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Seasonal Variation of Heavy Metal Concentrations in Crude Oil Polluted Water Around Major Tributaries in Ibeno, a Coastal Area, in Niger Delta. Nigeria

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Abstract Seasonal variation of heavy metal concentrations in crude oil polluted water around major tributaries in Ibeno, a coastal area, in Niger Delta. Nigeria was investigated using Atomic Absorption Spectrophotometer Unicam 939 model. The concentrations in mg L^{-1} of heavy metals in water during the dry season was in decreasing order of: Mn(2.80±0.93), V(1.53±1.42), Ni(1.50±1.53), Fe(0.86±0.25), Cd(0.27±0.21), Co(0.19±0.25), Zn(0.09±0.13), Pb(0.02±0.01), corresponding values obtained for the wet season were Mn (3.13±0.79), V(1.88±1.45), Ni(1.45±1.04), Fe(1.05± 0.25), Cd(0.10± 0.13), Zn(0.07± 0.10), Co (0.06±0.05), Pb(0.02± 0.02). All the eight heavy metals investigated were detected in all the water samples. The mean concentrations in mg L^{-1} of Ni(1.50), Cd(0.27), Co(0.19) and Zn(0.08) were higher during the dry season in comparison to corresponding mean concentration values obtained during the wet season. Conversely, mean concentrations in mg L^{-1} of V(1.88), Mn(3.13) and Fe(1.06) were higher in the wet season compared to similar dry season values. The measured concentrations were generally variable and inundating, except Pb which was consistent for both seasons. The mean concentrations of Ni, V, Cd, Pb, Fe and Mn, in the surface water samples in dry and wet seasons were higher than WHO, guidelines for heavy metal in water. The health implications of the heavy metals have been highlighted.

Keywords Contamination, Environmental pollution, bio-accumulation, concentration

1. Introduction

The presence of heavy metals in the environment is a major global concern not only to environmental scientists and engineers but also to the general public because heavy metals are not only harmful to humans and animals, but tend to bio-accumulate in the food chain, thus constituting a significant public health risk [1]. Heavy metals are generally and naturally found at very low concentrations while elevated concentrations are commonly associated with pollution from human activities. The contamination of water, sediments and aquatic biota with heavy metals is worrisome because of the toxicity, persistence and bio-accumulative nature of certain contaminants [2]. Metals which are discharged into natural waters at high concentrations in sewage, industrial effluents and or from mining operations can have severe toxicological effects on humans and aquatic ecosystems [3]. Fossil fuel combustion, agrochemical applications, metallurgical industrial activities, and industrial wastes generation over the last century have

undoubtedly intensified the emission of various heavy metals and other pollutants into the environment thereby distorting the balance of whole terrestrial, aquatic and atmospheric ecosystems. Some heavy metals like copper, manganese and zinc play important roles in the metabolic activities of organisms, while others like cadmium, arsenic and mercury have no metabolic roles and are toxic even at very low concentrations [4-5]. Unlike most organic pollutants such as organohalides, heavy metals are non-biodegradable and may only undergo relocation and species transformation across environmental compartments. Hence, the residence time of heavy metals in the environment is usually long. As a result, heavy metals have the propensity to constitute both short and long term serious health threats to humans and other organisms since they remain persistent in the environment for years.

Water quality is fundamental to the health and sustenance of aquatic ecosystems and to hydrology.

Water also plays a major role in the recycling of materials and thus can be a vector of critical importance in the spread of harmful substances and diseases [6]. The protection of water and aquatic ecosystem from adverse effects of pollutants such as heavy metals is central to environmental risk management [7]. Heavy metals contamination of rivers is one of the major quality issues in rapidly growing cities because maintenance of water quality and sanitation infra-structure do not increase along with population and urbanization growth especially in developing countries [8]. Humans are exposed to heavy metals in aquatic environments either directly from drinking water or indirectly through the food chain making heavy metals a culprit in many human disease conditions. The biotic component of the aquatic ecosystem which consists of fauna and flora are indispensable economic resources. Major components of aquatic fauna are the fin fish and shellfish (shrimps, prawns, crabs, lobsters, calms, scallops, periwinkles, oysters etc). Rural artisans who depend on fisheries as a means of livelihood concentrate on relatively shallow water bodies like rivers, creeks, lakes, lagoons, etc for their fishing expedition due to their inability to explore larger water bodies as a result of limited capital [9]. Water pollution is a remarkably peculiar environmental problem of Nigeria's Niger Delta region. In recent times, water bodies in the delta's coastal area have been subjected to various levels of pollution arising from increase in domestic wastes, industrial effluent, agricultural run-offs, accidental oil spillage**,** and unsafe fishing practices. The result is dwindled fortunes for fishers who depend on the resources in such polluted aquatic ecosystems for a living. The concentration of pollutants in water bodies around the Ibeno coastal area, which is seldom polluted by oil, has not been previously studied. Consumption of fish and shellfish caught from water bodies so polluted could pose severe health risks to consumers. Since one of such pollutants is heavy metals, monitoring the level heavy metal contaminants is important for safety assessment of environmental and particularly human health. Thus, the objective of this research was to investigate the concentrations of heavy metals in water samples around tributaries in the Ibeno coastal area.

Methodology

Study area

Ibeno Local Government Area has a coastal area of over 1,200 square kilometers. It is situated on the eastern flanks of the Niger Delta which in turn is part of the Gulf of Guinea. It is located at the south end of Akwa-Ibom State with latitude 7054' and 4034' north of the equator and longitude 7054' and 8002' east of Greenwich Meridian. Qua Iboe River estuary which lies within the study area coordinates, has Douglas Creek emptying into it. The Qua Iboe River estuary is also situated near the Exxon Mobil oil effluent treatment and discharge plant. The oily sludge from the plant is discharged into the Atlantic Ocean but may recede into the estuary due to tidal motion [10].

Sampling procedure

Experimental design method was adapted for this study. Fifteen composite water samples were collected in February 2014 and June 2015 representing dry and wet seasons respectively. The study area was divided into 15 sampling locations all of which are in close proximity to the Qua Iboe River estuary or the Atlantic Coast line, and are identified as follows : Location-1(Atabrikang), Location-2(Ntafre), Location- 3 (IkotInwang), Location-4 (Okoritip), Location-5 (Ukpenekang), Location-6 (Okpolom), Location-7 (IwoOkpom), Location-8 (Okoritip), Location-9 (Afia), Location-10 (AdahaUsuk), Location-11 (InuaEyetIkot), Location-12(ItakAfaha), Location-13

(Iwokwang), Location-14 (Okom Ita), and Location-15(Mkpanak) as shown in the map of the study area (Fig. 1).

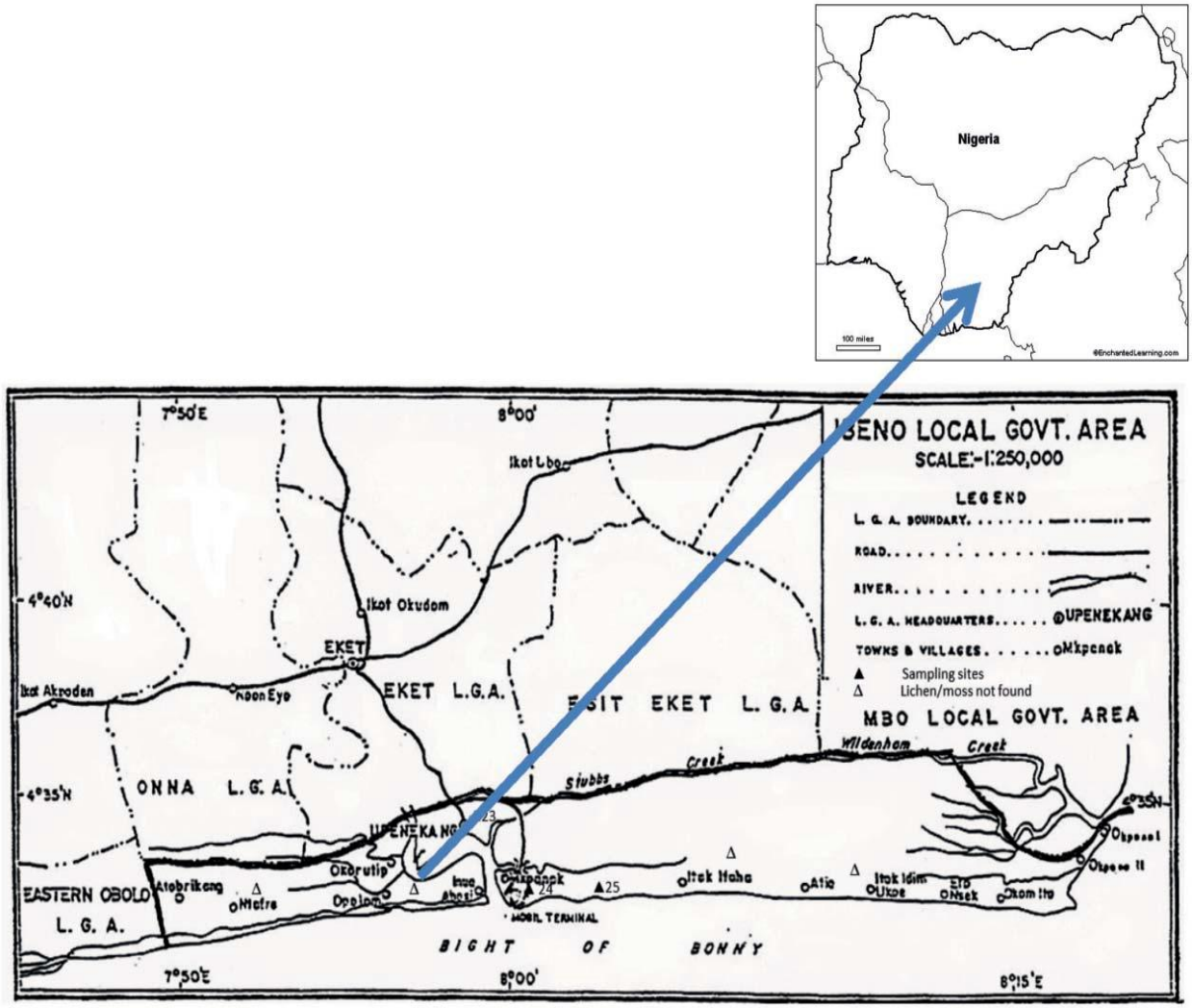

Figure 1: Map of the study area showing sampling locations

Source: *Survey and Geo-informatics Department Ministry of Lands and Housing, Akwa Ibom* State

Surface water samples were collected using clean plastic bottles. The sampling bottles were first filled with distilled water and taken to the site. At the site, the bottles were emptied and later rinsed several times with the water to be collected. Triplicate samples were collected systematically at 15 km apart in each location. The three samples were mixed to form one composite sample thus resulting in 15 samples from the study area. The sample bottles were labeled at each location, placed in a cooling unit, and taken to the laboratory for analysis.

Subsequently, each sample bottle was shaken thoroughly, and 100 mL of the sample measured into a beaker. 5 mL concentrated HNO_3 was added and the mixture was boiled slowly on a hot plate. The mixture was evaporated until a remnant of about 20 mL was left in the beaker. Another 5 mL concentrated HNO_3 was added to the mixture and the set-up was covered with watch glass and heated. Heating continued until the solution appeared clear and lighter in colour. This indicated that digestion was complete. 2 mL of concentrated HNO_3 was added again and heated slightly to dissolve any remaining residue. The watch glass was rinsed with distilled water in order to transfer condensed water droplets back into the beaker. The digest was transferred into a 50 ml volumetric flask, allowed to cool and made up to the 50 ml mark with distilled water. Blank sample was prepared in the same way but without the water sample. The concentrations of Ni, V, Cd, Pb, Co, Fe, Mn and Zn were determined using flame Atomic Absorption Spectrophotometer (Unicam solaar, model 969). A calibration

graph was plotted for each element using measured absorbance and the corresponding concentration. The calibration curve was then used to determine the concentrations of the metals [12].

Results

The amounts of the eight heavy metals (Ni, V, Cd, Pb, Mn, Fe, Co, and Zn) in the fifteen (15) surface water samples for dry and wet seasons in the study area are presented in Tables 1-3.

Table 1: *Concentrations (mg L^{-1}) of heavy metals in water during dry season*

Heavy Metal	H_{W1}	H_{W2}	H_{W3}	H_{W4}	H_{W5}	H_{W6}	H_{W7}	H_{W8}	H_{W9}	H_{W10}	H_{W11}	H_{W12}	H_{W13}	H_{W14}	H_{W15}	H_{WC}	Mean	SD	CV	%CV	Mean± SD
Ni	5.30	1.70	0.02	1.28	1.28	0.88	0.88	0.01	0.01	1.40	1.67	0.071	3.000	3.750	2.750	0.002	1.50	1.53	1.021	102.1	1.50±1.53
V	4.38	2.95	2.80	0.85	2.28	1.14	3.50	0.63	0.03	0.18	0.38	0.10	1.130	1.080	3.280	0.020	1.55	1.42	0.919	91.9	1.55±1.42
Cd	0.55	0.10	0.10	0.35	0.75	0.18	0.18	0.30	0.05	0.10	0.05	0.230	0.550	0.550	0.080	0.030	0.27	0.21	1.057	105.7	0.27±0.21
Pb	0.01	0.02	0.02	0.03	0.03	0.03	0.03	0.03	0.04	0.03	0.02	0.020	0.030	0.020	0.020	0.010	0.02	0.01	0.292	29.2	0.02±0.01
Mn	4.16	2.16	2.16	2.17	3.17	4.17	5.16	2.86	2.72	2.52	2.15	2.330	2.240	2.230	2.340	2.230	2.80	0.93	0.333	33.3	2.80±0.93
Fe	0.77	0.65	0.65	0.79	0.79	0.79	0.77	1.22	0.92	0.87	0.80	0.600	0.620	0.890	1.320	1.280	0.86	0.20	0.297	29.7	0.86±0.25
Co	0.01	0.13	0.13	0.12	1.10	0.13	0.14	0.13	0.12	0.16	0.17	0.170	0.160	0.160	0.100	0.120	0.19	0.25	1.331	133.1	0.19±0.25
Zn	0.06	0.07	0.07	0.06	0.45	0.39	0.03	0.02	0.02	0.04	0.01	0.040	0.060	0.050	0.050	0.007	0.09	0.13	1.500	150.0	0.09±0.13

HW = Heavy metals in water samples, HWC = Heavy metals in control water samples

Table 2: *Concentrations (mg L^{-1}) of heavy metals in water during wet season*

Heavy metal	H_{W1}	H_{W2}	H_{W3}	H_{W4}	H_{W5}	H_{W6}	H_{W7}	H_{W8}	H_{W9}	H_{W10}	H_{W11}	H_{W12}	H_{W13}	H_{W14}	H_{W15}	H_{Wc}	Mean	SD	CV	%CV	mean±SD
Ni	5.01	1.09	0.01	1.28	1.01	0.88	0.78	0.01	0.01	1.39	1.66	0.06	2.89	3.68	2.00	0.01	1.45	1.45	0.999	99.98	1.45±1.45
V	4.48	3.00	3.05	1.04	2.28	2.44	3.40	0.72	0.20	0.20	0.48	0.39	1.18	1.29	3.98	0.02	1.88	1.45	0.771	77.13	1.88±1.45
Cd	0.28	0.01	ND	ND	0.15	0.09	ND	0.03	0.10	0.03	0.06	0.02	0.25	0.45	0.04	ND	0.09	0.13	1.323	132.3	0.09±0.13
Pb	ND	0.02	ND	ND	0.06	0.03	0.03	0.04	0.05	0.03	0.05	0.07	0.04	0.03	0.01	0.01	0.02	0.02	0.920	92.0	0.02±0.02
Mn	4.27	2.16	3.00	2.29	3.20	4.27	4.90	2.87	2.99	2.52	2.65	2.97	2.33	3.38	3.14	0.10	3.13	0.79	0.253	25.30	3.13±0.80
Fe	1.40	1.00	1.05	0.79	0.99	0.78	0.98	1.37	1.00	0.98	1.00	0.99	0.76	1.70	1.00	0.02	1.05	0.25	0.241	24.10	1.05±0.25
Co	0.01	0.12	0.11	0.02	0.04	0.01	0.09	0.09	ND	0.16	0.06	0.04	0.06	0.08	0.04	0.01	0.06	0.05	0.740	74.0	0.06±0.05
Zn	0.03	0.05	0.07	0.03	0.33	0.29	0.06	0.07	0.01	0.02	0.01	0.02	0.05	ND	0.01	0.60	0.07	0.10	1.487	148.7	0.07±0.10

HW = Heavy metals in water samples, HWC = Heavy metals in control water samples

Table 3: Average concentrations of heavy metal for dry and wet seasons

Heavy metal	dry season	wet season	Average concentrations for dry and wet seasons	WHO standard
Ni	1.50	1.45	1.47	0.02
V	1.55	1.88	1.7	0.1
Cd	0.27	0.10	0.19	0.003
Pb	0.02	0.02	0.02	0.01
Mn	2.80	3.13	2.96	0.1-0.5
Fe	0.86	1.06	0.96	0.3
Co	0.19	0.06	0.12	0.1-0.5
Zn	0.09	0.07	0.08	3.0

Discussion

The results indicated that concentrations in mg L^{-1} of heavy metals in water for dry and wet seasons were in decreasing order of : (dry) Mn (2.80±0.93) > V (1.53±1.42) > Ni (1.50±1.53) > Fe (0.86±0.25) > Cd (0.27±0.21) > Co (0.19±0.25) > Zn (0.09±0.13) > Pb (0.02±0.01) and (wet) Mn (3.13±0.79) >V (1.88±1.45) > Ni (1.45±1.04) > Fe(1.05± 0.25) > Cd (0.10± 0.13) > Zn (0.07± 0.10) > Co (0.06±0.05) > Pb (0.02± 0.02). All the eight heavy metals investigated were detected in all the water samples of various locations in the study area. The mean concentrations in mg L^{-1} of Ni (1.50), Cd (0.27), Co (0.19) and Zn (0.08) were higher in dry season than wet compared to wet season. Conversely, mean concentration in mg L^{-1} V (1.88), Mn (3.13) and Fe (1.06) were higher in wet season compared to dry season. The measured concentrations were generally variable and inundating, except Pb which was fairly nearly consistent for both seasons. This is in agreement with the studies of Olatunde et al. (2012) [3] and Mondol et al. (2011) [11] respectively. The mean concentrations of Ni, V, Cd, Pb, Fe and Mn, in the surface water samples in dry and wet seasons were higher than WHO, and DPR guidelines for heavy metal in water. Mean concentrations of Co and Zn were within WHO and DPR guidelines for heavy metals in water Table 3. The results of this investigation are somewhat similar to those obtained by Ukpong et al. (2012) (12) who recorded Pb (3.45 mg L^{-1}), Fe (0.49 mg L^{-1}), Zn (5.00 mg L^{-1}), Ni (0.02 mg L^{-1}), Cd (0.02 mg L^{-1}, and Mn (0.07 mg L^{-1}) and Pb (3.90 mg L^{-1}), Fe (1.29 mg L^{-1}), Zn (5.20 mg L^{-1}), Ni (0.05 mg L^{-1}), Cd (0.03 mg L^{-1}), and Mn (0.26 mg L^{-1}) for wet and dry seasons respectively, in the study area 26 . Also, this results agreed with the of work of Essien et al. (2012) who documented a average concentration of Pb (2.94 mg L^{-1})

higher than WHO quality standard of Pb (0.01 mg kg^{-1}) in water samples [13]. The seemingly high concentration of Pb in water samples suggested pollution in the study area. Essien et al. (2012) also recorded high concentration of Ni, V and low concentration of Co in water samples in the study area [13]. The analytical results by Nwankwoala et al. (2011) [14], revealed that heavy metals concentrations in the groundwater sources in the area were high in majority of the locations, with iron (Fe) fluctuating between 0.06 mg L^{-1} to 43.09 mg L^{-1}, while manganese (Mn) ranged between 0.12 mg L^{-1} to 2.34 mg L^{-1} (14). Zinc (Zn) varied between 0.15 mg L^{-1} to 10.09 mg L^{-1} and nickel (Ni) concentrations fluctuated between below detectable limit (BDL) to 0.02 mg L^{-1}. Chromium (Cr) concentrations ranged between 0.01 mg L^{-1} to 0.18 mg L^{-1}, and lead (Pb) ranged between 0.21 mg L^{-1} to 0.42 mg L^{-1}. It is pertinent to note that the values obtained in this study for Ni, V, Cd, Pb and Mn which are higher than recommended WHO and DPR standards indicate pollution of the ecosystem by these heavy metals. Metals such as Cd and Pb serve no known function in any organism. Even in relatively minute quantities they can cause severe damage to fauna, flora and in humans. The elevated levels of some of the heavy metals imply that industrial and domestic activities have impacted negatively on the ecosystem of the study area.

Nickel (Ni)

The mean ± SD concentration of Ni in water samples for dry season in the study area was 1.50±1.53 mg L^{-1} while coefficient of variation (CV) was determined as 102.1 % as shown in Table 1. Also, mean ± SD concentration of 1.45±1.45 mg L^{-1} and % CV (99.99 %) Ni were recorded in water samples in the study area during wet season (Table 2). The concentration of Ni in the study locations was higher in dry season than wet season. The total average of Ni in dry and wet seasons was 1.47 mg L^{-1} greater than WHO standard of 0.2 mg L^{-1} for Ni in water (Table 3 and Figure 2), and concentration of Ni in back ground water. The highest concentrations of 5.30 mg L^{-1} Ni during dry season and 5.01 mg L^{-1} Ni during wet season were recorded in location 1 (Atabrikang). Also, the lowest concentrations of 0.008 mg L^{-1} and 0.001 mg L^{-1} for dry and wet seasons respectively were recorded in water samples of location 9 (Afia). In a similar work by Ukpong et al. (2012), 0.052 mg L^{-1} of Ni in dry season, 0.02 mg L^{-1} of Ni in rainy season with total average concentration of 0.27 mg L^{-1} Ni in water of the study were obtained [12]. Also, Essien et al. (2012) reported a high mean concentration of 7.78 mg L^{-1} in water sample [13]. In the work of Asia et al. (2007) in the study area, 0.05 mg L^{-1} Ni in the water of the study area was obtained below WHO limit [15]. Nickel and its water-soluble salts are potent skin sensitizers. Nickel ions can permeate the skin barrier and bind to carrier protein to form the allergen. Even minute quantity of Nickel or its water-soluble salt, will elicit or provoke an eczematous response. The high concentration of Nickel in the water sample, which is an important ingredient in many industrial processes, may be due to industrial and municipal wastewater and sludge discharge into the water. Moreover, Ni is one of the major metallic constituents of crude oil and could have probably been introduced into the ecosystem during petroleum activities. Humans need small amounts of nickel to produce red blood cells; however, in excessive amounts, it can become mildly toxic. Short-term exposure to Ni is not known to cause any health problem, but long-term exposure can cause weight loss, heart and liver damage and skin irritation [4]. Also, ingestion of nickel may cause hyper-glyanemia, depression of the central nervous system and kidney damage [16]. Nickel can also end up in surface water when it is a part of wastewater streams.

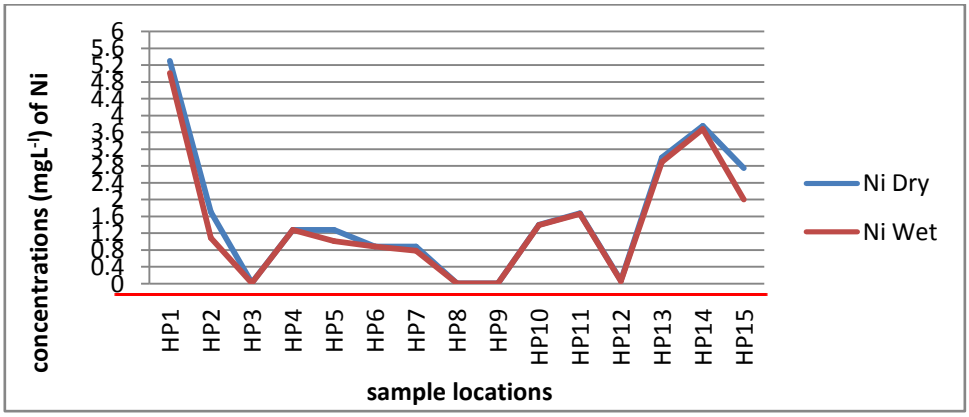

Figure 2: Seasonal variation of Ni concentration in water samples at different locations around Ibeno Coastal Area

Vanadium (V)

The concentration of vanadium in the water samples during dry season from Ibeno Coastal area was 1.55 ± 1.42 mg L^{-1} and % CV of 91.995 %. The results are presented in Table 1 and Figure 3 respectively. The total average concentration of V in dry and wet season was 1.711 mg L^{-1} greater than control water sample of 0.02 mg L^{-1} and WHO limit of 0.1 mg L^{-1}.The highest concentration of V (4.38 mg L^{-1}) in water samples was recorded in location 1 (Atabrikang) and the lowest concentration of 0.03 mg L^{-1} was recorded in location 9 (Afia). Essien et al. (2012) reported mean concentration of 1.35 mg L^{-1} of V in water of the study area [13].

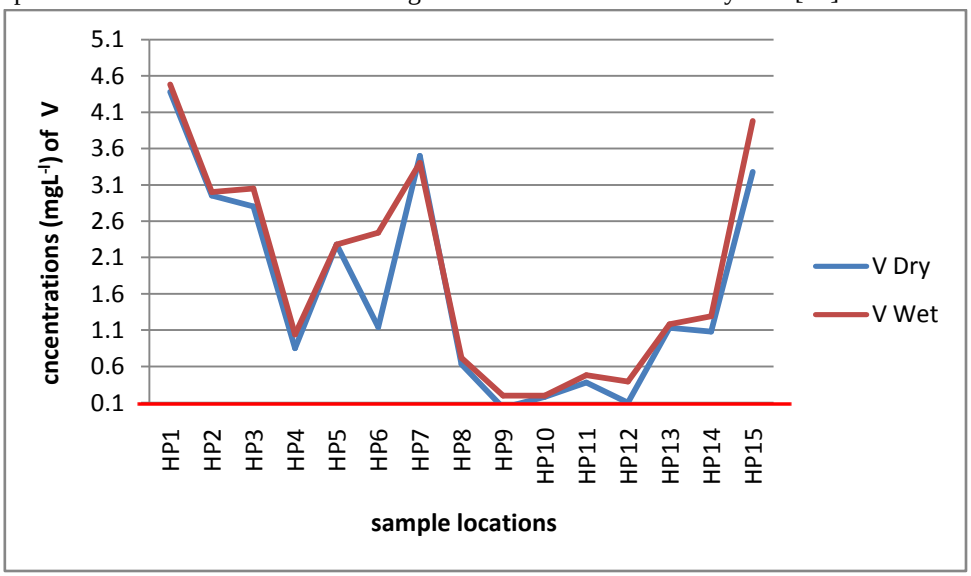

Figure 3: Seasonal variation of V concentration in water samples at different locations around Ibeno Coastal Area.

Cadmium (Cd)

The mean ± SD concentration and % CV of Cd in the surface water samples of the study area were 0.272 ± 0.207 mg L^{-1} and 105.76 % respectively for dry season (Table 1 and Figure 4). The investigation also revealed mean ± SD (0.098 ± 0.130 mg L^{-1}) and % CV (132.26 %) in the surface water samples of the study area for wet season, (Table 2).Total average concentration (0.185 mg L^{-1}) of Cd in surface water samples of the area for dry and wet seasons exceeded WHO (0.003 mg L^{-1}) maximum limit, and the normal range of Nigeria's Federal Ministry of Environment's standard for Cd in water (0.01 mg L^{-1}) (Table 3. The highest concentration of 0.55 mg L^{-1} was recorded surface water sample of location 1 (Atabrikang) during dry season. Cadmium was not recorded in locations 3, 4, 7, and control water samples. In a similar finding by Asia et al. (2007) a concentration < 0.005 mg L^{-1} was obtained in the water samples of the study area [15]. Also, Oribhabor et al. (2009) recorded (0.01-1.49) mg L^{-1} cadmium in surface water samples of the study area in dry season [16]. Minimum and maximum concentrations of heavy metals in the creek were 7.21-228.5 mg L^{-1} for Ca, (51.18 - 428.3) mg L^{-1} for Mg, (0.01- 6.78) mg L^{-1} for Fe, (0.010-0.43) mg L^{-1} for Zn, (0.01-0.61) mg L^{-1} for Pb, (0.01-0.11) mg L^{-1} for Cd, (0.01-1.49) mg L^{-1} for Cr, and (0.01-2.73) mg L^{-1} for Ni, while Hg and the total hydrocarbon content was approximately 0.01 mg L^{-1} throughout the study period. In a study by Oyekunle et al (2011) the seasonal means concentrations of Cd were 8.08±2.66 µg L^{-1} for and 15.19±8.73 µg L^{-1} for wet and dry seasons respectively [11]. The level of Cd exceeded WHO limit of Cd in water and can pose serious health problems for both the aquatic ecosystem and the humans who use the water for both domestic and agricultural purposes [1].The higher records of metals during the dry season could be attributed to low influx of fresh water and evaporation resulting in concentration of material in the creek. The intermittent high values of nickel in wet months could be due to influence of run-off from rainwater and human introduction. Heavy metals have been used as indices of pollution because of their high toxicity to human and aquatic lives.

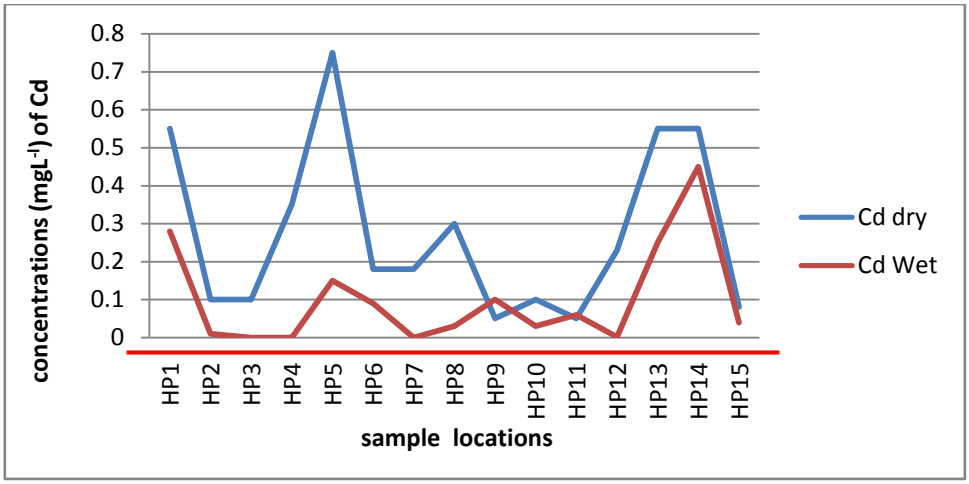

Figure 4: Seasonal variation of Cd concentration in water samples at different locations around Ibeno Coastal Area

Lead (Pb)

The level of Pb and % CV of Pb in surface water samples of the study area were 0.02 ± 0.01 mg L^{-1} and 29.26 % respectively for dry season (Table 1). Similarly, mean concentration (0.02±0.02 mg L^{1}) and % CV (91.99%) were obtained in wet season (Table 2). Total average concentration of Pb in surface water of the study area for dry and wet season was 0.02 mg L^{-1} (Table 3).The average concentration 0.02 mg L^{-1} was slightly higher than Pb concentration in control water (0.01 mg L^{-1}) and within the normal range of WHO standard of (0.01 – 0.05) mg L^{-1} of Pb in water, Figure 5 and Table 3. In related study by Ukpong et al. (2012) a mean concentration of 3.45 mg L^{-1} Pb in water samples of the study area for wet season and 3.90 mg L^{-1} Pb for dry season with total average of 3.68 mg L^{-1} [12]. Howard *et al.* (2006) recorded 0.22 mg L^{-1} Pb in the surface water samples of the study area [17]. Oribhabor and Ogbeibu reported (0.01-0.61) mg L^{-1} of Pb in surface water of the study area [16]. In a similar work by Kpee in the study area the result revealed that the average concentrations of heavy metals were in the order Pb (23.32 µg L^{-1}), Cu (17.32 µg L^{-1}), Ni (2.42 µg L^{-1}) and Cd (1.15 µg L^{-1}) respectively [18].

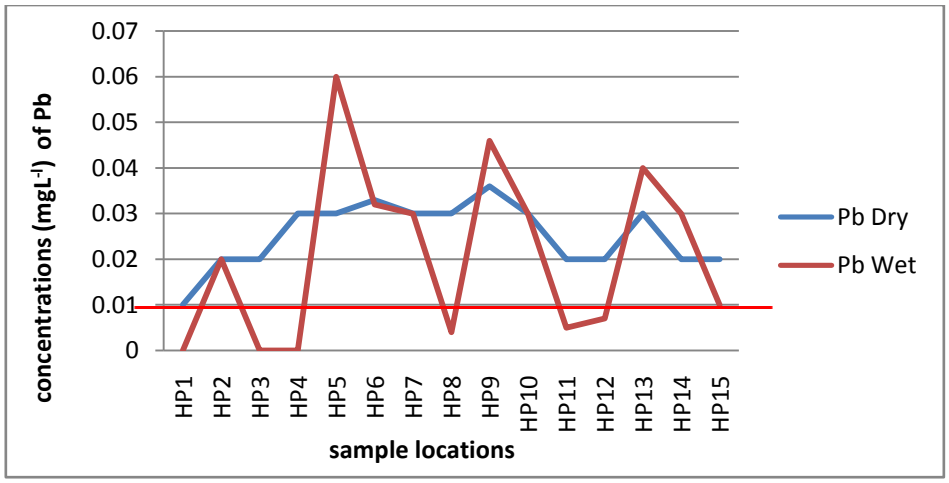

Figure 5: Seasonal variation of Pb concentration in water samples at different locations around Ibeno Coastal Area

Manganese (Mn)

The mean concentration and % CV of Mn in surface water samples of the study area were 2.80±0.93 mg L^{-1} and 33.377 % respectively for dry season (Table 1). Also, during wet season mean concentration (3.13±0.79 mg L^{-1}), and % CV (25.353 %) were recorded in the surface water samples of the study area (Table 2). The total average concentration of Mn in surface water of the study area was 2.96 mg L^{-1} (Table 3). The concentrations of Mn obtained were higher than concentration of Mn in control water (2.23 mg l^{-1}), and WHO standard for Mn

(0.1 - 0.5 mg L^{-1}) in water (Table 3 and Figure 6). The highest concentration of 5.16 mg l^{-1} Mn was recorded in location 7 (Iwo Okpom) and the lowest concentration of 2.15 mg L^{-1} recorded in location 11 (Inua Eyet Ikot). Ukpong et al. (2012) recorded a mean concentration of 0.17 mg L^{-1} of Mn in water samples of the study area, 0.07 mg L^{-1} and 0.26 mg L^{-1} in wet and dry seasons respectively (12).

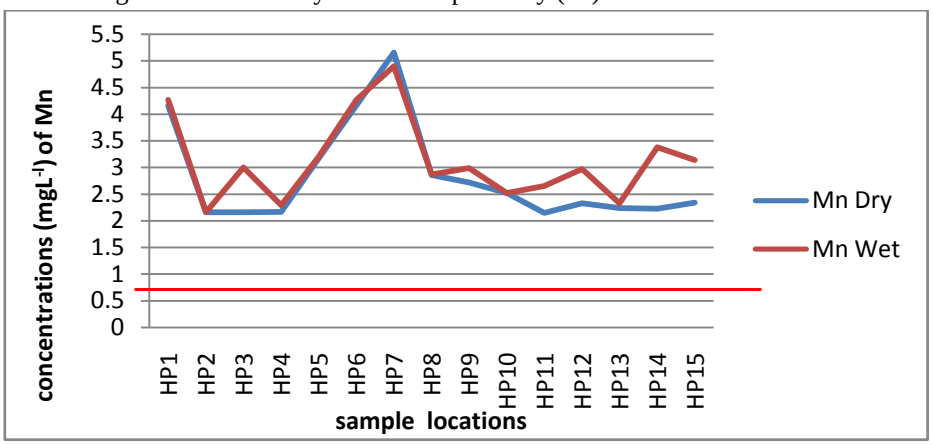

Figure 6: Seasonal variation of Mn concentration in water samples at different locations around Ibeno Coastal Area

Iron (Fe)

The mean level and % CV of iron in surface water samples of the study area were 0.86 ± 0.25 mg L^{-1} and 23.72 % for dry season (Table 1). Similarly, mean concentration (1.05 ± 0.25 mg L^{-1}) and % CV (24.07 %) of iron were recorded in the study area during wet season (Table 2). Total average concentration of Fe in surface water of the area for dry and wet seasons was 0.958 mg kg^{-1} (Table 3). Highest concentration of 1.32 mg kg^{-1} and lowest concentration of 0.62 mg L^{-1} were obtained during dry season. The mean concentration of 0.958 mg L^{-1} was lower than the concentration of Fe in control water samples and WHO standard (1.0 mg L^{-1}) for Fe in water (Table 4.1.0 and Figure 4.2.3) (12). Ukpong et al. (2012) recorded a mean concentration of 0.68 mg L^{-1} in dry season and 0.48 mg L^{-1} with a total mean concentration of 2.39 mg L^{-1} in the study area. Also, Essien et al. (2012) reported a mean concentration of 6.35 mg L^{-1} iron in the study area (13). Nwakwoala et al. (2011), obtained concentrations that ranged between (0.06 and 43.09) mg L^{-1} Fe (14). Oribhabor and Ogbeibu (2009) reported concentration of Fe that varied between (0.010 and 0.43) mg L^{-1} (16).

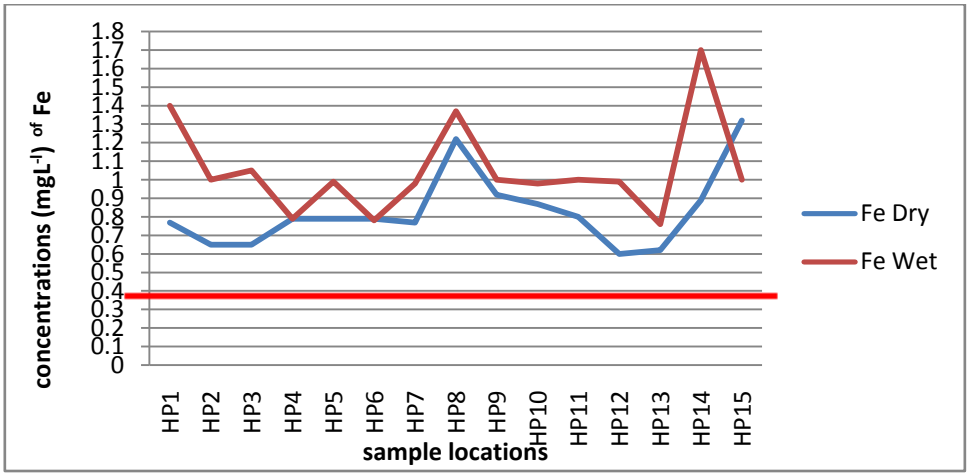

Figure 7: Seasonal variation of Fe concentrations in water samples at different locations around Ibeno Coastal Area

Zinc (Zn)

The mean concentration and % CV of Zn in surface water samples of the study area were 0.09±0.13 mg L^{-1} and 150.06 % respectively in dry season (Table 1). Also, mean concentration (0.07 ± 0.10 mg L^{-1}) and % CV (148.73 %) of Zn in water samples were recorded during wet season in the study area (Table 2). The total average of 0.079 mg L^{-1} of Zn was obtained for dry and wet seasons respectively, in the study area (Table 3).

The highest concentration of 0.45 mg l^{-1} was recorded in location 5 (Ukpenekang) and the lowest concentration of 0.01 mg L^{-1} was recorded in location 11 (Enua Eyet Ikot). The average concentration (0.08 mg L^{-1}) of Zn was higher when compared with the concentration of Zn in control water sample (0.007 mg L^{-1}) and lower than WHO and DPR standards of(3.0 mg L^{-1}) and (1.50 mg L^{-1}) respectively for Zn in water (Table 3 and Figure 8). Ukpong et al. (2012), reported mean concentrations 5.00 mg L^{-1} and 5.20 mg L^{-1} for wet and dry seasons respectively, with an average value of 5.13 mg L^{-1} of zinc in surface water samples in the study area (12). In a finding by Nwankwoala et al. (2011), mean concentrations of Zn in water samples of the study area ranged between 0.15 mg L^{-1} and 10.09 mg L^{-1} (14). Water pollution by zinc may be due to the presence of large quantities of Zn in wastewater of industrial plants. Also, from incessant deposition of Zn-polluted sludge into water bodies. Zinc can increase the acidity of waters. Some fishes can accumulate Zn in their bodies, when they live in Zn contaminated waterways. When Zn enters the bodies of these fishes, it becomes biomagnified in the food chain. Water-soluble zinc that is located in soils can contaminate ground water.

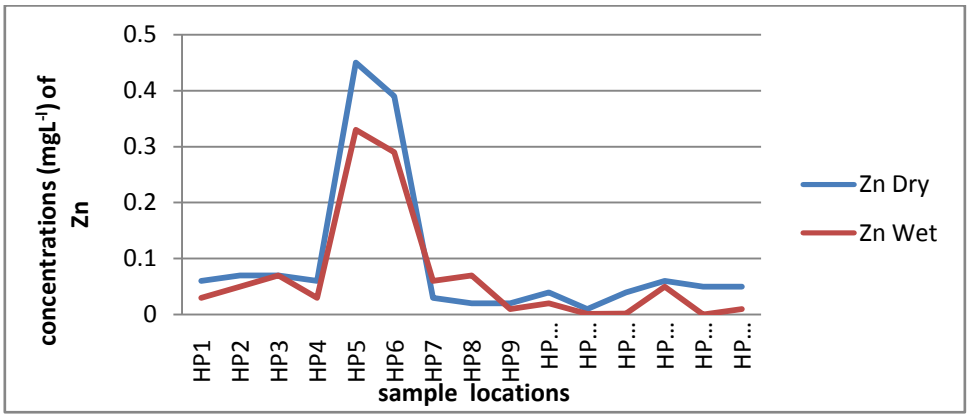

Figure 8: Seasonal variation of Zn concentration in water samples at different locations around Ibeno Coastal Area

Cobalt (Co)

The investigation also recorded a mean concentration (0.1903 ± 0.066 mg L^{-1}) and % CV (53.148 %) of Co in surface water samples of the study area for dry season (Table 1). During wet season, mean concentration of (0.061 ± 0.0458 mg L^{-1}) and % CV (74.023 %) of Co were recorded in water samples of the study area (Table 2). Total average concentration of Co for dry and wet season was 0.126 mg L^{-1} (Table 3). The water of the study area was not polluted by Co as indicated in the report of the research. Oyekunle et al 2011, recorded no significant difference between the wet season and dry season levels of Co in the river water indicating little or no anthropogenic influence [1].

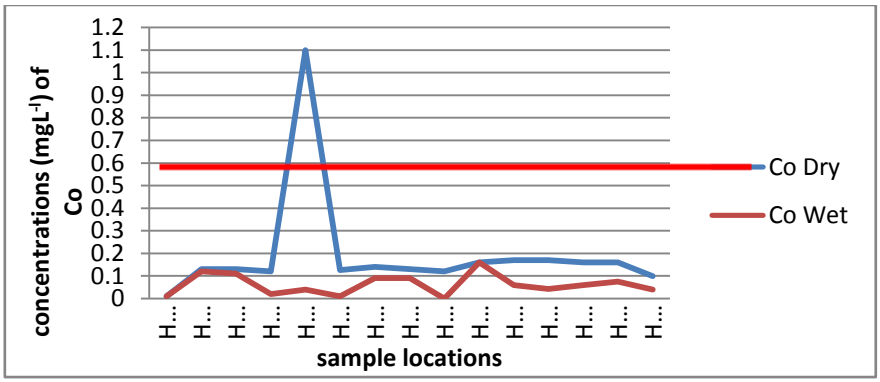

Figure 9: *Seasonal variation of Co concentration in water samples at different locations around Ibeno Coastal Area*

Conclusion

It could be concluded that - the mean concentrations in mg L^{-1} of Ni, Cd, Co and Zn were higher in dry season when compared to wet season.

- mean concentration in mg L^{-1} V(1.88), Mn(3.13) and Fe(1.06) were higher in wet season compared to dry season. The measured concentrations were generally variable and inundating, except Pb which was consistent for both seasons.
- the mean concentrations of Ni, V, Cd, Pb, Fe and Mn, in the surface water samples in dry and wet seasons were higher than WHO, and DPR guidelines for heavy metal in water.
- mean concentrations of Co and Zn were within WHO and DPR guidelines for heavy metals in water

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