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Assessing contaminants in Drain Sediments in Ogoni Niger Delta, Nigeria

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Abstract: This study was designed to investigate the status of drains using drain sediments. Thirty-five drain sediment samples were collected from thirty-five communities across the four local government areas of (Eleme, Tai, Gokana and Khana) in Ogoni land. The samples were evaluated using Atomic Emission Spectroscopy (AES) for Potentially toxic elements, Gas Chromatography-Flame Ionization Detector (GC-FID) for Total Petroleum Hydrocarbons (TPH). Gas Chromatography-Mass Spectrometry (GC-MS) for Benzene, Toluene, Ethyl-benzene and Xylene (BTEX). Chromium indicated concentrations ranged from 29.381 ± 0.552 mg/kg to 106.817 ± 0.433 mg/kg, Cobalt 42.268 ± 0.424 mg/kg to 69.162 ± 1.567 mg/kg, Copper 9.445 ± 4.499 mg/kg to 76.444 ± 0.65 mg/kg, Nickel 37.685 ± 0.375 mg/kg to 79.497 ± 0.65 mg/kg and Lead 33.257 ± 4.009 mg/kg to 102.924 ± 7.918 mg/kg. TPH ranged between 15.938 ± 3.934 mg/kg and 176.2 ± 7.852 mg/kg. BTEX ranged between 0.005 ± 0.005 mg/kg and 0.008 ± 0.006 mg/kg. The results obtained in this study indicate that the drains in these study areas are adversely impacted. Therefore, people from these communities should be involved in regular cleaning of their drains to be free from these contaminants.

Keywords: Potentially Toxic Elements, Organic Pollutant and Drain sediment

1. Introduction

Sediments can be defined as any settle-able particulate material found in storm water or wastewater that are able to form bed deposits in pipes and hydraulic structures [1]. These solids contain a wide range of very small to large particles, i.e. ranging from clays with a mean diameter of 0.0001 to 60 mm gravels [2] [3] and may originate from a variety of sources, such as large fecal and organic matter, atmospheric fall-out and grit from abrasion of road surface, among others. These particles move in the drainage catchment during storm events and, eventually, enter into the ecosystem.

Drainage is the natural or artificial removal of a surface's water and sub-surface water from an area with excess of water. The internal drainage of most agricultural soils is good enough to prevent severe water logging (anaerobic conditions that harm root growth), but many soils need artificial drainage to improve production or to manage water supplies.

The term Potentially Toxic Elements, refer to any metallic element that has a relatively high density and is toxic or poisonous at low concentration [4]. Heavy metals cannot be degraded including bio treatment and are very toxic even at low concentration (1.0–10.0 mg/L). Some of elements are essential in trace amounts, namely Cu, Fe, Mn, Cr, Cd, Pb etc. But higher concentration of these metals in the ecosystems may lead to an excessive accumulation of metals, becoming toxic to soil and possible danger to human health problem [5][6][7]. Higher level of metals may



frequently react with biological systems by losing one or more electrons and forming metal cations, which have affinity to the nucleophilic sites of vital macromolecules. Several acute and chronic toxic effects of heavy metals affect different body organs. Gastrointestinal and kidney dysfunction, nervous system disorders, skin lesions, vascular damage, immune system dysfunction, birth defects, and cancer are examples of the complications of heavy metals toxic effects. Simultaneous exposure to two or more metals may have cumulative effects [8][9]. A number of cases of health problems related to environmental Cr- poisoning and elevated levels of Pb in the blood of infants have been reported [10][11]. Some heavy metals are considered as serious contaminants of aquatic ecosystems, due to their high potential to enter and accumulate in food chains [12][13]. Heavy metal pollutants most common in the environment are Cr, Mn, Ni, Cu, Zn, Cd, and Pb [14].

Organic pollutants are toxic substances made of organic compounds. They can be found anywhere, in water, soil, sediments, dust and air. These pollutants are especially dangerous because their toxins don't break down easily, because they persist in the environment and are therefore known as Persisting Organic Pollutants (POPs). They can accumulate in the body fat of humans and other animals. Small amounts of these compounds can cause nervous system damage, immune system diseases, reproductive disorders, and cancer [15].

Organic pollutants in sediments are a worldwide problem because sediments act as sinks for hydrophobic, recalcitrant and hazardous compounds. Pollutants from gas flares, oil spills and vandalized oil pipe lines discharges into river leach into soil increasing the accumulation of metals in sediments, biota and ultimately humans [16]. Depending on biogeochemical processes these hydrocarbons are involved in adsorption, desorption and transformation processes and can be made available to benthic organisms as well as organisms in the water column through the sediment–water interface. Most of these recalcitrant hydrocarbons are toxic and carcinogenic, they may enter the food-chain and accumulate in biological tissue. Distribution of these contaminants in various parts of the environment is influenced by many factors some are industrial activity that spills or flushed into the environment etc), activity of man (Oil pipeline vanderlization etc) and even natural occurrences like oil spillage or gas flaring in to the atmosphere, aquatic and terrestrial ecosystems, they are considered ubiquitous environmental contaminants. Their affinity for the aquatic environment is minimal, but they are readily sorbed to solid particles as it ash, dust, soil or sediment. Due to the fact that accumulation of these substances in sediments may last for many years, sediments are considered to be an important reservoir of contaminants and material often monitored for environmental pollution, [17].

Total petroleum hydrocarbon (TPH) is a term used to describe a large family of several hundred chemical compounds that originally come from crude oil. Crude oil is used to make petroleum products, which can contaminate the environment. However, it is useful to measure the total amount of TPH at a site. Scientists divide TPH into groups of petroleum hydrocarbons that act alike in soil or water. These groups are called petroleum hydrocarbon fractions. Each fraction contains many individual chemicals. Some chemicals that may be found in TPH are hexane, jet fuels, mineral oils, benzene, toluene, xylenes, naphthalene, and fluorene, as well as other petroleum products and gasoline components. However, it is likely that samples of TPH will contain only some, or a mixture, of these chemicals, [18].

Benzene, Toluene, Ethylbenzene and Xylene (BTEX) are naturally occurring components of crude oil, they are found in small concentration in refined oil products such as diesel, gasoline and aviation fuel [19]. BTEX are toxic to human and are found in the class of chemicals known as Volatile Organic Compound (VOCs). They are composed of Benzene 15%, Toluene 20%, Ethylbenzen 11%, o-xylene 12%, m-xylene 11% and p-xylene 8% [20].

2. Materials and Methods

Study Area and Sample Locations

The Ogonis are an indigenous people in the Niger Delta region of Nigeria. According to the Ogoni Bill of Right [21] the land covers an area of about 404 square miles of the caostal plains terraces to the East of the Niger Delta, it lies in an area between approximately latitude 4.050 and 4.200 North, and longitude 7.100 and 7.300 East. Ogonis have over 500,000 rural population as at 1963 census. Rainfall is seasonal, variable as well as heavy and occurs between the months of March and October through November. The wet season peaks in July, lasting more than 290 days.



Total annual rainfall decreases from about 4700 mm (185 in) from the coast to about 1700 mm (67 in) North. Average temperatures are typically between 25°C - 28°C. The Vegetation of the Ogonis was formally that of a very thicken forest, where different mammals, reptiles and amphibians were found, but now, there is alot of deforestation due to little development (building of houses, roads, installing electrical polls) and also since farming is the major occupation of the Ogonis, their vegetations is just an uncultivated farm land presently [22].

The Ogonis settle on this territory as farmers and fishermen before the British colonialists invaded them in 1901. The Ogoni ethnic minorities are made up of seven clan: Eleme, Tai, Gokana, Babbe, Ken-khana, Nyokhana and Bori as the traditional headquater, which comprises of four Local Government Areas (Eleme, Tai, Gokana Khana), [23].

Sampling

Samples were collected from different drains of the thirty-five (35) communities, giving a total of thirty-five (35) samples. The variation in the number of communities from each Local Government Area is because, not all communities have drainages.

Sample Preparation

The samples were air dried, sieved, weighed and stored in clean sample containers in the laboratories.

Sample Analysis

Potentially Toxic Elements Levels For potentially toxic Elements determination, 0.5 grams of sample was weighed in triplicate from the 30 or 35 samples into the beaker using the analytical balance. Nitric acid and hydrochloric acid were measured in the ratio of 1:3, mixed together and swirled, 20ml of the mixed acids was measured and added to the sample in the beaker, and the mixtures was heated for 20 minutes and allowed to cool. The heated mixture was filtered with filter paper into the volumetric flasks and make up to 50ml deionized water. Finally, the filtrate was turned into the sample bottle, the process was repeated for all the ninety samples and sent for further analysis with Atomic Emission Spectrophotometer (AES) [24].

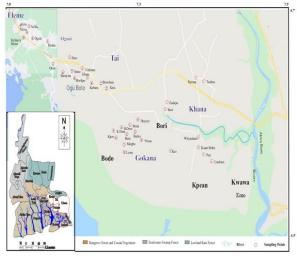
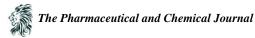


Figure 1: Map of the locations and sample area

Total Petroleum Hydrocarbon

For Total Petroleum Hydrocarbon (TPH) Gas Chromatography - Flame Ionization Detector (GC-FID) by Agilent Technologies 7890, was used. Extraction: The sample, 10g was weighed into a 120ml glass bottle for extraction, 20ml of Dichloromethane (DCM) and Acetone (1:1) mixture was added into the bottle, 50µl of surrogate (o-Terphenyl) was added and extracted with a vortex mixer for 90 minutes. The extract was transferred into a clean beaker through glass funnel with filter paper stuffed with sodium sulphate at the aperture. The sample was allowed to concentrate to 1ml in the fume hood and was sent to clean-up. Clean up procedure: The activated Silica gel was heated over night at 1300C in 50ml of Dichloromethane to make a slurry and mixed well, the slurry was poured into a 10mm diameter Chromatographic column. The column was gently tapped to settle the Silica gel and eluted with 30ml Dichloromethane, 1cm layer of anhydrous sodium sulphate was added to the top of the silica bed, the column



was pre-eluted with 60ml of Hexane and discarded prior to exposure of the sodium sulphate layer to the air, 2ml of extract exchange was transferred with Hexane onto the column, additional 19ml Hexane was made to complete the transfer for the Aliphatic TPH [25].

Benzene, Toluene, Ethyl-benzene and Xylene (BTEX)

For Benzene, Toluene, Ethyl-benzene and Xylene (BTEX), 1g of the sample was weighed into a clean extraction bottle each from the samples collected from the communities. Extraction: To 1g of sample, 10 ml of extraction solvent (Dichloromethane) was added, mixed thoroughly and allowed to settle. The mixtures were carefully filtered into clean solvent extraction bottles using filter paper fitted into Buchner funnels. The extracts were concentrated to 2 ml and then transferred to cleanup/separation section.

Clean-up procedure: Gas Chromatography–Mass Spectrometry (GC-MS) by Agilent Technologies 5975C, was used for the analysis. The column concentrated aliphatic fractions were transferred into labeled glass vials with rubber crimp caps of GC analysis. 1 ml of the concentrated sample was injected by means of hypodermic syringe through a rubber septum into the column. Separation occurs as the vapour constituent partitions between the gas and liquid phases [26].

3. Results and Discussion Potentially Toxic Elements: Chromium (Cr)

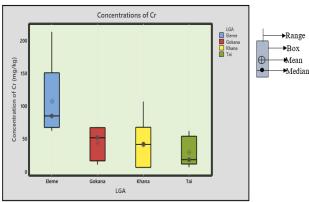


Figure 2: Indicates the average distribution of Cr concentration in the four Local Government areas

The results shows that Cr concentration in Eleme Local Government is 106.817 mg/kg \pm 0.433 mg/kg, Gokana Local Government 43.232 mg/kg \pm 0.702 mg/kg, Khana Local Government 41.583 mg/kg \pm 5.575 mg/kg and Tai Local Government 29.381 mg/kg \pm 0.552 mg/kg, Cr is lower in Tai and higher in Eleme. **Cobalt (Co)**

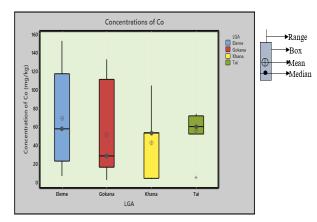


Figure 3: Shows the average distribution of Co concentration in the four Local Government Areas.



The result indicated that Eleme Local Government obtained the highest Co concentration with value 69.162 mg/kg \pm 1.567 mg/kg, Gokana Local Government 50.911 mg/kg \pm 4.973 mg/kg, Tai Local Government 55.499 mg/kg \pm 0.560 mg/kg and Khana Local Government 42.268 mg/kg \pm 0.424 mg/kg. Co was high in all locations except in Khana.

Cupper (Cu)

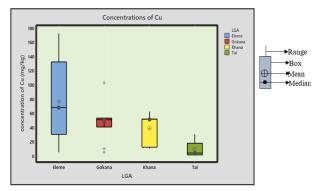


Figure 4: The concentration of Cu in the various Local Government Areas are depicted here.

The results showed that Eleme Local Government had the highest concentration value in Cu, which is 76.444 mg/kg \pm 0.65 mg/kg, Gokana Local Government 50.94 2mg/kg \pm 0.719 mg/kg, Khana Local Government 38.891 mg/kg, Tai Local Government 9.445 mg/kg \pm 4.499 mg/kg. Shows that Cupper was high in all the locations except in Tai that it indicated a lower concentration.

Lead (Pb)

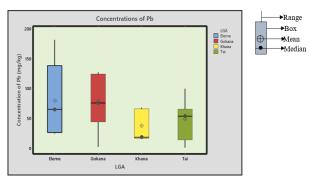


Figure 5: Indicates the average concentration of Lead in the Local Government Areas.

Eleme Local Government showed the highest concentration in Pb with value 79.497 mg/kg \pm 0.65 mg/kg, Gokana Local Government 78.403 mg/kg \pm 3.609 mg/kg, Tai Local Government 53.575mg/kg \pm 1.516mg/kg and Khana Local Government 37.685 mg/kg \pm 0.375 mg/kg.

Nickel (Ni)

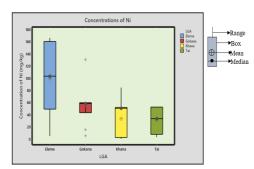


Figure 6: Shows concentration of Nickel in all the Local Government Areas investigated.



Eleme Local Government had the highest concentration value of 102.924 mg/kg \pm 7.918 mg/kg in Nikel, Gokana Local Government 58.116 mg/kg \pm 3.068 mg/kg, Tai Local Government 33.583 mg/kg \pm 0.904 mg/kg and Khana Local Government 33.257 mg/kg \pm 4.009 mg/kg.

All five metals indicated different concentrations in drain sediment samples from the thirty-five communities across the four local government areas of Ogoni, Eleme local government area indicated the highest concentration in all five metals due to industrialization and commercial activities, which suggest pollution in the study areas, while some showed low concentrations. The presence, despite the low concentrations of Ni and Pb, could still lead to serious health hazard considering their cumulative effects in human body [27]. Several acute and chronic toxic effects of heavy metals affect different body organs. Gastrointestinal and kidney dysfunction, nervous system disorders, skin lesions, vascular damage, immune system dysfunction, birth defects, and cancer are examples of the complications of heavy metals toxic effects. Simultaneous exposure to two or more metals may have cumulative effects [28].

Organic Pollutants

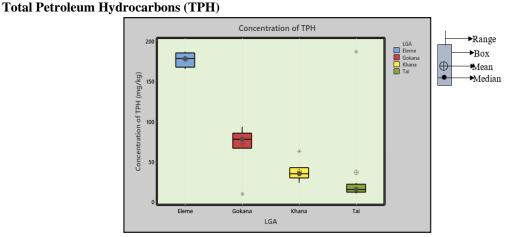


Figure 7: Indicated the Mean concentration of TPH from the study Areas.

Eleme Local Government had the highest concentration of 176.2 mg/kg \pm 7.852 mg/kg, Gokana Local Government 72.639 mg/kg \pm 8.863 mg/kg, Khana Local Government 37.968 mg/kg \pm 9.722 mg/kg and Tai Local Government 15.938 mg/kg \pm 3.934 mg/kg, This could be due to the high rate of artisanal refining of crude oil activities that takes place in Eleme and Gokana local government areas. Total petroleum hydrocarbons (TPH) is a pollutant that affect public health in urban areas.

Benzene, Toluene, Ethyl-benzene and Xylene (BTEX)

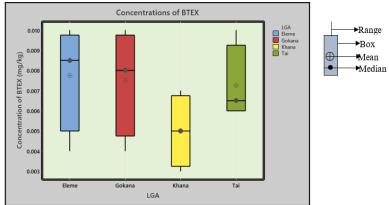


Figure 8: Indicated the concentration of BTEX in the various study areas.



which shows that Eleme Local Government had the highest BTEX concentration of $0.0077 \text{ mg/kg} \pm 0.006 \text{ mg/kg}$, Gokana Local Government $0.0074 \text{ mg/kg} \pm 0.003 \text{ mg/kg}$, Tai Local Government $0.007 \text{ mg/kg} \pm 0.004 \text{ mg/kg}$ and Khana Local Government $0.005 \text{ mg/kg} \pm 0.005 \text{ mg/kg}$. This may be due to commercial activities in these areas. Mitra and Roy [29] reported that human exposure to BTEX compounds over a long period of time results in skin and sensory irritation, adverse respiratory health effects and central nervous system irritation. In spite of the negative effects they pose to human health, BTEX compounds remain overlooked and untreated in municipal systems, thereby increasing the risk of water-related diseases through their ingestion.

4. Statistical Analysis

Correlations

Correlation matrix of BTEX, TPH, Cr, Co, Cu, Pb, Ni in drain sediment from four LGAs **Method**

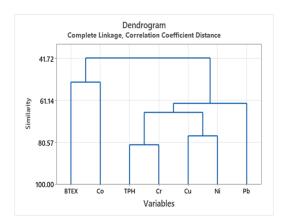
	Co	Correlation type			Pearson	
	Nu	mber of	rows use	d 35		
	BTEX	ТРН	Cr	Со	Cu	Pb
TPH	0.181					
Cr	-0.033	0.637				
Co	0.057	0.157	-0.117			
Cu	-0.026	0.543	0.338	0.292		
Pb	-0.166	0.357	0.254	-0.030	0.308	
Ni	0.010	0.583	0.409	0.075	0.555	0.475

◆ TPH correlated positively and moderately with Cr (r = 0.637), Cu (r = 0.543) and Ni (r = 0.583).

Cr, Cu and Pb correlated positively and moderately with Ni (r = 409, 555 and 475) respectively.

Note: r = Correlation Coefficient

The correlation nature of these variables shows their relationship and that they are from the same source. **Cluster Analysis: Dendrogram of Variables**

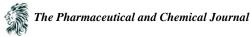


BTEX, and Co clustered into the same group with same similarity, suggesting that they originate from same source. TPH, Cr, Cu, Ni and Pb clustered in the same group with differences in their similarities

The clustered nature of these variables shows their relationship and that they originate from the same source.

Conclusion

From the investigations of this study, the five selected potentially toxic metals (Cr, Co, Cu, Pb and Ni) were present in drain sediment from the study areas at concentration above the USEPA permissive limit.



The presence of these pollutants Total Petroleum Hydrocarbon (TPH) and Benzene, Toluene, Ethyl-Benzene and Xylene (BTEX), indicates pollution in the study areas.

The Elevated concentrations of the investigated contaminants are sufficient data to trigger clean up of the drains, since they are more likely to be exposed to the local population.

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