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Research Article

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Physico-Chemistry and Heavy Metal Concentration in Shallow Groundwaters Around A Semi-Controlled Dumpsite in Eneka, Rivers State, Nigeria.

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Abstract The Eneka dumpsite, Rivers State, Nigeria, has been in existence for over 20 years, which is long enough to impact the chemistry of the nearby shallow groundwater. An assessment of some heavy metals:chromium (Cr), cadmium (Cd), lead (Pb), nickel (Ni), zinc (Zn) and copper (Cu), and some physico-chemical properties of shallow groundwater around Eneka dumpsite was carried out using American Society for Testing and Materials (2010) standard methods. Groundwater flowed in the NE-SW direction. Static water levels ranged from 1.61m – 2.11m. Water samples were collected from 4 sampling points-three boreholes and a hand dug well. One borehole was located upslope, which was used as control and the others downs lope. Groundwater samples were analyzed for the six heavy metals using Atomic Absorption Spectrometry (AAS) and physico-chemical parameters including Total Dissolved Solids (TDS), Electrical Conductivity (EC), temperature (T) and hydrogen ion concentration (pH) were measured in-situ using a hand-held PCS Tester 35. pH values ranged from 4.36 to 6.2 which is below the WHO acceptable limit for drinking water. Average temperature of water was 28 °C. TDS values ranged from 13.6 to 527 ppm, water with TDS above 500 ppm is saline and not suitable for drinking. EC values ranged from 19.6 to 746µS. Cd and Pb concentrations were below detection limits for the AAS instrument. Ni concentrations were 0.08 and 0.09 which is slightly above World Health Organisation (WHO) limit of 0.07 mg/l but was not detected in two samples. Cu concentrations ranged from 0.02 to 0.04mg/l, Zn concentrations from 0.04 to 0.13mg/l. These concentrations are below those set by the Federal Environmental Protection Agency (FEPA) and WHO. All the water samples analyzed contained detectable concentrations of Cr (0.13 - 0.59mg/l), these concentrations are well above WHO acceptable limits for drinking water. It is recommended that people living SW of the dumpsite should monitor their water frequently for heavy metal contamination and low pH to determine if the water can be used for human consumption.

Keywords groundwater, heavy metals, physico-chemical parameters

Introduction

Groundwater is the water present beneath the surface of the earth in soil pore spaces in the saturated zone and in the fractures of hard rock formations. Groundwater constitutes about 96% of the world's total fresh water resources. Ground water can be polluted in numerous ways in spite of the protective mechanisms that nature provides. Liquid pollutants canjs originate from waste water discharge, sludge lagoons, runoff, septic tank leaching fields or seepage pits. Pollutants can also originate from the leachates of decomposing solid wastes as in the case of open dumps and sanitary landfills [1]. One of the major problems associated with dumpsites is the formation of leachate and eventual contamination of groundwater due to contaminant migration [2].

Groundwater pollution results from the elevation in the concentration of its constituent anions and cations (for example, Cu^{2+}, Fe^{2+}, Zn^{2+}, NO^{3-}) and also the introduction of bacterial, viral and parasitic micro-organisms. The extent and seriousness of groundwater quality degradation depend on the geohydrologic setting, nature of contaminants, Climate of the area and the interplay of physico-chemical processes that operate in the subsurface environment [3].

Waste dumps abound in every city in Nigeria. When it rains or when water comes in prolonged contact with these dumps, the effluent or leachate forms. This leachate contains a variety of suspended or dissolved constituents, including heavy metals that can contaminate water supplies through their migration in soil and into ground water.

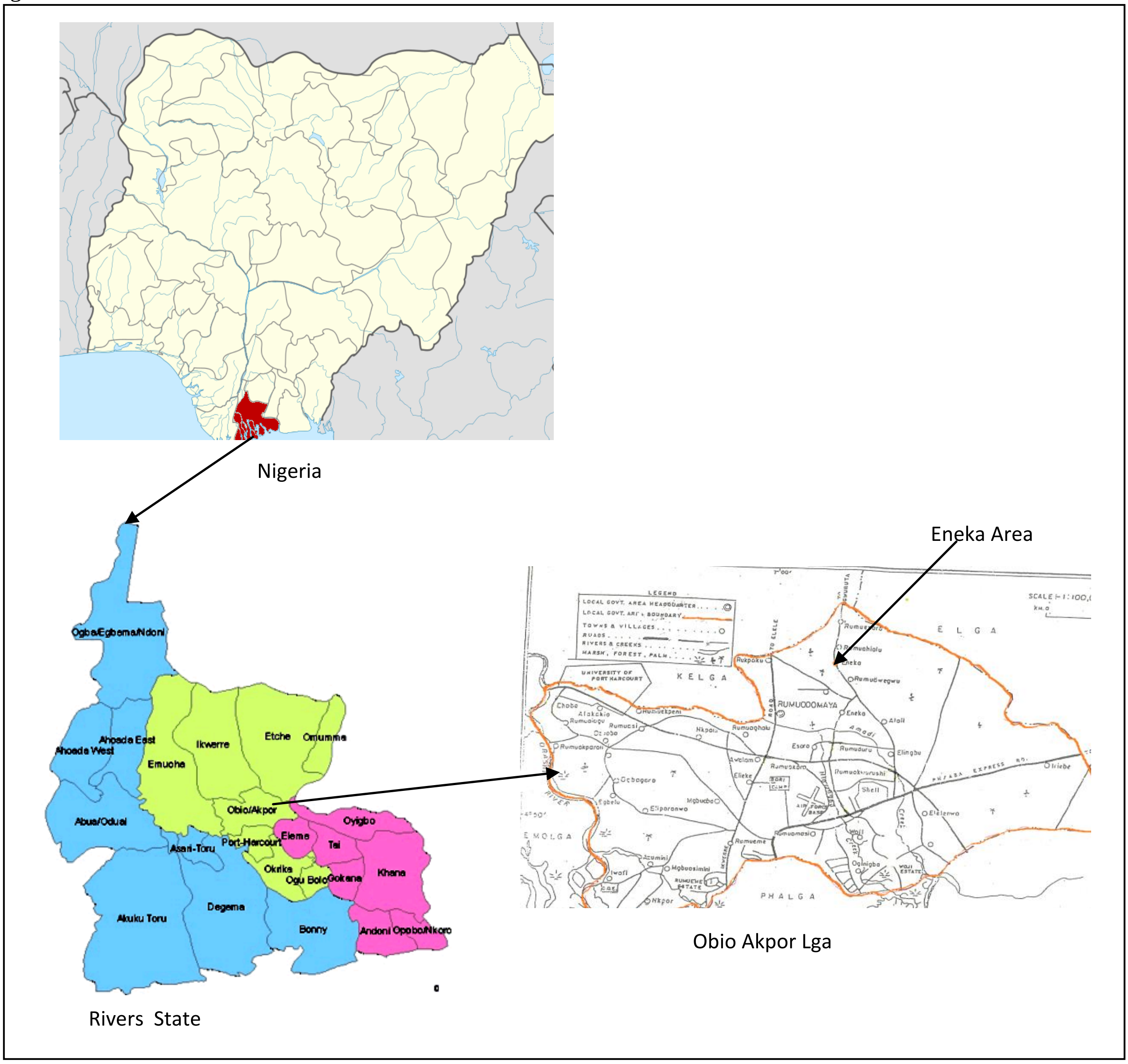


Figure 1: Maps showing location of study area

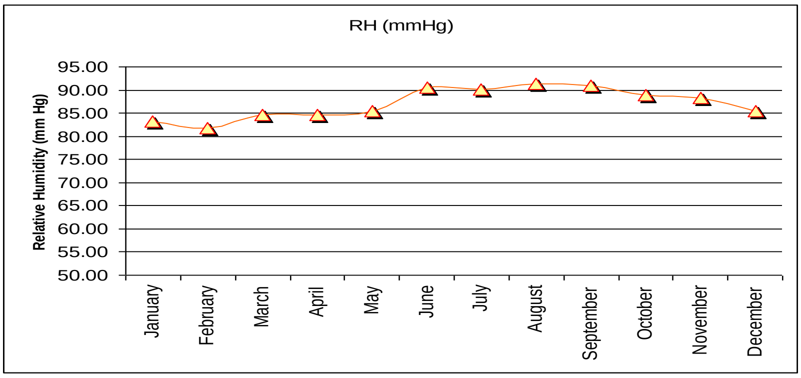
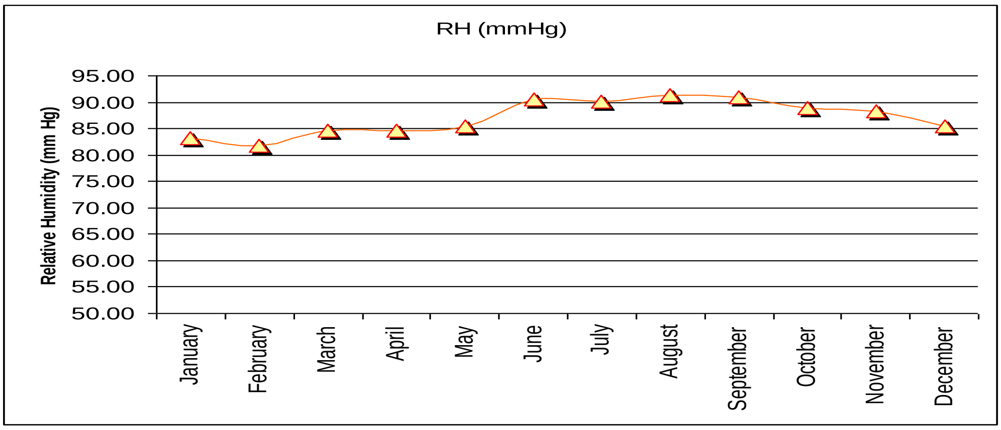


Figure 2: Mean monthly relative humidity of Port Harcourt from 1994 - 2004
Source: Federal Department of Meteorological Services, Oshodi – Lagos (1994 – 2004)



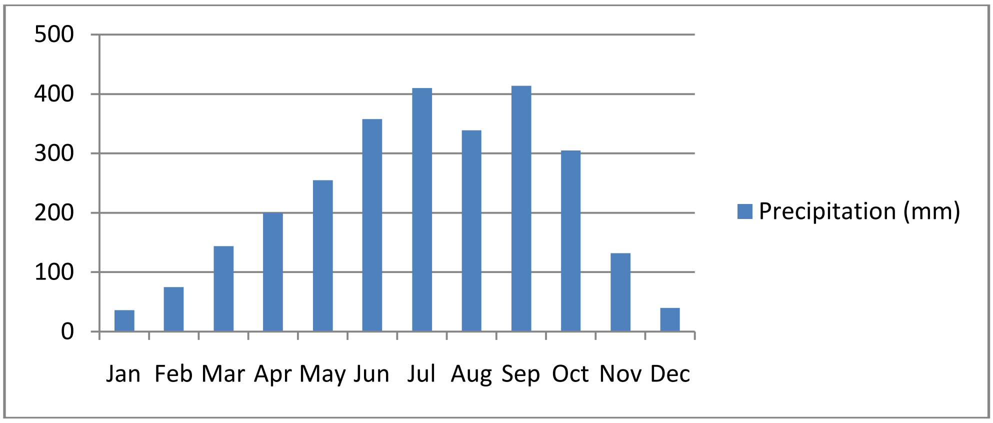


Figure 3: Mean monthly precipitation of Port Harcourt.

Source:climate-data.org/location /528

In the Niger Delta, rainfall is heavy and flooding a common phenomenon, the risk of pollutant migration from leachate into the groundwater system remains very high. The waste dump at Eneka has been in existence for over 20 years and is a threat to groundwater systems as heavy metals in the leachate could infiltrate through the soil and pollute groundwater. A very large proportion of the human population of Port Harcourt depend on hand dug wells or private boreholes for drinking water, thus further increasing the risk of potential pollutant consumption. This is what has led to this research, which aims at studying the concentration levels of heavy metals in groundwater and the physico-chemical properties of shallow groundwater in Eneka.

Description of Study Area

The study area is in Obio-Akpor Local Area of Rivers State (Fig 1), which is one of the states in the South-South geopolitical zone. This geopolitical zone is within the Niger Delta which is one of the world's largest wetlands with a total land area of approximately 29,000 Km^2 excluding the continental shelf [4]. ObioAkpor local Government Area is one of the major centres of economic activities in Nigeria, and one of the major cities of the Niger Delta, located in Rivers State (Fig 1). The Local Government Area covers 260sq.Km and at the 2006 census, held a population of 464,789 persons (NBS, 2006) and has her headquarters at Rumuodomaya. Enekaarea had a population of 4,423 persons in 1991 [5], 7,607 persons by the 2006 census (NBS, 2006) and population projection with the exponential growth model is 10,659 inhabitants by 2016 [6].

The area is characterized by high humidity. Relative humidity is high (75-99%) all year round (Fig 2). This is due mainly to the coastal nature of the area, dense vegetation cover, greater cloud cover together with the influence of the moisture laden tropical maritime air mass, and annual average rainfall exceeding 2800 mm (with peaks in July and September (Fig 3)).Port Harcourt city experiences moderately high temperature (24 °C-34.5 °C) and long periods of sunshine. It rains for about eight months of the year (March – October), and even the months considered to be dry months are not free from occasional rainfall [7].

The vegetation is typical of the tropical rain forest dominated by oil palm (*Elaiesguineensis*) and raphia (*Raphiahookeri*), surrounded by farmlands and fallow grounds. Although, there are two seasons (wet and dry), measurable precipitation occurs in all the months of the year.

The neighbouring settlements to Eneka town include Rumuokwurushi/Elimgbu in the North, Igwuruta in the south and Rumuduru town (in Oroigwe) in the east. The nearest building to the dumpsite is located about 50m

away, although initially the area was dominated by thick bush and has been designated by the state government as an industrial area.
The Eneka waste dump is located along the Igwuruta/Eneka Express Roadon 282888.25mE and 540948.49mN UTM Zone 32N and covers an area of 29000.84 square meters and accommodates the Chiroda International Company Ltd corporate offices, a leachate treatment plant an engineered dumpsite cell and a dump heap. The dumpsite itself covers about a third of the total surface area (Fig 4). The site is currently used for the disposal of domestic non-hazardous waste mainly kitchen waste from offices, operational and residential locations and wastes arising from estate management activities, including but not limited to garbage and trash.
The dumpsite receives an estimated 12,757 cm^3 of wastes annually comprising of kitchen, garden and office wastes from SPDC which includes food wastes, papers, broken furniture, food containers, plant parts etc.
The study area is low lying with a gently sloping surface such that low surface runoff is expected. Owing to high rainfall pattern typical of the Niger Delta, rain water collects in a large depression (from where waste materials were removed to the engineered portion) at the eastern part of the compound. The topography is undulating and drainage is poor, thus pools of water stand in depressions for long periods after a rainy episode.

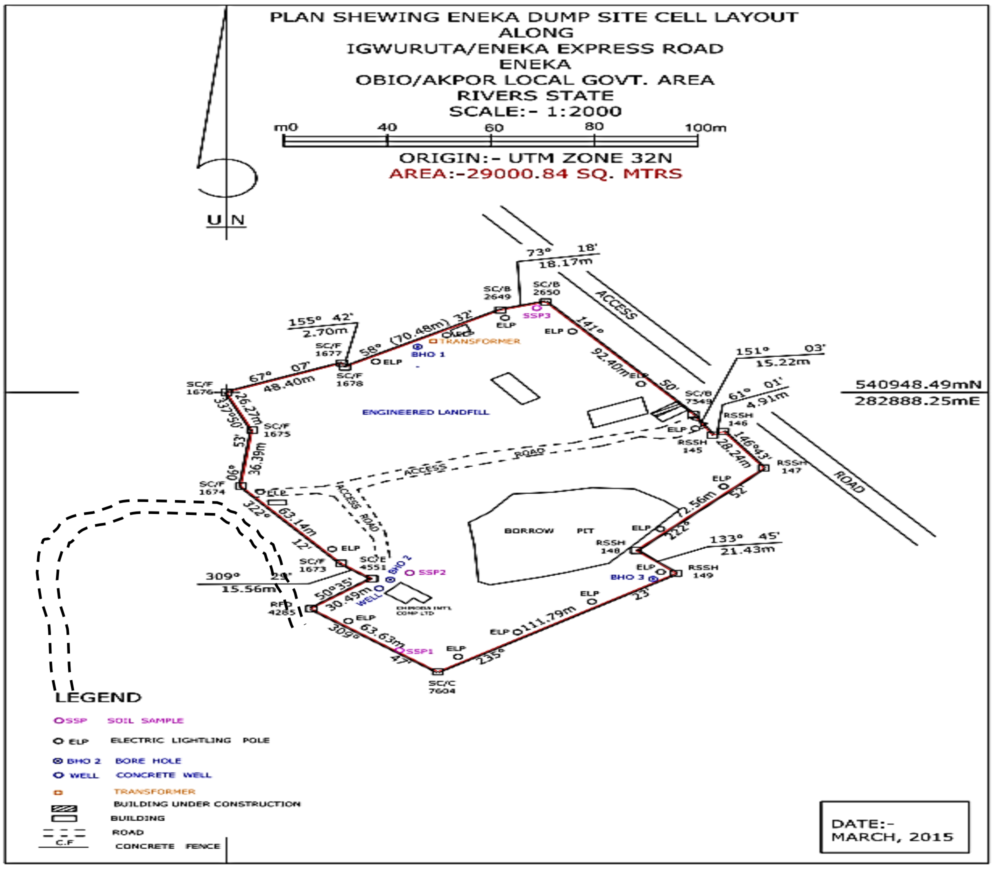


Figure 4: Plan showing sampling points at Enekadumpsite layout

Materials and Methods

Three boreholes and a hand dug well were identified on the site and were used as the sampling points for this study. One sampling point was located upslope, which was used as control, and the others downslope. The Geographic positions of the boreholes were noted using a hand-held GPS. Groundwater gradient and flow directions were calculated using the triangular method (Fig 5). Groundwater samples were collected from the boreholes and hand dug well using a stringed glass bottle. The glass bottle and the 1 litre plastic bottles for conveying the samples to the lab were rinsed with portions of the water being sampled.
Eight water samples were collected; two samples were collected from each sampling point, one for heavy metal analysis and the second for general physicochemical parameters. The sampling points were –borehole 1upslope (283008.0mE, 540968.5mN,), and the other sample points downslope: borehole2 (282965.0mE, 540832.0mN,) a hand-dug well (282950.0E, 540812.0N,) and borehole 3 (283078.0mE, 540848.0mN,). Because samples were vulnerable to microbial degradation and transformation over time, the samples collected from the dumpsite were analysed as quickly as possible time after collection. Samples for general physicochemical parameters were immediately subjected to measurements of pH, temperature, TDS, and Electrical Conductivity in the field using

a waterproof PCS.

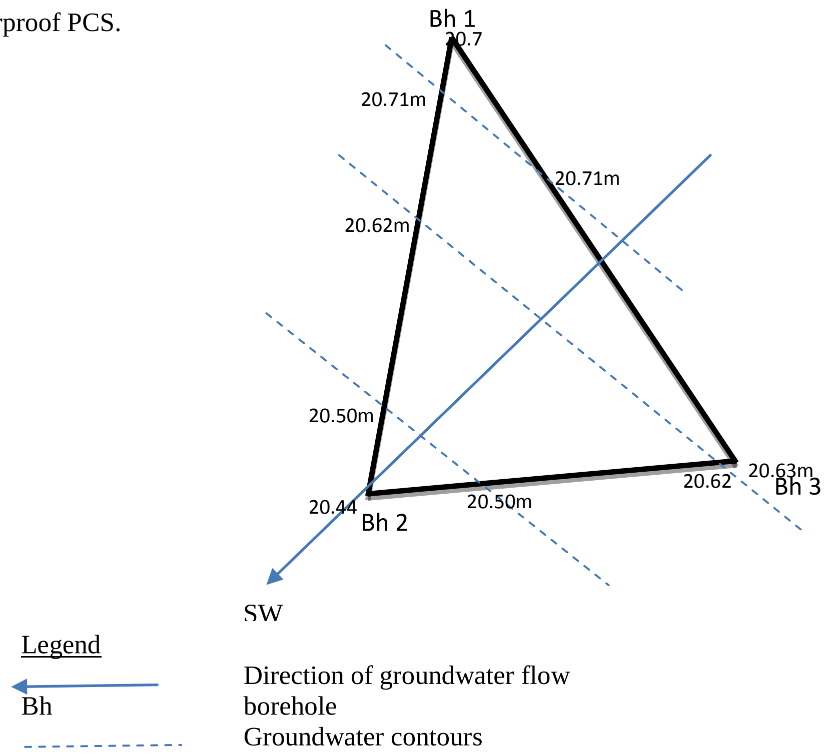


Figure 5: Hydraulic gradient and flow direction in the study area

Testr 35 multi-parameter test instrument. The equipment was calibrated using automatic calibration mode. Each 1 litre sample for heavy metals analysis was acidified by addition of 1:1 Analar (about 3ml) grade concentrated nitric acid to pH $\leq$ 2. The samples were stored in polythene containers, and kept in an ice chest and quickly transferred to the Laboratory. Heavy metals were analyzed using an AAS equipment with accuracy of 0.0001 following the ASTM (2010) method.

Results

Table 1 lists the measured physico-chemical parameters (Temperature (T), Total Dissolved Solids (TDS), Electrical Conductivity (EC) and Hydrogen ion concentration pH) of groundwater in the study area. Results from analysis for heavy metal concentration are listed in table 2.

Table 1: Physico-chemical analysis of the groundwater Samples

Borehole	Location	T (^{o}C)	TDS (ppm)	E C(µS)	pH
1	540968.5mN, 283008.0mE	27.7	13.6	19.6	6.2
2	540832.0mN, 282965.0mE	29.2	527	746	4.36
3	540848.0mN, 283078.0mE	27.3	13.4	19.9	6.1
Well	540812.0N, 282950.0E	28.8	38	23	5.1

Table 2: Concentrations of Heavy Metals in the Groundwater Samples and Concentration Limits set by FEPA and WHO.

Water Samples	Cd (mg/l)	Cr (mg/l)	Cu(mg/l)	Pb(mg/l)	Ni(mg/l)	Zn(mg/l)
BH 1	<0.001	0.13	0.02	<0.001	0.08	0.04
BH 2	<0.001	0.58	0.03	<0.001	< 0.01	0.13
BH3	<0.001	0.59	0.02	<0.001	0.09	0.06
WELL 1	<0.001	0.48	0.04	<0.001	< 0.01	0.08
FEPA	0.01	0.05	1.00	0.05		5.00
WHO	0.003	0.05	2.00	0.01	0.07	5.00

Discussion

Groundwater flow direction is NE-SW and pollutants are mostly flowing in this direction. Borehole 2 is directly in the flow direction and the most likely heavily impacted by the dump since contaminants would flow with the water in the direction of groundwater flow. This borehole had the lowest pH values of 4.36, TDS measured in-situ at borehole 2 was high (527mg/l). At a high TDS concentration, water becomes saline. Water with a TDS above 500mg/l is not recommended as use for drinking water [8].

Cd and Pb concentrations were below detection limit. Cr was present in all the water samples – 0.13mg/l in BH1, 0.58mg/l in BH2, 0.59mg/l in BH3 and 0.48mg/l in the hand dug well, these values were all in excess of WHO (2006) and FEPA (1991) limits for drinking water. Cu values ranged between 0.02mg/l and 0.04mg/l [9-10].

The apparent lack of Cd and Pb and the low values of Zn, and Cu in the groundwater samples could be due to high clay content and presence of a thin layer of organic matter at the surface resulting in sorption of the pollutants as reported elsewhere [11]. Zn was present in all the samples at very low concentrations 0.04mg/l in BH1, 0.13mg/l in BH2, 0.06mg/l in BH4 and 0.08mg/l in the Well. The results for the presence of heavy metal pollution of groundwater recorded for the Eneka dumpsite are much lower than that reported by Oyeku and Eludoyin (2010) in Lagos State [12]. The water is slightly acidic with pH values ranging from 4.36 – 6.2.

Ni concentrations in BH2 and the hand dug well were below detection limit but was detected in BH1 measuring 0.08mg/l and 0.09mg/l in BH4. These concentrations are slightly higher than the limit of 0.07mg/l recommended by WHO. The larger part of all nickel compounds that are released to the environment will adsorb to sediment or soil particles and become immobile. In acidic ground however, nickel is bound to become more mobile and it will often rinse out to the groundwater. For animals nickel is an essential foodstuff in small amounts. But nickel is not only favorable as an essential element; it can also be dangerous when the maximum tolerable amounts are exceeded. This can cause various kinds of cancer on different sites within the bodies of animals. Nickel is not known to accumulate in plants or animals. As a result nickel will not bio magnify up the food chain [13].

Groundwater in and around the Eneka dumpsite have been found to be contaminated with Chromium (0.13 – 0.59mg/l) up to ten times the acceptable limit for household use and drinking purposes.Chromium may be present in domestic waste from various synthetic materials. Through waste incineration it may spread to the environment when protection is insufficient. Chromium is a dietary requirement for a number of organisms. This however only applies to trivalent chromium. Hexavalent chromium is very toxic to flora and fauna. Chromium (III) oxides are only slightly water soluble, therefore concentrations in natural waters are limited. Chromium (III) ions are rarely present at pH values over 5, because hydrated chromium oxide ($Cr(OH)_3$) is insoluble.

Chromium (VI) compounds are stable under aerobic conditions, but are reduced to chromium (III) compounds under anaerobic conditions. The reverse process is another possibility in an oxidizing environment. Chromium is largely bound to suspended particles in water. Chromium (VI) compounds are toxic at low concentrations for both plants and animals. The mechanism of toxicity is pH dependent. These compounds are more mobile in soils than chromium (III) compounds, but are usually reduced to chromium (III) compounds within a short period of time, reducing mobility. Soluble chromates are converted to insoluble chromium (III) salts and consequently, availability for plants decreases. This mechanism protects the food chain from high concentrations of chromium. Chromate mobility in soils depends on both soil pH and soil sorption capacity, and on temperature. Trivalent chromium is an essential trace element for humans. Together with insulin it removes glucose from blood, and it also plays a vital role in fat metabolism. Chromium deficits may enhance diabetes symptoms. Chromium can also be found in RNA. Chromium deficits are very rare, and chromium feed supplements are not often applied.

Chromium (III) toxicity is unlikely, at least when it is taken up through food and drinking water. It may even improve health, and cure neuropathy and encephalopathy.

Hexavalent chromium is known for its negative health and environmental impact, and its extreme toxicity. It causes allergic and asthmatic reactions, is carcinogenic and is 1000 times as toxic as trivalent chromium. Health effects related to hexavalent chromium exposure include diarrhoea, stomach and intestinal bleedings, cramps, and liver and kidney damage. Hexavalent chromium is mutagenic. Toxic effects may be passed on to children through the placenta.

Chromium (VI) oxide is a strong oxidant. Upon dissolution chromium acid is formed, which corrodes the organs. It may cause cramps and paralysis. The lethal dose is approximately 1-2 g. Most countries apply a legal limit of 50 ppb chromium in drinking water [13].

Conclusion and Recommendation

The dumpsite has impacted the chemistry of the adjacent shallow groundwater resulting in low pH and high TDS and EC values as reflected in results from borehole 2 which is directly in the flow direction of groundwater SW of the dump. Elevated concentrations of Cr with respect to the control have been established. It is therefore important that groundwater in the area be treated before domestic use. There is also the need to correct the pH of the water to make it suitable for household use.

Since the groundwater flow direction is NE-SW, it is recommended that inhabitants on the SW side of the dumpsite should monitor their groundwater often against any degradation.

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