: weathering of rocks; leaching of soils; discharge of aerosol particles into the atmosphere; mining activities; use of metal base fertilizers; incinerator ash from municipal wastes and untreated industrial effluents. Onitsha the study area plays host to many industries that product a range of products and commercial activities and about the most densely populated urban center south east of the River Niger in terms of the per capita space that is available. Numerous markets and street markets are a common place in Onitsha. The presence of numerous small scale industries and markets in Onitsha led to unprecedented increase in human activities. The said activities as vast as they are occur in less than one hundred square kilometers land area, which also serve as habitat to an estimated population of about 100300 persons. The city of Onitsha is located on the adjourning buffer strip of the River Niger.

It is also unfortunate that man ingest heavy metals either directly in drinking water which is contaminated by the metals. Or indirectly through contaminated food – vegetables, fish etc. Various intestinal problems such as gastro-intestinal diseases, chronic renal diseases, and structural alterations in membranes of the endoplasmic reticulum, also important is the fact that disorder in central nervous system are linked to heavy metals poisoning (Lewis et al., 2001). Recall that heavy metals disrupt the natural ecosystems functions. Their accumulations in the hydrologic environment from natural and anthropogenic sources are of serious concerns for two notable reasons: these reasons include (i) due to their ability to bio-accumulate in biota from where it constitutes serious threat to public health; (ii) possible contamination of groundwater for which it can persist for longer times. Source of heavy metals in the environment was widely believed to be mainly from rock weathering or mineralization of soils an opinion also held by Merian, (1991). and Ralph, (1982). Soluble iron (Fe^{2+}: ferrous and ferric ions: Fe^{3+}) are found in many groundwater because of the reducing conditions which favor the soluble Fe^{2+} oxidation state of this metal. Thus, iron is common in many aquifers and is found in trace amounts in practically all sediments and rock formations. Effluent from waste causes de- oxygenation in the ground, which results in dissolution of this metal. The iron content of groundwater is important because iron is a low level pollutant and can therefore affect the usefulness of water for some domestic and industrial purposes even at levels as low as 0.3-0.6mg/l. It has been stated that excess concentration of iron in water affects laundering operations, supports bacterial growth in water pipes and imparts taste to water (Ogwueleka, 2002).

Groundwater results from precipitation that has reached the zone of saturation in the earth through infiltration and percolation (O'Neil and Robson, 2000). Water in the natural reservoirs (aquifers/river channels) may spend as little as 2 to 6 months for rivers, or as much as 10,000 years for deep groundwater (Cherry, 1987). Seepages from poorly designed landfills, leakages from ponds and lagoons used as surface waste dumps, hazardous wastes disposal by deep well injection below an aquifer can be of great danger to the groundwater reservoir as these could migrate upwards by capillary action, laterally along the groundwater flow line or downwards through the pore spaces into deeper groundwater aquifers.

Annual industrial discharge of water polluted to varying degrees would be about 6,000 billion gallons in the USA (Chanlett, 2004). Most of these was said to have come from metal cleaning, pickling and plating, bleaching and dyeing, pulping, canning of fruits, vegetables and beef, sugar refining, milk products, brewing, and bakery among others. In Nigeria, the top major polluting industries are steel works, metal fabrication, food processing, tanneries, textile, pharmaceuticals, petroleum refineries and associated activities are also a source of groundwater contamination. The production of plastic vessel and building materials is practically associated with the emission of chlorine into the air, it mixes with atmospheric moisture to produce acid rain, and this acidified rain hits the soil surface, infiltrates through the soil and some reaching the water table zone of the aquifer.

Groundwater Quality Impact

Alao (1994), studied traced metallic chemicals found in surrounding well waters in Ibadan, to nearby waste dumps. It was thereafter concluded that the wells were infestations by pathogens as a result of infiltrations from decomposing organic solid waste material into the wells. Such waste materials include saw-dusts and shavings from wood work industries, and wastes from food preparation centers, including peelings or left-over. Chemical stability and movement in groundwater lead to arsenic poisoning of 13 construction workers in Perham, Minnesota, who drank water from a nearby shallow temporary well (Cherry, 1987). The lithologic sections from some boreholes in the study area showed the aquifer system as composed of a sequence of sand beds from red earth at the surface through various sand columns and good quality waters were intercepted at about 200m – 240m and the lithologic sections show that the water bearing formation is unconfined.

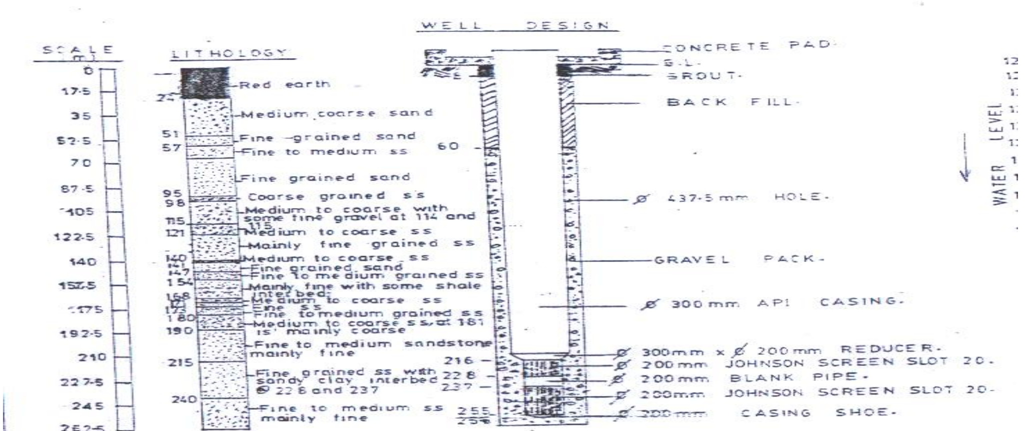

Fig.1. Borehole log showing lithologic units of Ameki Formations (after Anunobi,

As it is now, recent researches have revealed tremendous increase in concentrations which are practically traced to human activities as also submitted by Merian, (1991). Other sources include paints, pesticides, fungicides and preservatives. Also mercury generation is posited to occur naturally by the degassing process of the earth's crust, and from volcanic emissions (Goyer, 1996). He further submitted that mercury exists in three forms including elementary mercury, organic and inorganic mercury. However it is to be dispersed across the earth by winds and returns to the earth through precipitation (Clarkson, 1990). The use of lead in making PVC pipes/plastics and in plumbing, ammunition, fuel additives, in paints/pigments and these are widely use in developing countries. It was expected that both chemicals and their containers should contain information on Safety Handling of Chemicals (SHOC) regarding the very chemical in stock inscribed on the containers. Such inscriptions as intended will ensure public safety from unexpected exposure to toxic substances. In parts of Nigeria today, used plastic cans are discarded without their SHOC cards attached and the result is that the unsuspecting persons use these cans in storing water. Also water tanks are painted to avoid rust and the chemistry of

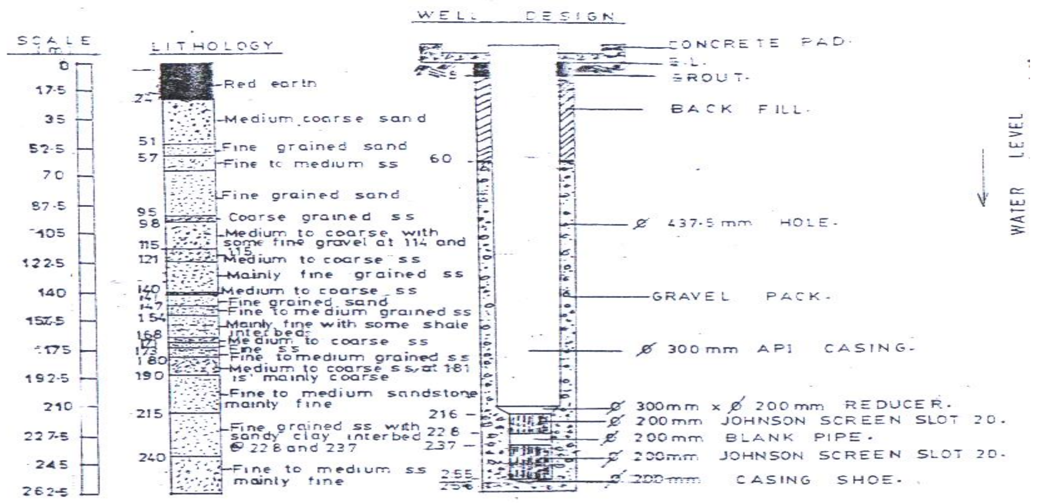

Fig.2. Borehole log showing sequence of sandstone, sand and clay rich rich unit of Ameki Formation (after Anunobi, 1998).

the paint (which may include one or two of these toxic metals) may remain unknown to both the painter and the user. These paints in time weather and interact with the water that it contains either temporary if water vendors using tankers made of metals are involved. It is worse still if the water tend to stand long in storage in metal tanks which are sometimes painted with aluminum paints. The worst is not over yet as the current way of water delivery to nearby homes from borehole owners is by the use of plastics pipes. These pipes tend to impact strong odor to the water which persists long after the water delivery (Ibezueet al., 2013).

The current study is limited to some metals selected from most of the first twenty metals listed by Agency for Toxic Substances and Diseases Registry (ATSDR). The sampling was during rainy periods of which the water volumes were slightly higher than normal times and this may influence concentration levels for metals measured. Expected effects include Ion- exchange depending on the immediate chemistry of the reservoir. What this implies is that the result may vary from season to season. Over six hundred groundwater sources of water supply exist in Onitsha but ten were selected systematically for this analysis. This was to follow up an earlier research in which case surplus ions were observed from a hydrochemical facies survey of groundwater in the same vicinity. Ten out of about 100 water boreholes earlier sampled were selected just to ascertain if these heavy metals could account for the surplus ions observed (Ibezue,2014).

3. METHODOLOGY

The water samples were collected and pre-treated-they were first filtered, stabilized using 2-3 drops of dilute Hydrochloric Acid to forestall hydrolysis, absorption and sorption, de-sorption. The research adapted the standard methods for water quality examination of APHA-AWWA-WPCF (1995). Heavy metals concentrations in the water samples were determined by atomic absorption spectrophotometer (AAS) methods. This method is based on the absorption of radiation by free atoms in vapor state.

Each water sample was converted to atomic vapor by spraying a solution (end-point indicator) in series from a photo flame – monochromatic light – a detector that measures the amount of light absorbed by the atomized elements in the flame. Source lamps made of the same element which is to be analyzed was used to avoid spectral or radiation interferences due to variations in wavelengths as each element has its own characteristic wavelength. The rate of absorption of light energy is same for both the incident light from the lamp source and atomized element from the sample since they operate at the same wavelength. The amount of light energy absorbed by the flame is proportional to the ionic concentration of the element under consideration at that wavelength. Temperature, turbidity, conductance, and pH were also measured using a digital meter (Gallenkamp, Hach and DREL meters) that measures all three simultaneously.

4. RESULT AND DISCUSSION

The result of the analysis is presented in table 1 below. Following the table are figures 3-8 that illustrated the relationships between parameters and across samples.

Table 1. Heavy Metals Concentration Across Samples

Sample	Temp ^oC	pH	Fe^{2+} mg/l	Mercurymg/l	Cadmium mg/l	Lead mg/l	Arsenic mg/l
S_1	27	4.7	0.83	0.001	0.002	0.002	0.01
S_2	27	6.8	0.55	0.002	0.001	0.009	0.01
S_3	28	6.5	0.65	0.006	0.004	0.008	0.02
S_4	29	6.4	0.21	0.003	0.007	0.005	0.01
S_5	28	6.9	3.91	0.001	0.002	0.035	0.01
S_6	29	5.2	2.54	0.005	0.002	0.006	0.01
S_7	27	6.2	2.45	0.002	0.002	0.071	0.01
S_8	28	6.1	2.01	0.004	0.001	0.002	0.01
S_9	28	5.1	2.33	0.001	0.003	0.000	0.01
S_{10}	29	5.5	1.81	0.001	0.001	0.002	0.01
WHO LIMITS	-	-	0.3	0.002	0.005	0.015	0.01

The figures following tried to illustrate the relationships between the various water quality parameters measured during the course of the analysis. The graphical configuration comparing the heavy metals characteristics in samples on inter parameter basis and with WHO limits showed the groundwater in the study area as having serious problems with iron ions. Concentration levels fall between 0.01mg/l and < 1.0 mg/l for Hg, As, Cd, and Pb except for samples 5 and 7 which presented slight variations from normal; others are within limits acceptable by WHO for almost all samples. The fact remains that Onitsha as a city grapples with problems associated with heavy commercial activities in a haphazard manner. This poses a problems to groundwater supply sources and a health risk to the public who are less likely aware of this trending contamination by human activities judging the owner developer attitude to groundwater development and supply in the study area. Heavy metals concentration in the environment and the groundwater which is a part of the hydrologic environment to a greater extent has been attributed to human activities. The inhabitants are more likely to face the consequences of their undoing, since they are the polluter and the victim of the polluting activities

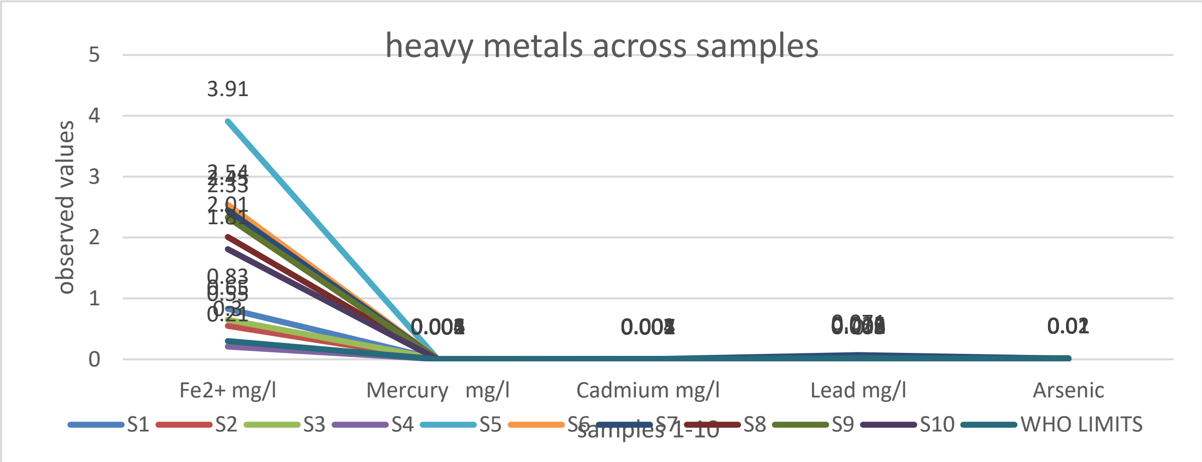

Fig. 3. Heavy metals concentration across samples

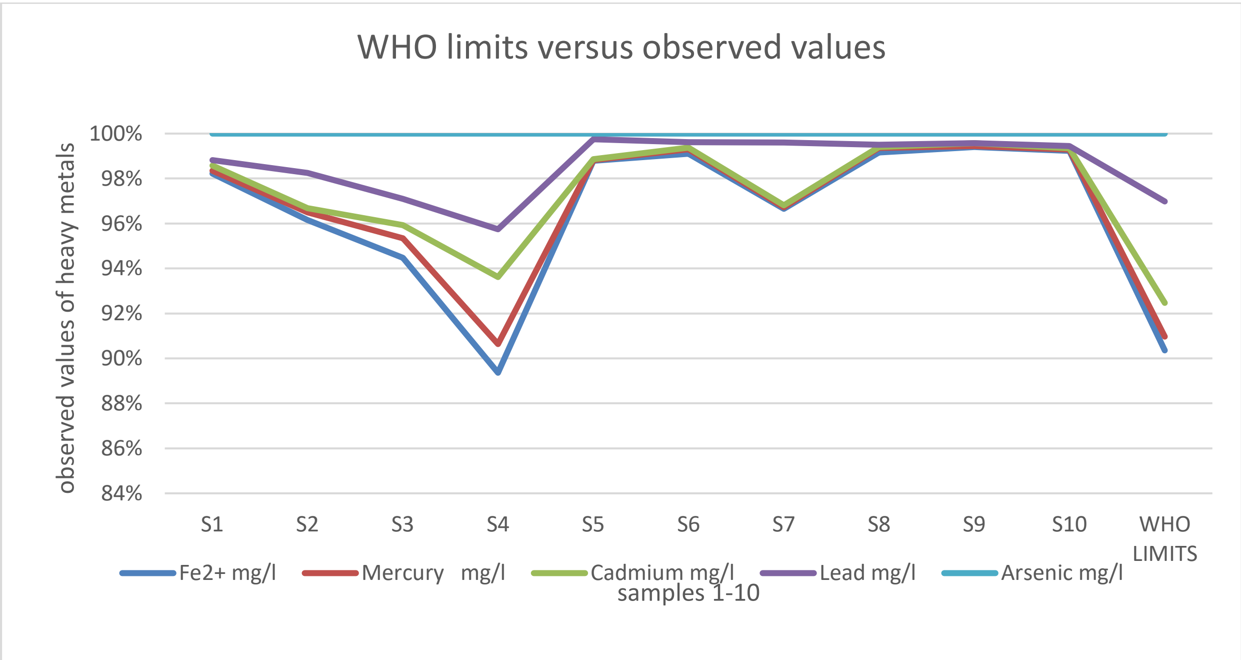

Fig. 4. Heavy metals concentration across samples versus WHO limits

Take for instance, the mercury which is carcinogenic which presents slight elevation in its level of concentration in sample number 4; where it is 0.007mgl^{-1} as against 0.005mgl^{-1} set as the acceptable limit set by WHO. It follows that, the consumer is liable to cancer in his/her lifetime if he/she consumes the water from the said source for long enough time to allow for bioaccumulation. The same goes for iron, under normal circumstances, iron ion concentration in drinking is set at 0.1mgl^{-1} but because of the peculiar chemistry of the Nigerian groundwater and especially the South Eastern Region which present problems with iron and pH, the standard was elevated to 0.3mgl^{-1}. The groundwater samples show problems with iron except in one (sample 4 with 0.21mgl^{-1}). This trending problem with iron borders on the level of ferruginization of the water bearing formations within the region and the Eocene Ameki Formation is a typical example. The dominant red earth material that consist the overburden may have contributed its quota of the iron ions. Besides this, possible sources could also be leaching from the surface and younger deposits with of Ogwashi-Asaba Formation which is also ferruginized. According to Hems, (1989), ferrous Fe^{2+} and ferric Fe^{3+} ions are found in groundwater because of the reducing conditions in the environment which favour soluble iron oxidation, it also occur in many aquifers in trace amounts in practically all sediments and rock formations. Presence of iron in drinking and domestic water supply sources presents problems with laundry operations, supports bacterial growth and imparts taste (Hems, 1989), this makes the water unpalatable to the consumer.

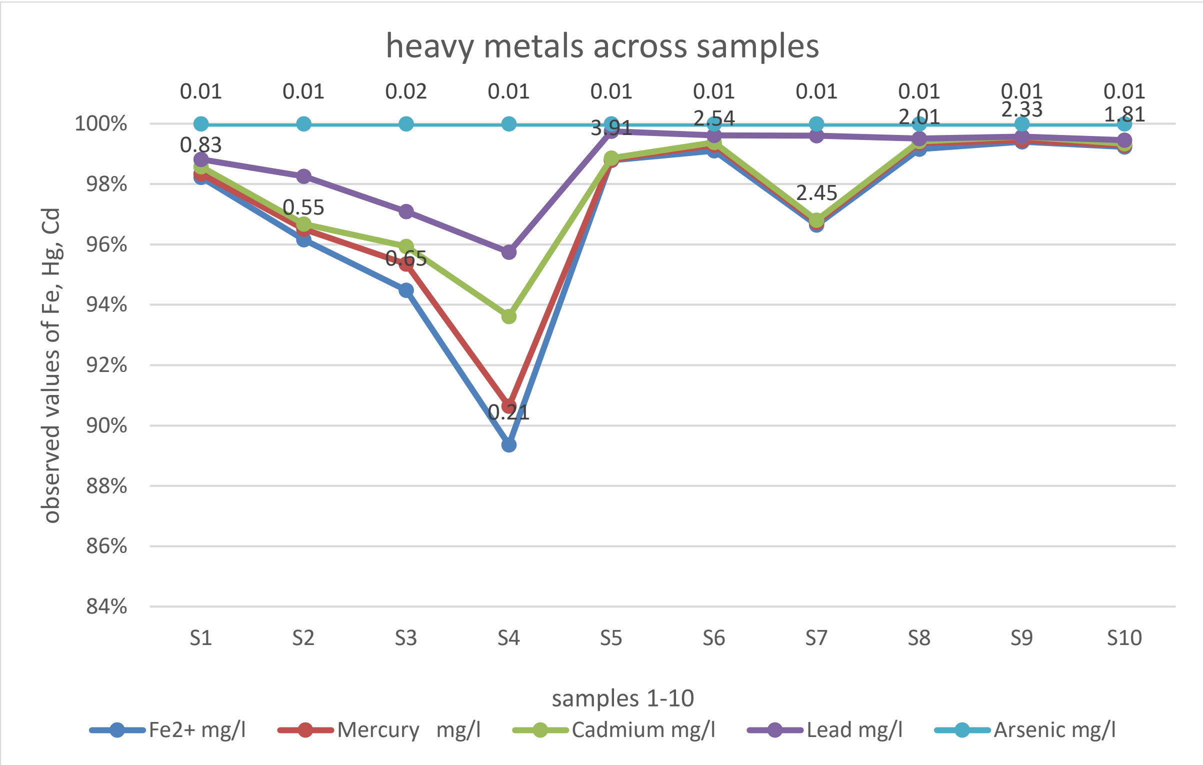

Fig. 5. Heavy metals concentration across samples in a reverse plot.

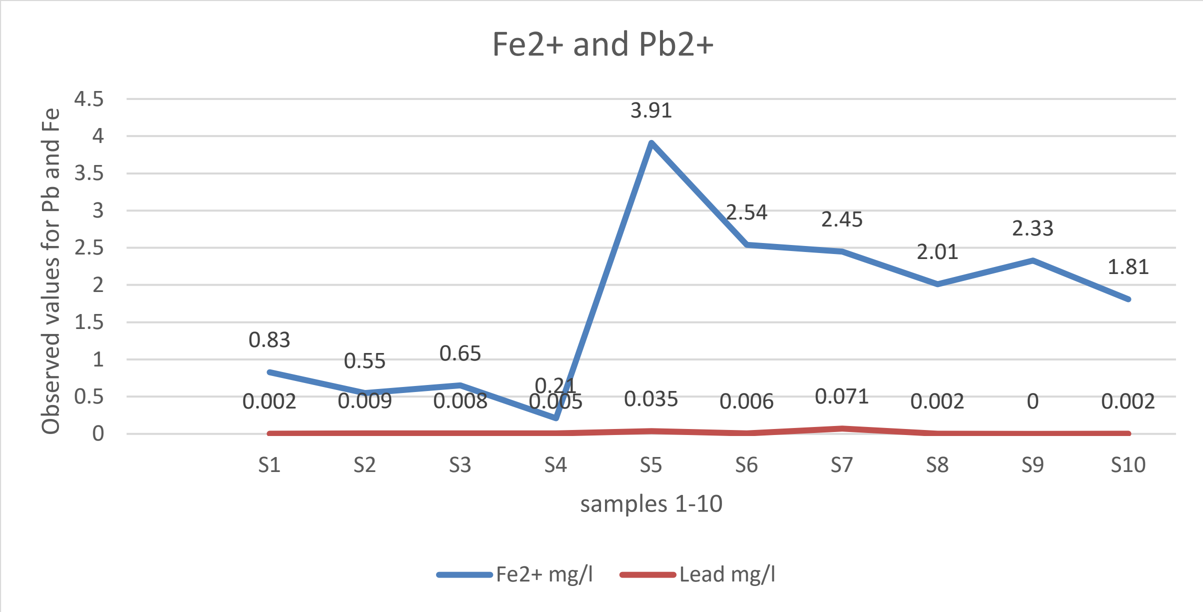

Fig. 6. Lead and Iron concentrations across samples compared.

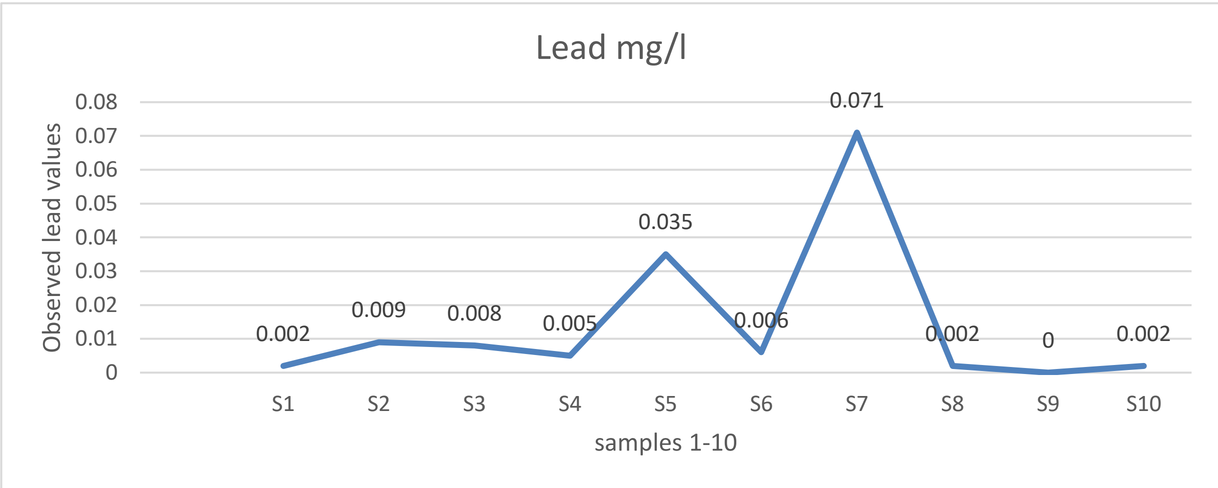

Fig. 7. Lead concentration across samples

Lead poisoning looms for the users of the water from sample numbers 5 and 7 where concentration levels were observed to be 0.035mgl^{-1} and 0.071mgl^{-1} respectively as against 0.015mgl^{-1} standard limit acceptable as set by WHO. Pb is known to be tetratogenic in that it causes birth defect to the unborn if consumed by pregnant women, it is also carcinogenic. From the observations made, heavy metals concentration in the groundwater supply of the Eocene deposits within Onitsha calls for prudent action including quality monitoring to ensure that their concentrations does not escalate to epidemic proportions. There is also the need for treatment before use and centralized water supply system will help quality monitoring, proper treatment (where necessary) and safe drinking and domestic water supply for all.

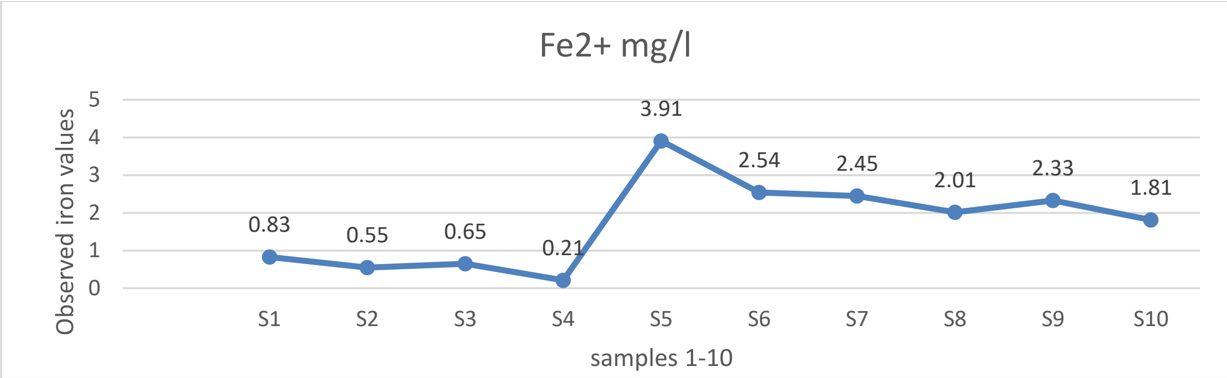

Fig. 8. Iron concentration across samples

5. SUMMARY

Waste effluents from industries may be a global issue but in developing countries it is much more than just a problem but it is synonymous with the production phenomena and as such part of life in such environments. Environments in these areas are fed with all forms of pollutants whether they are gaseous, liquid or solid as polluters are less likely to be held accountable to their polluting activities. This is unlike what obtains elsewhere in the developed industrialized societies where a level of monitoring is involved. The fact however remains that these activities (i) go on in diverse places unchecked (ii) some of the polluting raw materials are obtained from across borders (iii) and some of the products may also cross borders, an opinion also held by Ralph, (1982), (iv) the pollutants may also be exported or imported across borders as acid rains are known to have formed from acidification of water vapors resulting from gaseous emissions from far away cities. This implies that pollution transcends boundaries and as such will require global approach that emphasizes formulation and implementation of policies that will ensure correction in these trends in the antisocial behaviors and unethical stance of the industrial world.

The need to develop the world economies is imperative but it should be followed by the need to protect the environment on which we live and depend on by sticking to sustainable principles and practices. The issue of freshwater looming hydrocide should be treated as a global challenge other than localized issue which is restricted to the have-nots. It may eventually become a scourge like the HIV which traversed all social classes and all ages. Certain water borne infections have a way of crossing borders and with potentials to put every other race at risk. Proper effluent management by the suspected feeder activities will no doubt control the trend in heavy metals accumulation in the soils which leaches down into the groundwater. Layouts should be designed for efficient effluent and solid waste management schemes for industries and residential areas.

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