Dry And Wet Seasons' Dynamics In Concentrations Of Ni, V, Cd, Pb, Mn, Fe, Co And Zn In Soil Samples Within Farm Lands In Ibeno Coastal Area, Akwa Ibom State, Niger Delta, Nigeria.

Nwadinigwe, Chukwuemeka A., Udo, Godwin J., Nwadinigwe, Alfreda O., Ubuo, Emmanuel E.

Abstract: Increase in demand for crude oil, petrochemicals and natural gas have resulted in exploration for more oil wells in Niger Delta Region of Nigeria with consequent pollution of the environment. The terrestrial ecosystem and shorelines in the oil producing communities are under continuous cultivation. Environmental pollution by the industrial and domestic activities may therefore have far reaching implication on the agricultural productivity of the area and multiplier effect on the socio-economic wellbeing of people. It is on this background that this investigation "Dry and wet season's dynamics in concentrations of Ni, V, Cd, Pb, Mn, Fe, Co and Zn in soil samples within farmlands in Ibeno Coastal Area, were investigated using atomic absorption spectrophotometer Unicam 939 model was carried out. The rank profile of mean concentrations of the heavy metals in mg kg^{-1} in the soil samples during dry and wet seasons was : Fe (12.09±4.98) > Mn (9.66 ± 2.18) > Zn (0.50±0.26) > Co (0.27±0.27) > Pb (0.26±0.39) > Ni (0.05±0.03) > V (0.04±0.01) > Cd (0.04±0.02) and Fe (12.09±4.98) > Mn (9.66 ± 2.18) > Zn (0.50±0.26) > Co (0.27±0.27) > Pb (0.26±0.39) > Ni (0.05±0.03) > V (0.04±0.01) > Cd (0.04±0.02) respectively. The concentrations of iron ranked the highest in both seasons. The amounts of the heavy metals in soil samples were higher in dry season than wet season. The pollution consequences of investigated heavy metals as well as their attendant health hazards on humans, livestock and economic crops have been discussed based on the results obtained, international standards, controls and available related literatures. All the metals investigated showed a significant increase in concentrations when compared to control samples but within maximum permissible range as recommended by World Health Organization (WHO) and Department of Petroleum resources (DPR) limits. This implies that the level of pollution of the soil of the studied area as regard the investigated heavy metals is insignificant. Hence, domestic animals, plants and human being are not at risk of contamination.

Key words: heavy metals; pollution; soil; variation; environment.

1 INTRODUCTION

Metal pollutants have been a part of human history since the dawn of civilization. However, toxic metals pollution of the biosphere has intensified rapidly since the onset of the industrial revolution, posing major environmental and health problems [1]. Recently, environmental scientists have raised concern on the increasing ecological and toxicological problems arising from pollution of the environment [2].

- *Prof. Nwadinigwe, Chukwuemeka A. Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka, Nigeria.*
- *Udo, Godwin J. Department of Pure and Industrial Chemistry University of Nigeria, Nsukka, Nigeria., email acmejames@yahoo.com Phone: +2348083661932*
- *Dr. Nwadinigwe, Alfreda O. Department of Plant Science and Biotechnology, University of Nigeria, Nsukka, Nigeria.*
- *Ubuo, Emmanuel E. Department of Chemistry, University of Hull, England.*

Heavy metals occur naturally in small quantities in soil though rarely at toxic level, but human activities have raised these to exceptionally high levels at many polluted land and water sites [3]. The extent of soil pollution by heavy metals and base metal ions, some of which are soil micronutrients is very alarming. Industrial wastes are the major sources of soil pollution and originate from mining industries, chemical industry, metal processing and petroleum industries [4]. Nigeria as a major producer and exporter of crude petroleum oil continue to experience oil spill and this exposes the environment to hazards and its effects on agricultural lands as well as on plant growth [5]. Oil pollution of soil leads to the buildup of essential (organic carbon, P, Ca, Cu) and non-essential (Mn, Pb, Zn, Fe, Co, Cu) elements in soil and the eventual translocation in plant tissues [6]. The main causes of soil pollution in Nigeria include discharge from sludge, production test, drilling mud, and spills from pipelines, well blow-outs, gas flaring and sabotage [7]. Oil spills are known to have long effects on soil, an immediate effect of petroleum products in the soil is a depression in population of soil micro-organisms.Besides the economic and aesthetic damages caused by oil spills, plants and animals life in both aquatic and terrestrial environment are affected as most life forms die rapidly following spillage. Some distinctive species of medicinal, ornamental plants, vegetables and animals in Niger Delta are now extinct due to pollution [8]. Contamination of the ecosystem by toxic metals during man's activities poses serious concern because heavy metals are not biodegradable and are persistent in the ecosystem. Once metals are introduced and contaminate the environment they will remain for a very long time. Metals do not degrade

easily like carbon-based organic moleculesIn recent, there is increase in industrial activities in the study area as a result of discoveries of new oil wells with consequent oil spillage and increase in effluent discharge. The situation is increasingly becoming a concern to the people of the area as oil companies are expanding and waste treatment facilities are either inadequate or not available. Seemingly, most of the terrestrial ecosystem and shorelines in the oil producing communities are under continuous cultivation. Environmental pollution by the industrial and domestic activities may therefore have far reaching implication on the agricultural productivity of the area and multiplier effect on the socio-economic wellbeing of people. Therefore, there is need for regular, comprehensive and a more extensive work on the level of heavy metals in the soil of the study area to protect the public health from the hazard of toxic metals pollution. It is on this basis that this research work was designed to investigate the variation in concentrations of heavy metals in soil samples within farmlands in the study area during wet and dry seasons.

2. Materials and methods

2.1 The study area:

Ibeno Local Government Area has a coastal area of over 1,200 square kilometers. It is situated on the eastern flanks of Niger Delta which in turn is part of gulf of Guinea. It is located at the south end of Akwa Ibom State with latitude $7^{o}54$ and $4^{o}34$ North of equator and longitude $7^{o}54'$ and $8^{o}02'$ east of Greenwich Meridian.The communities on the west bank of Qua Iboe River do not have access to the hinterland except by boat through the river and creeks. Qua Iboe River estuary which lies within the study area coordinates, has Douglas Creek emptying into it. This creek is about 900 m long and 8 m deep. It is the point where petroleum exploration and production (E and P) waste from the Exxon Mobil Qua Iboe Terminal (QIT) tank farm are transferred to the lower Qua Iboe River Estuary and adjourning creeks through two 24 cm diameter pipes. The Exxon Mobil oily sludge dumpsite is located adjacent to this creek and the flare stack, where gas is flared continuously is also situated. Some communities in Ibeno Local Government Area are located at the bank of Qua Iboe River while others are located on the Atlantic Littoral, Mkpanak, Ukpenekang, Iwu-achang, are located on the east bank of Qua Iboe River, Okoritip and Ikot Inwang are located on the west bank while Iwokpom-Opolom, Itak Abasi, Akete, Okoritak are located on the Atlantic Coast line. Qua Iboe River estuary situates in close proximity to the Exxon Mobil oil effluent treatment and discharge plant. The wastes are discharged into the Atlantic Ocean but may recede into the estuary due to tidal motion [9-10].

2.2 Sample collection

The study area was divided into 15 sampling locations, identified as : 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). Samples from 5 points of each location were mixed together to form a composite sample representation of that location. A total of 15 composite samples were collected and analyzed for heavy metals concentrations.

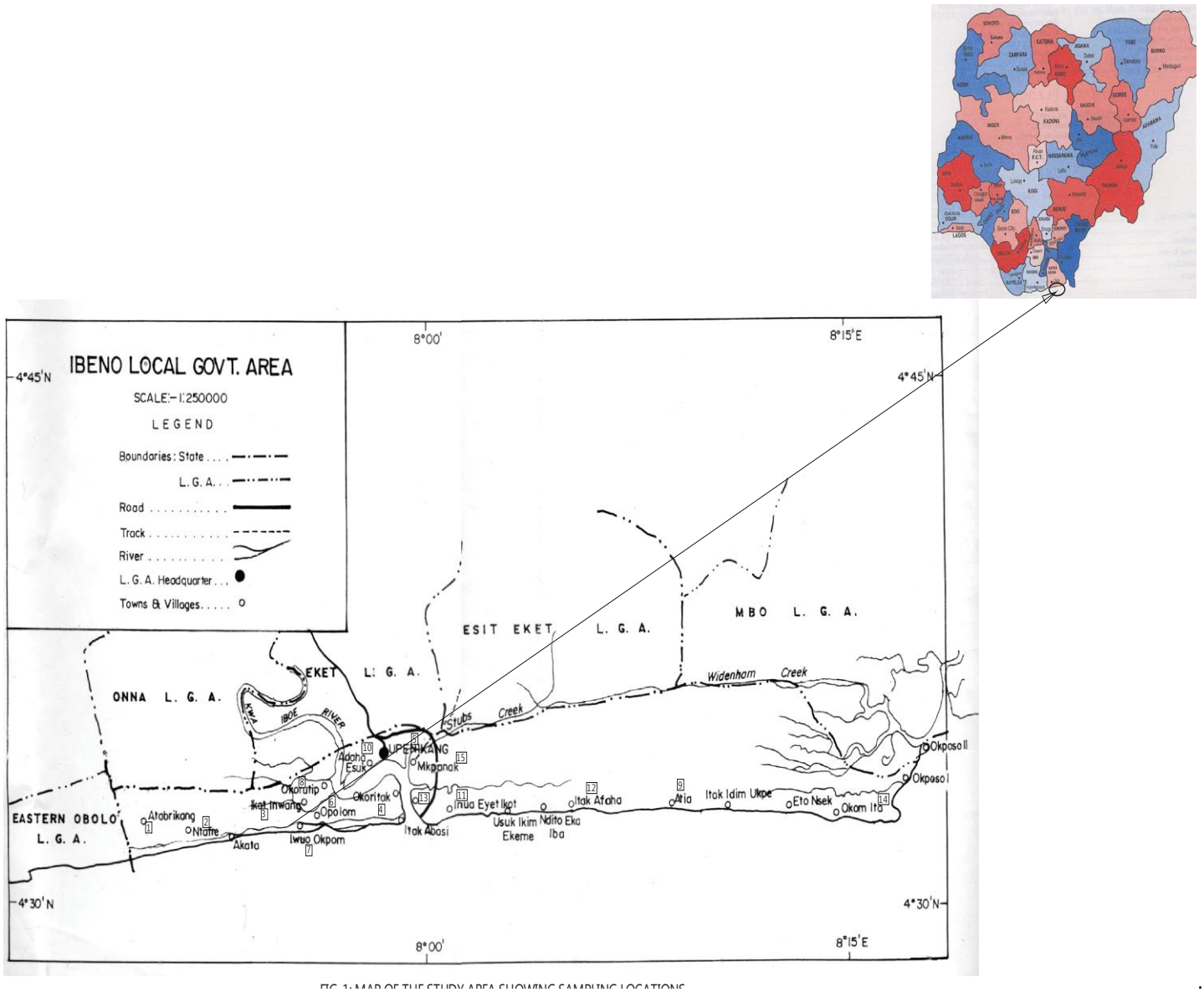


FIG. 1: MAP OF THE STUDY AREA SHOWING SAMPLING LOCATIONS

At each sampling collection point all material and organic detritus were removed from the surface of the soil, the soil sampler (auger) was used to gather the soil sample to a depth of 15 cm. The soil samples were put in clean polyethene bags, labeled appropriately and taken to laboratory for pre-treatment and analysis. Sampling took place on the 11th November 2012 for dry season and 23rd July 2013 for wet season respectively.

Sample treatment and analysis

The soil samples were air dried at 32 ^{0}C and mechanically ground using mortar and pestle, sieved to pass through a 2-mm mesh size. The soil samples (1.0 g) were weighed into Kjeldahl flasks. Aqua regia (15 ml) was added, swirled to wet the samples and kept overnight. The flasks were heated on a hot plate to 50 ^{o}C for 30 mins; temperature was later adjusted to120 ^{o}C and heated continuously for 2 hours. The samples were cooled, and 0.2 M HNO_3 (10 ml) added to the mixtures. The resulting mixtures were filtered through a Whatman (no. 541) filter paper. The flasks and filter papers were washed with small aliquots of 0.2 M HNO_3. Filtrates were transferred into 50 ml standard flasks and made up to the mark with 0.2 M HNO_3. A blank sample was prepared using the same methods but excluding the sample. The concentrations of Ni, V, Cd, Pb, Co, Fe, Mn and Zn were determined using flame Atomic Absorption Spectrophotometer Unicam 939 model according to Radojevic (1999).

3. Results and discursion

The mean concentrations, coefficient of variance (CV), % coefficient of variance (% CV), total average for dry and wet seasons and standard deviation of the eight heavy metals (Ni, V, Cd, Pb, Mn, Fe, Co and Zn), in the in soil samples within farm lands in Ibeno Coastal Area are presented in (Tables 1 - 3) for dry and wet seasons respectively.

Table 1: Concentrations (mg kg^{-1}), of heavy metals in soil during dry season.

Heavy Metal	HS_1	HS_2	HS_3	HS_4	HS_5	HS_6	HS_7	HS_8	HS_9	HS_{10}	HS_{11}	HS_{12}	HS_{13}	HS_{14}	HS_{15}	HS_C	CV	%CV	Mean ± SD
Ni	0.99	0.07	0.07	0.093	0.07	0.02	0.02	0.01	0.03	0.04	0.001	0.001	0.003	0.004	0.002	0.00	2.633	263.3	0.10±0.25
V	0.10	0.08	0.08	0.093	0.02	0.03	0.03	0.01	0.06	0.05	0.04	0.22	0.21	0.43	1.13	ND	1.666	166.6	0.17±1.12
Cd	0.03	0.35	0.20	0.023	0.03	0.05	0.10	1.15	ND	0.23	0.02	ND	0.18	0.23	ND	ND	1.445	144.5	0.22±0.31
Pb	0.05	0.02	0.02	0.017	0.03	0.01	0.07	0.03	0.03	0.04	0.03	0.03	0.02	0.03	0.02	0.02	0.482	48.2	0.03±0.01
Mn	10.02	12.09	6.46	6.00	10.10	8.90	8.40	10.00	8.09	6.89	10.01	13.92	13.18	14.42	17.02	6.02	0.307	30.7	10.37±3.18
Fe	9.16	9.91	7.96	6.758	11.98	11.72	13.01	14.92	15.97	16.77	17.98	20.01	25.01	26.20	16.96	1.00	0.390	39.0	15.15±5.91
Co	0.08	0.09	0.07	0.075	0.08	0.07	0.07	0.09	0.10	0.10	0.15	0.22	0.24	0.22	0.22	0.02	0.531	53.1	0.12±0.07
Zn	0.10	0.07	0.07	0.093	0.07	0.09	0.10	0.04	0.04	0.04	0.04	0.04	0.04	0.10	0.08	0.03	0.396	39.6	0.07±0.03

HS = heavy metals in soil samples, HSC = heavy metal in control soil sample, ND= Not detected

Table 2: Concentrations (mg kg^{-1}), of heavy metals in soil during wet season

Heavy metal	HS_1	HS_2	HS_3	HS_4	HS_5	HS_6	HS_7	HS_8	HS_9	HS_{10}	HS_{11}	HS_{12}	HS_{13}	HS_{14}	HS_{15}	HS_C	CV	%CV	Mean± SD
Ni	0.10	0.17	0.08	0.21	0.02	0.09	0.01	0.12	0.05	0.002	ND	0.001	0.002	0.007	0.002	0.003	1.18	118.40	0.058± 0.68
V	0.03	0.10	0.06	0.003	0.01	0.05	0.004	0.01	0.06	0.01	0.10	0.06	0.06	0.01	0.004	0.002	0.92	92.03	0.038± 0.04
Cd	0.01	0.003	0.02	0.07	0.01	0.01	0.001	ND	ND	0.02	0.17	0.02	0.02	0.02	0.01	0.01	1.81	181.1	0.024± 0.04
Pb	0.01	0.19	0.08	0.77	0.10	0.11	0.67	0.01	0.05	0.99	0.56	ND	0.21	0.12	0.09	0.10	1.21	120.8	0.264± 0.39
Mn	10.10	11.00	10.10	7.50	8.30	9.70	4.50	12.00	6.50	10.11	11.6	9.40	10.00	12.10	12.00	2.00	0.23	22.58	9.661± 2.18
Fe	9.00	9.10	5.05	6.01	10.50	7.00	6.99	12.90	13.00	14.04	14.1	15.77	19.99	20.90	17.00	3.50	0.41	41.14	12.09± 4.99
Co	0.05	0.88	0.60	0.07	0.03	0.60	0.55	0.01	0.09	0.20	0.10	0.19	0.22	0.11	0.31	O.30	0.99	99.06	0.268± 0.27
Zn	0.08	0.66	0.70	0.78	0.58	0.78	0.89	0.29	0.30	0.30	0.29	0.28	0.30	0.39	0.89	0.6o	0.52	52.72	0.501± 0.26

HS = heavy metals in soil samples, HSC = heavy metal in control soil sample, ND= Not detected

Table 3: Average concentrations (mg kg^{-1}) of heavy metals soil during wet and dry seasons.

Heavy metals	dry season	wet season	Average concentrations for dry and wet seasons	DPR standards
Ni	0.095	0.058	0.077	100
V	0.172	0.038	0.105	50-100
Cd	0.216	0.024	0.120	0.1-2
Pb	0.029	0.264	0.147	2-200
Mn	10.366	9.661	10.014	20-1000
Fe	15.154	12.093	13.624	25 -1000
Co	0.124	0.268	0.196	0.5 - 6.5
Zn	0.066	0.501	0.066	1 - 9.0

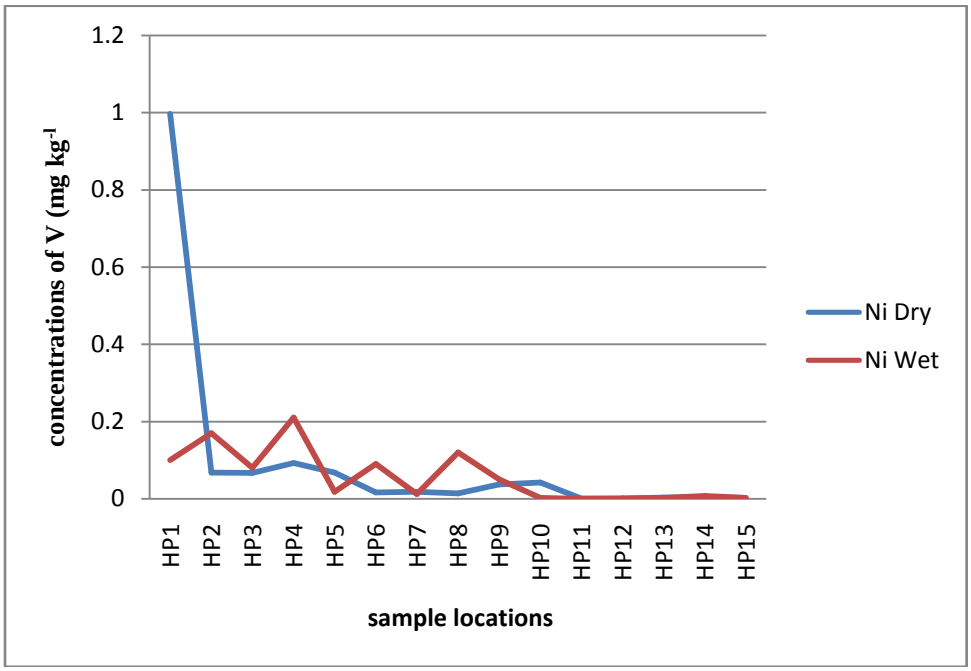
DPR standards source: Environmental Laws governing Petroleum and Other Related Operations in Nigeria Offshore from Mobilisation to Decommissioning of such Operations (including Seismic and Fishing Activities) in the areas of Waste and Hazardous Materials Toxic Chemicals including Carriage and Disposal. 2010. The order in mean concentrations of the heavy metals in mg kg^{-1} in the soil samples for dry season and wet seasons was in descending order Fe (12.09±4.98) > Mn (9.66 ± 2.18) > Zn (0.50±0.26) > Co (0.27±0.27) > Pb (0.26±0.39) > Ni (0.05±0.03) > V (0.04±0.01) > Cd (0.04±0.02) and Fe (12.09±4.98) > Mn (9.66 ± 2.18) > Zn (0.50±0.26) > Co

(0.27±0.27) > Pb (0.26±0.39) > Ni (0.05±0.03) > V (0.04±0.01) > Cd (0.04±0.02) (Tables 1-3). All the heavy metals investigated showed significant increase in concentrations when compared to control soil samples. The amounts of the investigated heavy metals were within WHO and DPR limits. All the heavy metals investigated in the soil samples were detected in all the sample locations. Soil samples collected during the wet season recorded lower concentrations of heavy metals in the study area except Co. The higher concentrations of the heavy metals during dry season could be attributed to low influx of fresh water and higher evaporation rate with consequent concentration of material in the area. The seasonal variations in the concentrations of the heavy metals could also be attributed to differences in individual metal solubility, pH, leaching by acidic rain during the wet season and topography of the area Iwegbue (2007) [12]. The amounts of iron ranked the highest compared to other metals and higher in both seasons. The high Fe content compared with other metals in this study is expected, because iron occurs at high levels in Nigerian soil Adefemi (2006) [13]. Similarly, the results of chemical analysis by Myung (2008) [14] indicated that the heavy metals in soils decreased with distance from the source, controlled mainly by water movement and topography. This agreed with the work of Iwegbue et al. (2006) [12] and Udosen et al. (2012)[3] who reported a trend in concentrations of Fe (396.35 ± 261.71 mg kg^{-1}) > Zn (30.49 ± 2.18 mg kg^{-1}) > Pb (21.16 ± 20.10 mg kg^{-1}) > Ni (8.78 ± 5.20 mg kg^{-1}) > V (8.41 ± 4.49 mg kg^{-1}) > Cd (1.12 ± 1.27 m kg^{-1}) in soil samples of the study area. The experimental data indicated that the mean concentrations of the heavy metals in soil samples were relatively lower than the critical levels except for Fe which far exceeded the optimal range and critical values for toxicity (> 300 - 500 mg kg^{-1}). Also, Ideriah et al. (2013) [15] revealed that the dry season concentrations of the various forms of the heavy metals except Cr were higher than the rainy season concentrations. The enhanced concentrations of the heavy metals raised concern because of long term exposure since heavy metals are bio-accumulative.

3.1 Seasonal dynamics of the individual element.

3.2. Nickel (Ni)

The results revealed mean concentrations of 0.095 mg kg^{-1} and 0.056 mg kg^{-1} of Ni in soil samples of the study area for dry and wet seasons respectively Tables 1-2. Total average concentration of Ni in the soil of the study area for dry and wet seasons was 0.0765 mg kg^{-1} (Table 3), quite insignificant when compared with DPR standard of 140.0 mg kg^{-1} (Table 3). The highest concentration of 0.997 mg kg^{-1} of Ni was recorded in location 1 (Atabrikang) during dry season Table 1. The mean concentration of Ni was higher in dry season than wet season .Comparison of this data highlighted the relatively high concentration of Ni load in dry than wet season (Fig. 1). Similar variations were observed at the control sites. These observations could be attributed to the cleansing effect of rainfall during the rainy season and the accumulation of heavy metals due to human activities. The mean concentration of Ni in soil was also within the limit guidelines for heavy metals in soil according to Alloway (1999) [16]. In a research by Asia et al. (2007) [17], Ni concentration vary from (1.60 – 13.80) mg kg^{-1} .Though Ni is a micronutrient, excessive level of the metal in soil might be toxic to some soil fauna, like earthworms, which are adjacent to micro flora in organic matter decomposition and may also reduce heterotrophic activities of the micro flora. Ni can cause various kinds of cancer on different sites within the bodies of animals, mainly of those that live near refineries Raymond (2012) [19].



HP1to HP15=sample locations

Fig. 2: *Seasonal Variations of Ni in soil*

3.3. Vanadium (V)

The mean concentrations of V in the soil samples were 0.172 mg kg^{-1} and 0.0379 mg kg^{-1} for dry and wet seasons respectively Tables 1-2. The concentrations of V were higher in the dry season than wet season [Fig.3]. The total average concentration of V for dry and wet season was 0.105 mg kg^{-1} [3].The concentration of V in soil samples were within limit guidelines for heavy metals in soil according to Alloway (1999)[16] Figure 2. Vanadium was not detected in control soil samples. The highest concentration of V (1.13 mg kg^{-1}) was recorded in location 15 (Mkpanak) and the least concentration of 0.014 mg kg^{-1} was recorded in location 8 (Okoritip).The concentration was high compared with background soil and low compared to guidelines for concentration of heavy metals in soil (3 – 500) mg kg^{1} Vanadium is widely dispersed in the environment in several ways including the leaching of rocks, the combustion of coal or petroleum products, and the contamination from the use of fertilizer and residual slag from steel industry. In spite of the low concentration of V in the soil of the study area, effort should be intensified toward reducing the amount of vanadium introduced into this environment since it is not completely absent as compared to the background soil samples.

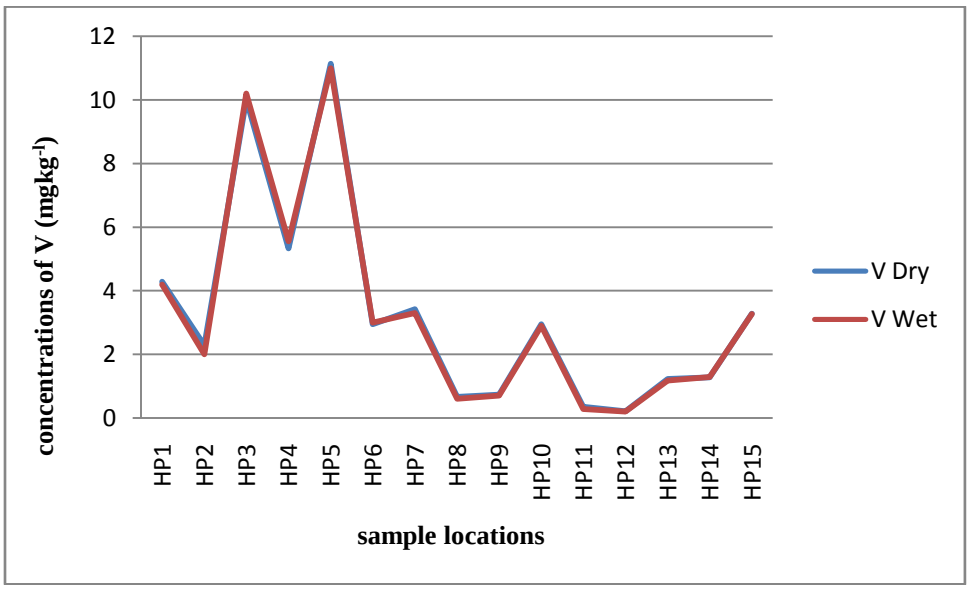


Fig. 3: *Dry Seasonal Variations of V in soil*

3.4. Cadmium (Cd)

Also, the mean concentration of 0.216 ± 0.33 mg kg^{-1} and % CV of 144 % of Cd were obtained in soil samples of the study area for dry season (Table 1 and Fig. 4). Similarly, concentration of 0.024 ± 0.044 mg kg^{-1} and % CV of 181.14 % were recorded in wet season (Table 2 and Fig. 4). The total average concentration of Cd in soil of the study area for dry and wet seasons was 0.120 mg kg^{-1}. Cd was not detected in the control soil samples. The highest concentration of 1.15 mg kg^{-1} was detected at location 8 (Okoritip) and lowest of 0.004 mg kg^{-1} was detected at location 1 (Atabrikang). Cadmium was not detected in soil of locations 9, 12 and 15. The mean concentration in dry season was higher compared to wet season (Fig. 4). Ideriah et al. [15] recorded % CV of 31.5 % and 13.6% Cd in dry and wet seasons respectively. Myung (2010)[14] obtained 0.200 mg kg^{-1} of Cd. Udosen and Awak-ama (2005) [2] reported a mean concentration of 0.05 mg kg^{-1} Cd in the soil samples of the study area and Osuji et al. (2001)[4] reported < 0.2 mg kg^{-1} Cd in the soil of the study area. Similar findings were also made by Onwerenmadu et al. (2007) [19] on "assessment of Cd concentration of crude oil polluted arable soil" a mean concentrations of 0.76 mg kg^{-1} of Cd in soil was obtained. Though the average concentration of 0.120 mg kg^{-1} Cd was within (0.01-2.0 mg kg^{-1}) guidelines for heavy metals in soil according to Alloway (1999)[16], WHO and DPR. There is need to check its increase to avoid accumulation by the biotas and subsequent assimilation by human and animals as Cd is not need at any concentration in human and animals. Cd concentrations of 1.15 mg kg^{-1} recorded at location 8 (Okoritip) may constitute a serious agronomic and environmental hazard in the study area. When compared to typical neutral levels of Cd in soil, the mean concentration of 0.120 mg kg^{-1} and highest concentration of 1.15mg kg^{-1} in Okoritip location 8 where high and exceeded the lower limit of 0.1mg kg^{-1} for heavy metal in soil. There is need to prevent this trend since there is a high tendency of heavy metals to accumulate in the environment. Cd is a highly toxic to most organisms, having toxicity 2 – 20 times higher than many other heavy metals. Cd content in soil can be available for plant uptake and subsequent human uptake, thus Cd is readily available for uptake in a range of crops. There is a clear association between Cadmium concentration in soil and the plant grown on that soil.

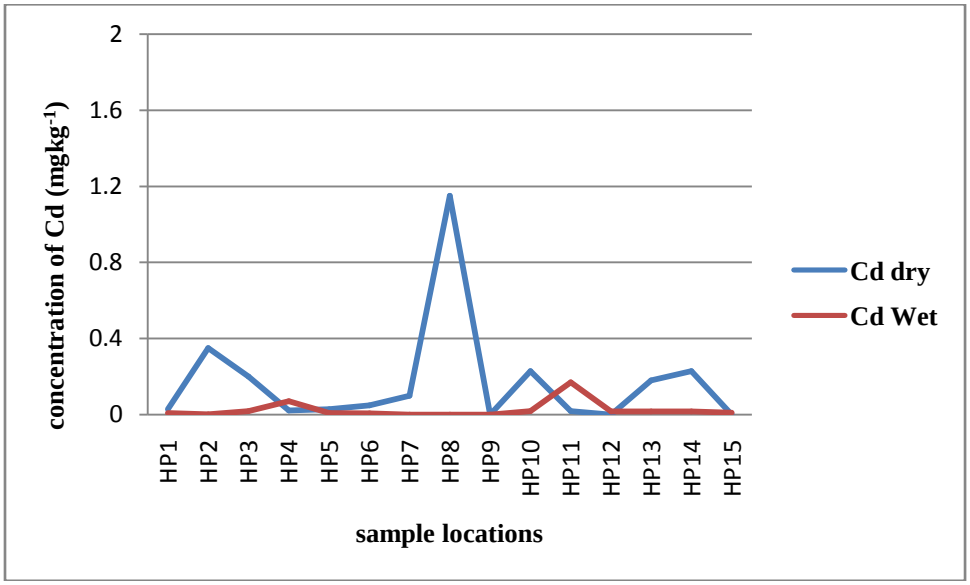


Fig. 4: *Seasonal Variations of Cd in soil*

3.5. Lead (Pb)

The results obtained from this investigation showed a mean ± SD concentration of 0.029 ± 0.014mg kg^{-1} and % CV (48.25 %) of Pb in the soil samples of the study area during dry season (Table 1 and Fig. 5). Also, mean ± SD (0.0275 mg kg^{-1}) and % CV (134.24 %) were recorded (Table 2 and Fig. 5).The total average of Pb in the soil of the study area was 0.147mg kg^{-1} Table 3. When compared with the back ground soil level (0.02 mg kg^{-1}), the mean concentration of 0.029 mg kg^{-1} in the soil sample is quite low and within guidelines values for concentrations of heavy metals in soil. The average amount of Pb (0.147 mg kg^{-1}) recorded in this study was lower compared to 21.16 mg kg^{-1} recorded by Udosen et al. (2012)[20] Ideriah et al.[15] recorded 2.38 mg kg^{-1} for dry season and 1.33mg kg^{-1} of Pb during wet season in the soil samples of the study area. Asia observed a variation of (3.40 to 99.40 mg kg^{-1} higher than Toxicity Characteristic limits (TCL) of 5.00 mg kg^{-1} for lead. Also, Nwajei et al. (2012) [21] obtained a mean concentration of 10.14±2.04 mg kg^{-1} and % CV 4.05% lead in the soil of the study area. Lead is toxic to many plants species, although a few are relatively tolerant. When ingested, lead can cause a disease called plumbism; lead also is known to damage the brain, the central nervous system, kidney, liver and the reproductive system". Lead content in soil varies in a very wide range. Pb concentration in soil may have been due to lead discharged from the battery waste as well as gasoline, engine oil and used container carried by runoff in the sampling locations.

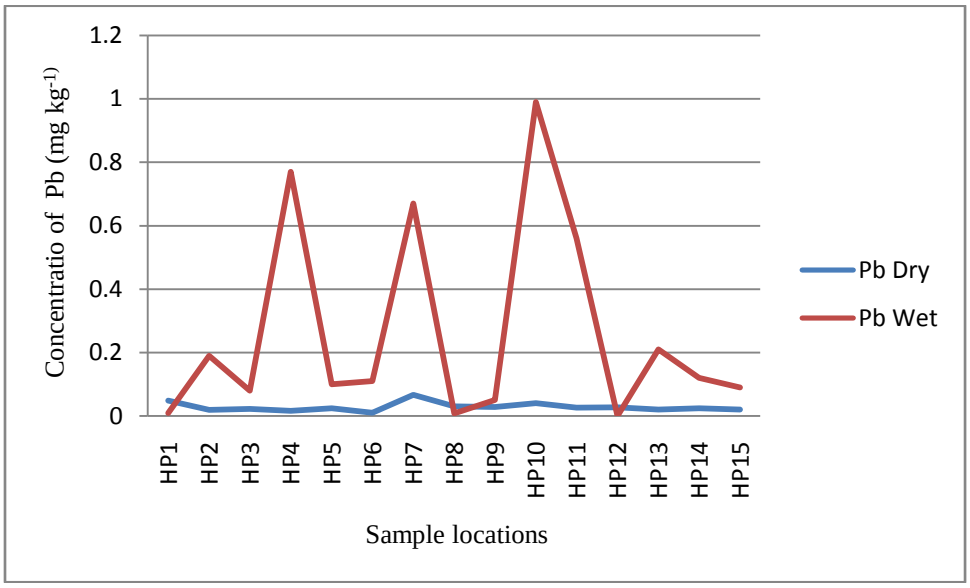


Fig. 5: *Dry Seasonal Variations of Pb in soil*

3.6. Manganese (Mn)

The mean ± SD concentration and % CV of Mn in the soil of the study area were 10.3663 ± 0.187 mg kg^{-1} and 30.749 % for dry season (Table 1 and Fig. 6). Correspondingly, mean ± SD (9.661 ± 2.177 mg kg^{-1}) and % CV (22.537 %) were obtained during wet season (Table 2 and Fig. 6). Total average of average of 10.014 mg kg^{-1} of Mn higher than control sample 6.00 mg kg^{-1} was obtained. The highest concentration of 17.019 mg kg^{-1} was recorded in location 15 (Mkpanak) and lowest concentration of 6.00 mg kg^{-1} was recorded in location 4 (Okoritip) as shown (Fig. 6) below. In a similar study, Nwajei et al. (2012) [21] a mean concentration of 14.53 ±.2.05 mg kg^{-1}, % CV 14.11 % of Mn was obtained in the soil of the study area. Ideria et al. (2013)[15] also revealed 42.80 mg kg^{-1} and 26.97mg kg^{-1} Mn for dry and wet seasons respectively.

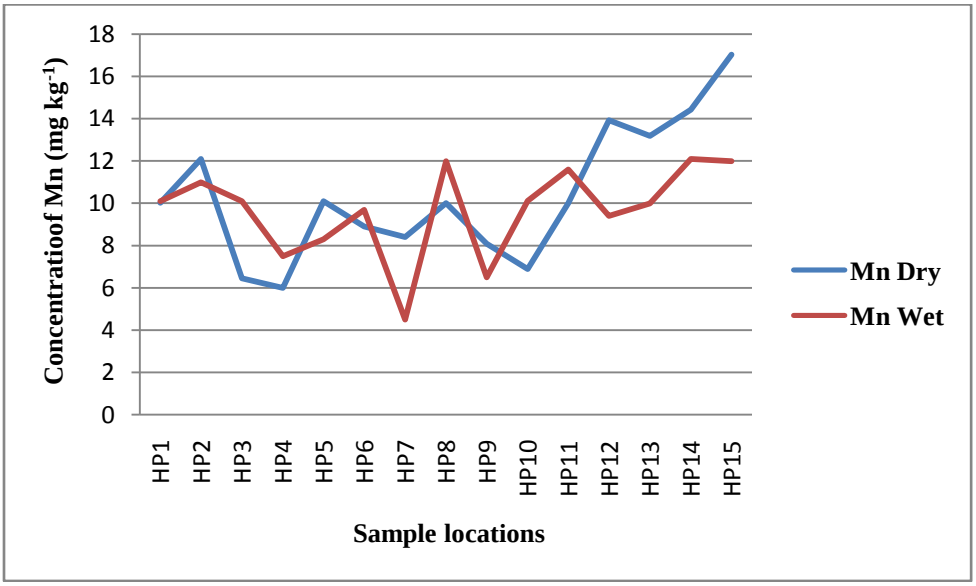


Fig. 6 *Seasonal Variations of Mn in soil*

3.7. Iron (Fe)

The investigation also revealed mean ± SD concentrations and % CV of 15.154 ± 5.912 mg kg^{-1}, 39.014 % and 12.093 ± 4.976 mg kg^{-1}, 28.47 % of Fe in the soil samples of the study area for dry and wet seasons respectively (Tables 1-2 and Figure 7). The highest and lowest concentrations of 26.198 mg kg^{-1} and 6.758 mg kg^{-1} Fe was recorded in location 14 (Okom Ita) and location 4 (Okoritip) respectively. Total average concentration of 13.624 mg kg^{-1} was high when compared with the background soil samples of 0.998 mg kg^{-1} and 3.500 mg kg^{-1}; and mean concentrations of other metals obtained in this study. Udosen, et al. (2012) [20] recorded a mean level of 39.635 mg kg^{-1} Fe in the study area. Nwajei et al. (2012) [21] recorded mean concentration 66.00 ± 10.50 mg kg^{-1} and % CV 15.91 % of Fe in the study area. The increase in

concentration of Fe may be due to poor drainage or permanently flooding state of the soil. This could also be as a result of the accumulation of the metal from the leached top soils which were not taken-up by plants, or washed-off during the rainy season. It could also be due to non-volatilization of the metallic compounds in solution in the soil. Fe is not generally considered a soil pollutant because it a component of the hemoglobin. The critical concentration in solution for the occurrence of Fe toxicity varied widely and reported values range from (10 – 1,000) mg kg^{-1}. The solubility of Fe and resultant migration potential is influenced by the pH and redox equilibrium between Fe^{2+} and Fe^{3+}. Scientists have demonstrated that while Fe is an essential element for normal cell function and metabolism, an excess of cellular Fe become highly toxic by inducing reactive oxygen species production. Foremost organs and cell type affected by Fe overload are liver, heart, kidney pancreatic beta and testis.

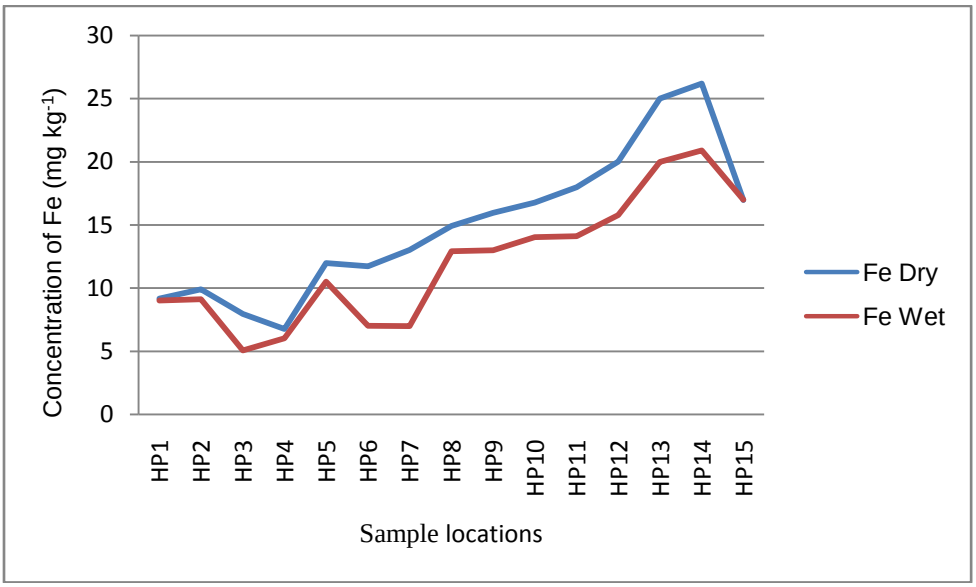


Fig.7: *Seasonal Variations of Fe in soil*

3.8 Zinc (Zn)

Investigation of Zn in soil of the study area indicated mean ± SD (0.066 ± 0.026 mg kg^{-1}) and % CV (186.72 %) during dry season (Table 1). Also, in wet season mean ± SD (0.5011 ± 0.264 mg kg^{-1}) and % C V (52.72 %) were recorded (Table 2 and Fig. 8). Total average concentration of Zn in soil of was 0.066 mg kg^{-1} for dry and wet seasons. The highest and lowest concentrations of 0.099 mg kg^{-1} and 0.035 mg kg were obtained in location 7 (Owo-Okpom) and location 10 (Adaha Usuk) respectively (Fig. 8). The average concentration of 0.066 mg kg^{-1} Zn was higher than the control sample 0.034 mg kg^{-1} but below critical level. Ideria et al. (2013) [15] recorded 18.50 mg kg^{-1} and 8.86 mg kg^{-1} of Zn for dry and wet seasons respectively. Essien and Benson [3] (2012) obtained a mean concentration of 30.49 mg kg^{-1} with % CV of 7.10 % in soil of the study area. Nwajei et al. (2012)[21] recorded a mean concentration of 7.88±1.58 mg kg^{-1} and % CV 20.05 % Zn in soil of the study area. Zinc although is essential in low concentration, is toxic in high concentration. Ingestion of zinc in excess of 12 mg per day may cause lung disturbance which can cause death. Plants often have a Zn uptake that their systems cannot handle, due to the accumulation of Zn in soils. Zn can interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthworms, thus retarding the breakdown of organic matter. Zinc can be a pollutant, especially in areas close to industrial plants engaged in processing of petroleum, because zinc is directly added to the drilling fluids as zinc carbonate and act as corrosion inhibitor for mud formations and part of the zinc can be trapped by the soil layer.

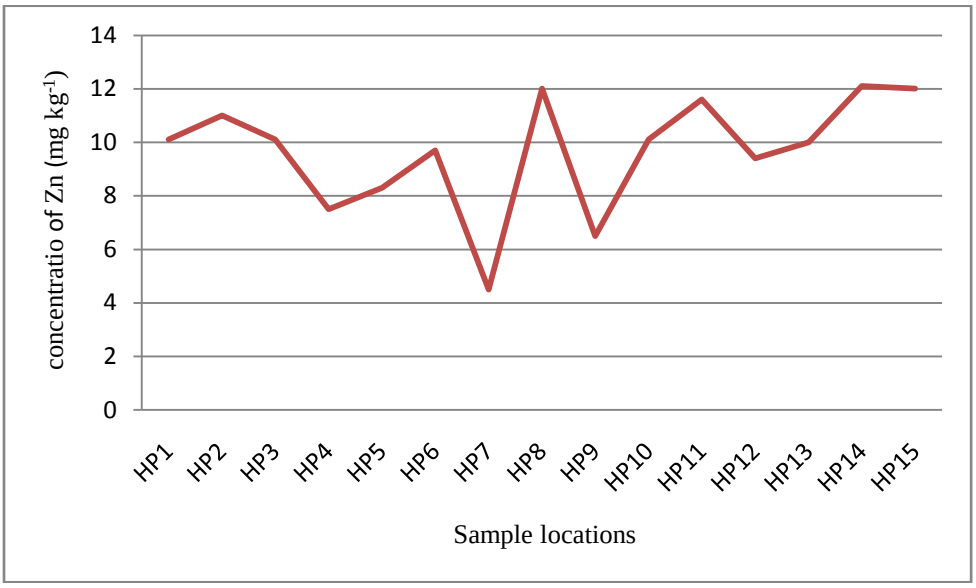


Fig.8: *Seasonal Variations of Zn in soil*

3.9. Cobalt (Co)

The result revealed a low concentration of Co in soil with mean ± SD concentration of 0.124 ± 0.066 mg kg^{-1} and % CV (53.148 %) recorded during dry season (Table 1). Mean ± SD concentration of (0.267±0.265mg kg^{-1}) and CV % (43.44 %) were also recorded during wet season (Table 2). Total average concentration of 0.196 mg kg^{-1} was recorded Table3. The highest concentration of 0.235 mg kg^{-1} was recorded in location 13 (Ikwokwang) and the lowest concentration of 0.067mg kg^{-1} was recorded in location 3 (Ikot Inwang). Figure 9. Nwajei et al (2012)[21] revealed 0.01 ± 0.00 mg kg^{-1} mean of Co in soil of the study area.

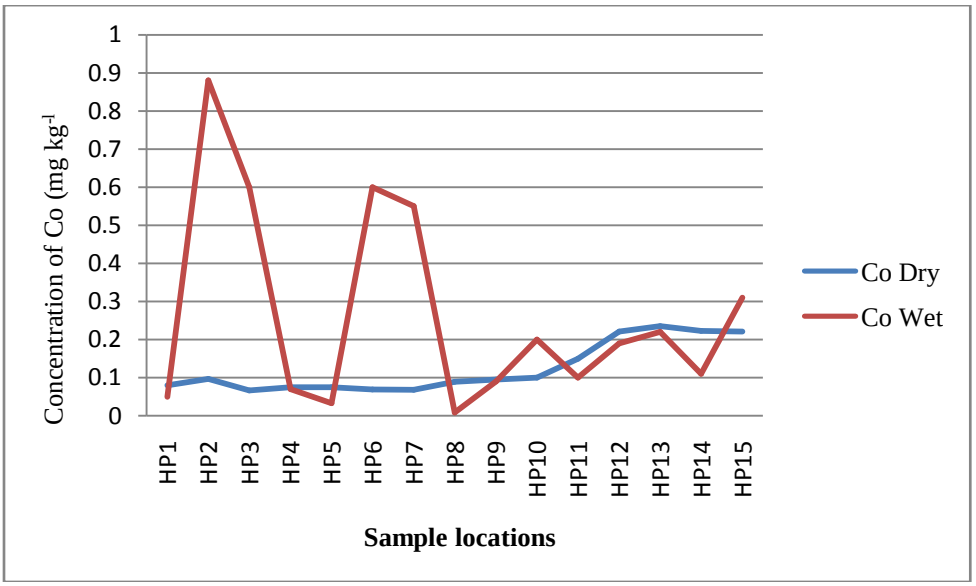


Fig.9: *Seasonal Variations of Co in soil*

4. Conclusion

The data obtained in the findings indicated that the concentrations of all the investigated heavy metals in soil were within permissible range as recommended by DPR, but higher than the control soil samples. From The results obtained it could also be infer that industrialization, oil exploration and indiscriminate disposal of industrial and domestic wastes have contributed to enhanced levels of heavy metals in the soil of the study area. In view of fact that heavy metals are bio-accumulative and with increased industrial and domestic activities in the area, there is need to monitor more closely the environment under review and put in place appropriate proactive check and balance measures to preserve the health of the communities. The relationship between the levels of the heavy metals in the soil and in vegetables and other edible crops should be investigated. Also, there is need to study the level of polyaromatic hydrocarbons (PAHs) as emerging contaminants in vegetables and other edible crops in the study area. The local populations are unaware of the effects

of environmental contaminants hence researchers are forced to pay heavily for samples with resultant increase in cost of the research.

References

[1] Bhaskar, R. Lena, Q. Tolerance of Heavy Metals in Vascular Plants; Arsenic Hyper Accumulation by Chines ebraker fern (pterzs vzttatal) .Pteridology in the new millennium. Kluwer Academic publisher, Netherlands. 2005; p 397-420

[2] Udosen, ED, Awak-Ama, JJ. The Concentration of some Toxic Metals ions in a Tropical Ultisol from coastal plain area of Akwa Ibom State, Nigeria. Global Journal of pure and Applied Sciences. 2005; 7 (3), 427-431.

[3] Essien, JP, Benson, NU. Trend in Heavy Metals and Total Hydrocarbon Burdens in Sub creek, a Tributary of Qua Iboe Estuary, Nigeria. Trends in Applied Science Research. 2012; 2: 312 – 319.

[4] Osuyi, CL, Chukwunedum, MO. The Ebocha-8 oil spillage fate of Associated Heavy Metals six months after. Petroleum chemistry research group, Department of industrial and pure chemistry, University of Port Harcourt, Choba, Port Harcourt, Nigeria. 2001; 1-9

[5] Essiett, UA, Effiong, GS, Ogbenudia, FO, Bruno, E.J. .Heavy metal concentrations in plants growing in crude oil contaminated soil in Akwa Ibom State, Nigeria. African Journal of Pharmacy and Pharmacology. 2010;4 (7), 466-470.

[6] Vwioko, DE. Anoliefo, GO. Fashemi, SD. Metal concentration in plant Tissues of *Ricinus Comnismu L*. (castor oil plant) Grown in soil contaminated with spent lubricating oil. Journal of Applied Science and Environmental Management. 2006; 10 (30), 127-134.

[7] Edema, NE. Obadoni, BO, Erhani, H, Osakwumi, UE Eco-phytichemical studies of plants in a crude oil polluted terrestrial Habitant located at Iwhreken, Ughelli North Local Government Area of Delta State. Nature and Science 7(9) (2009) 78-79.

[8] Ud, GJ. Determination of heavy metals (Ni, V, Cd , Pb) in soil and colocasia spp in oil polluted Qua Iboe River Coastal Area. M.Sc Research Project. Department of Pure and Industrial Chemistry University of Nigeria, Nsukka. 2006; pp 20-45

[9] Unilag Consult. Environmental Impact Assessment for the Proposed QIT 750TBD (crude) expansion project, Akwa Ibom State, Nigeria, Onshore Facilities, Mobil Producing Nigeria Unlimited, Lagos Nigeria. 1997; 12-13.

[10] University of Calabar Consultancy Services (Unical Cons) Draft Final Report of Environmental Impact Assessment (EIA) of the Proposed Iko-Atabrikang – Akata – Okpolom - Ikot-Inwang – Okoritip – Iwoachange Road Project by NDDC. 2003; 2 – 5.

[11] Radojvic, M. Bashkin, VN. Practical Environmental Analysis. The Royal Society of chemistry. Thomas Graham Honse, Science Park, Milton Road, Cambridge UK. 1999; pp 405-500.

[12] Iwegbue, CM, Egobuez, FE, Opuene, K. Preliminary assessment of heavy metals levels of soils of an oil field in the Niger Delta, Nigeria. International Journal of Environmental Science and Technology. 2006; 3(2). 167-172.

[13] Adefemi, O, Olaofe, O, Asaolu, SS. Seasonal Variation in Heavy Metal Distribution in the Sediment of Major Dams in Ekiti-State. Pakistan Journal of Nutrition. 2007; 6(6): 705-707.

[14] Myung, CJ. Heavy Metal Concentrations in Soils and Factors Affecting Metal Uptake by Plants in the Vicinity of a Korean Cu-W Mine. Sensors. 8 (2008) 2413-2423.

[15] Ideriah, TJ, Ikpe, K, Nwanjoku, FN. Distribution and Speciation of Heavy Metals in Crude Oil Contaminated Soils from Niger Delta, Nigeria. World Environment. 2013; 3(1): 18-28.

[16] Alloway, BJ. Processes and the behavior of heavy metals Heavy in soil. Blackie and son Limited. Bishop Briggs, Glasgow. 1999; PP 43-56.

[17] Asia, IO, Jegede, SI, Jegede, DA, Ize-Iyamu, OK, Akpasubi, EB. The effects of petroleum exploration and production operations on the heavy metals contents of soil and groundwater in the Niger Delta. International Journal of Physical Sciences. 2007; 2(10): 271-275.

[18] Raymond, AW, Felix, EO. Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation. Ecology. 2012; 3:9-18

[19] Onwerenmadu, EU, Duruigbo, OI. Assessment of Cd concentration of crude oil polluted arable soil. International journal of Environmental Science and Technology. 2007; 4(3): 409-412.

[20] Udosen, DE, Ukpong, ME, Etim, EE. Concentration of heavy metals in soil samples within Mkpanak in Ibeno coastal Area of Akwa Ibom State, Nigeria. International Journal of Modern Chemistry. 2012; 3(2):74 – 81.

[21] Nwajei, GE, Okwagi, P, Nwaje, RI, Obi-Iyeke, GE. Analytical Assessment of Trace Elements in Soils, Tomato Leaves and Fruits in the Vicinity of Paint Industry, Nigeria. Research Journal o.f Recent Sciences. 2012; 1(4): 22- 26.