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Chronic Kerosene Contamination and Variation in the Physicochemical and Heavy Metal Content of the Soil in Calabar, Cross River State, Nigeria.

[1]Nseabasi N. O, [2]Antai S. P, [2]Bassey I. U.[2]Iwatt G. D& [2]UnimkeA. A.
[1]Department of Biological Sciences, College of Science, Federal University of Agriculture, Makurdi, Benue State, Nigeria
[2]Department of Microbiology, Faculty of Biological Sciences, University of Calabar, Calabar, Nigeria.

***Abstract**: Soil physicochemical parameters such as pH, organic carbon, total nitrogen, available phosphorus, effective cation exchange capacity, base saturation, total petroleum hydrocarbon and heavy metal concentration were investigated in chronic kerosene contaminated soil samples and compared against pristine agricultural soil sample. The value for the above parameters in the pristine control sample were 4.75, 3.40, 0.22, 40mg/kg, 9.22cmol/kg, 87.74% and 40mg/kg respectively. In chronic kerosene contaminated soil samples, values for the same parameters ranged from 4.96-6.40, 7.63%-9.92%, 0.06%-0.16%, 25.06-39.61 (mg/kg), 9.16-12.13 (cmol/kg), 85.56%-90.84% and 380-23300 (mg/kg) respectively. Statistical analysis showed significant difference ($p \leq 0.05$) in the levels of lead, chromium, zinc, copper, manganese and nickel between pristine control and chronic kerosene-contaminated soil samples. Chronic kerosene-contaminated soil samples indicated insufficient mineralization and persistence of heavy metals which results to bioaccumulation in plants, soil organism, dependent animal population and contamination of water aquifer.*

Keywords: *chronic, Kerosene-contamination, physicochemical, heavy metals, bioaccumulation, persistence, mineralization.*

INTRODUCTION

The effect of spillage of petroleum products over the past decades can not be over emphasised owing to the fact that the menace seemed to persist due to industrial and sub-industrial activities. The advent of industrialization and particularly the strive for development and lack or inadequate enforcement of environment laws in third world countries such as Nigeria has led to the use and abuse, deliberate and indeliberate disposal of petroleum products. Kerosene is thin oil distilled from petroleum or shale oil, used as a fuel or alcohol denaturant (Mouwerik*et al.*, 1997). Thus, due to its relative availability, affordability and application over a vast majority of processes and machinery, spillage or seepage of this product occurs though not frequently in large quantities at a given time but consistently over a period of time. Owing to this, kerosene has been seen to accumulate and result in chronic contamination in the soil especially around retail outlets such as surface tanks. The employment and wide application of kerosene as a pesticide control in citrus cultivation (agriculture) is however, of particular concern due to the enduring and damaging effects. Via metabolism, co-metabolism and transformation, most organic chemicals are degraded by soil microbiota to maintain equilibrium. However, a number of soil microbiotacan not withstand the stress imposed on them by these chemical toxicants. The effect of these chemicals on indigenous microbiota disrupts the biogeochemical cycling of elements (Gadd, 1992, Deni and Pennickx, 1999).

The objective of this study was to evaluate the variation in the physicochemical parameter and heavy metal content between pristine soil and chronic kerosene contaminated soil.

MATERIALS AND METHODS

Study area

Soil samples were collected around kerosene surface tanks located at Diamond-Hill (latitude 4.97992, longitude 8.32744), Old Odukpani Road (latitude 5.00204, longitude 8.33938), Egerton Street (latitude 4.9536, longitude 8.31168), Hart Street (latitude 4.94428, longitude 8.32436) and pristine soil sample was collected from the agricultural garden behind biological garden behind biological science building, University of Calabar (Latitude 4.95179, longitude 8.34386) in Calabar, Cross River State.

Collection of samples

Soil samples were collected from surface (0-15cm) and sub-surface (15-30cm) soil by excavation with a spade. The sample were collected from different location and mixed to obtain a composite sample. Five (5kg) of each of the samples were weighed into perforated polyethylene bags.

Soil physicochemical analysis

Physicochemical parameters analysed includes moisture content, soil pH, organic carbon content, total nitrogen, available phosphorus, exchangeable cations, exchangeable acidity (EA) effective cation exchange capacity (ECEC), base saturation (BS), total petroleum hydrocarbon (TPH).

Soil pH

The hydrogen ion concentration was determined by dissolving one part of the soil sample in two parts of distilled water. The suspension was agitated to ensure homogeneity and afterwar), ds, the sample was read using a pyeUnicam model Mk2 pH meter.

Organic carbon

Organic carbon was determined colorimetrically using modified Walkey-Black method as described in *Methods of Applied Soil Microbiology and Biochemistry* (Alef and Nannipiere, 1995).

Total nitrogen

Total nitrogen was estimated by macro-kjeldahl digestion methods as outlined by *Jou (1979).*

Available phosphorus

Available phosphorus was extracted with acid fluoride using the Bray P-1 Method (Bray and Kurtz, 1945). Phosphorus in the extract was determined colorimetrically by blue colour of Murphy and Riley (1962) as outlined by Jou (1979).

Exchangeable cation

Exchangeable cation (Ca, Mg, K and Na) were extracted with 1N NH4OAC pH 7.0 using 1:10 solution ratio. Potassium and sodium in the extract were determined by flame photometry while calcium and magnesium were determined by versenate EDTA titration (Jackson, 1962).

Exchangeable acidity

Titration methods as outlined in *Selected Methods for Soil and PlantsAnalysis* of Jou (1979) was used for this determination. The sample was extracted with 1N. K solution and extract were titrated with 0.05N NaOH to a permanent pink end point using phenolphthalein as indicator.

Effective cation exchange capacity

This was determined by extrapolation using the values of the total exchangeable bases (Ca, Mg, K and Na) which were added to exchangeable acidity.

$$ECEC = (Ca + Mg + K + Na + EA)$$

Base saturation (BS)

This was determined by extrapolation studies. Total exchangeable base (Ca + Mg + K and Na) were divided by ECEC and multiplied by 100.

$$BC = \frac{Ca + Mg + K + Na}{ECEC} \times 100$$

Total petroleum hydrocarbon (TPH)

The amount of total petroleum hydrocarbons in the soil sample was determined using air-dried soil that was sieved through 1mm mesh. Ten (10) grams of the soil sample was extracted with n-hexane by shaking with mechanical shaker for 30 minutes according to methods reported by Okolo*et al.*, 2005. The extracted soil sample was then measured using Jen way Uv/Vis spectrophotometer at a wavelength of 430nm

Heavy metal analysis

Heavy metals were extracted out via employing aqua regia digestion technique adopted by *Etesin (2002)*. The heavy metals analyzed for were lead (Pb), chromium (Cr), zinc (Zn), copper (Cu), nickel (Ni), manganese (Mn), cadmium (Cd), cobalt (Co), and iron (Fe).

Statistical analysis

Collected data were subjected to analysis of variance (ANOVA) using completely randomised design (CRD). Means were separated using least significant difference (LSD) test.

RESULTS

Table 1 presents the physiocochemical parameters of the soil samples for both the pristine control (PC) and chronic kerosene-contaminated soil samples (Q, R, S and T). The pH value of the pristine soil sample was 4.75 while those of kerosene-contaminated soil samples ranged from 4.96 - 6.40. The value of organic carbon in the pristine soil sample was 3.40% while in chronic kerosene-contaminated soil sample, its value ranged from 9.63%-9.92%. The level of total nitrogen in the pristine soil sample was 0,22% while in the chronic kerosene contaminated soil samples, its value ranged from 0.06%-0.16%. The carbon nitrogen ratio in the pristine soil sample was 15.46 while in chronic kerosene contaminated soil samples, C:N ratio ranged from 47.69-165.33.

The level of available phosphorus P in the pristine control soil sample was 40mg.kg^{-1}while its level in chronic kerosene-contaminated soil ranged from 25.06-39.61mg.kg^{-1}.The calcium level in pristine soil sample was 5.22cmol.kg^{-1} while its level in chronic kerosene contaminated soil samples ranged from 5.08-6.56cmol.kg^{-1}. The magnesium level in pristine control soil sample was 2.30cmol.kg^{-1}while its level in chronic kerosene-contaminated soil sample ranged from 2.6-3.8cmol.kg^{-1}. The sodium level in the pristine soil was 0.13cmol.kg^{-1} while its value in chronic kerosene contaminated soil ranged from 0.19-0.61cmol.kg^{-1}. The level of potassium in the pristine soil sample was 0.27cmol.kg^{-1} while its level in chronic kerosene-contaminated soil samples ranged from 0.05-0.21cmol.kg^{-1}. The exchangeable acidity in pristine soil sample was 1-13cmol.kg^{-1} while its level in chronic kerosene contaminated soil samples ranged from 1.06-1.11cmol/kg. The value of effective cation exchange capacity of the pristine soil sample was 9.22cmol/kg while in chronic kerosene contaminated soil samples, its values ranged from 9.16-12.3cmol/kg. the percentage base saturation (BS value in the pristine soil was 87.74% while in chronic kerosene contaminated soil samples, its value ranged from 88.20-90.84 cmol/kg. the total petroleum hydrocarbon level in the pristine soil was 40mol/kg while its value in chronic kerosene contaminated soil samples, its value ranged from 358-23,300mol/kg.

Table 2 presents the heavy metal content of the soil for both pristine (PC) and chronic kerossene contaminated soil samples (Q,R,S,T). A total of nine heavy metals were analyzed for in both sample types. In pristine soil sample, a total of seven heavy metals were detected in varying concentrations. Iron (Fe) 96.007ppm, manganese (Mn) 5.571ppm, chromium (Cr) 2.601 ppm, lead (Pb) 0.546ppm, zinc (Zn) 0.384ppm, nickel (Ni) 0.290ppm and copper (Cu) 0.071 ppm. In the chronic kerosen contaminated soil samples, the heavy metals detected were also in varying concentrations. Those with higher concentration such as iron (Fe) ranged from 96.082-100.102 ppm, manganese (Mn) ranged from 2.63-3.74 ppm and chromium (Cr) ranged from 2.350-3.001 ppm. Other heavy metals detected in lower concentrations included zinc (Zn) which ranged from 0.436-0.465 ppm, copper (Cu) which ranged from 0.046-0.072 ppm, nickel (Ni) which ranged fom 0.157-0.216 ppm and lead (Pb) which ranged from 0.307-0.375 ppm. Heavy metals such as cadmium (Cd) and colbalt (Co) were below detectable levels in both sample types.

DISCUSSIONS

The hydrogen ion concentration pH value of the soil is very useful in measurement of other soil parameters. It yields information on the availablilty of nutriebts and elements such as calciummmagenesium, sodium , potassium etc in the soil. In this studt, the pH value of pristine soil was 4.75 which is indicative of acidic soil while that of chronic kerosen contaminated soil samples ranged from 4.96-6.40. Obire*et al.,* (2002) observed pH values in the range 6.1-6.5 in kerosene contaminated soil. Statistical analysis indicated a significant difference ($P \leq 0.05$) in organic carbon betwween sample types. There was a marked increase in the organin carbon content in the chronic kerosene contaminated soil and a corresponding marked decrease in the level of toatal nitrogen. Thus, a remarkable increase in the C:N ratio in chronic kerosene contaminated soil samples. This result corresponds with Shi *et al.*, (2002) which reported that petroleum hydrocarbon contaminated soils were characterized with high organisc carbon content. C:N ratio higher than 35-40 generally indicates inadequate nitrogen which is a required for mineralization of pollutant (WDNRERRP, 1994). Available phosphorus being a major soil requirement was determined since organic carbon make up to over 80% of the phosphorus content in tropical soil, its availability is microbiologically induced (Bray and Kurtz, 1945). However, statistical analysis showed that there was no significant difference ($P \geq 0.05$) in phosphorus content between chronic kerosene contaminated and pristine soil samples. It was observed that calcium and potassium level between both sample types fell within similar range. There was no significant difference ($P \geq 0.05$) in the EA, ECEC and BS of both pristine and chronic kerosene contaminated soil samples. The total petroleum hydrocarbon content of chronic kerosene contaminated soil samples were significantly higher ($P \leq 0.05$) than in pristine soil samples. Abbiotic process of voliatilization and transsformation aid in TPH reduction. The higher C;N ratio in the range 47.69-165.33 in chronic kerosene contaminated soil samples is indicative of inadequate minerialization and hence, the high TPH values.The total petroleum hydrocarbon can be reduced overtime through effective mineralization of hydrocarbon contaminated soil (Atagana, 2008).

Statistical analysis showed that there was significant difference ($p \leq 0.05$) in the level of lead, chromium, zinc, copper, manganese and nickel between pristine soil and chronic kerosene contaminated soil i.e there was a decrease in the level of lead, manganese and nickel and an increase in the level of zinc and copper in chronic kerosene contaminated soil samples. The increased level of zinc and copper in chronic kerosene contaminated soil samples may have a direct relationship with the poliferatiion of hydrocarbonclastic microorganisms, as these elements at certain levels possilbly activate enzyme kinetics of these microorganisms enabaling them poliferate and metabolize the hydrocarbon contaminant. There was no significant difference ($P \geq 0.05$) in the iron content of the soil while cadmium and colbalt were below detectable levels.

Heavy metals are toxic to plants and animals if absorbed in large quantities and a good number of them act as enzyme inhibitors at certain levels and interfer with microbial metabolism. It follows that their persistence inthe environment encourages bioaccumulation which is injurious to most forms of life. Compounds of cadmium, nickel and some forms of chromium (chromates) are carcinogenic (Mishra *et al.,* 2001). Thus, there is variation between the physiochemical and heavy metal content between chronic kerosene contaminated and pristine soil samples.

CONCLUSION

The decrease in nitrogen level as observed in the chronic kerosene contamniated soil samples renders such soil inadequate for sustainable agricultural practices due to reduction in mineralization vis-a vis depleting microbial and other soil communities. Thus, the use of kerosen as a pesticide especially in citrus cultivation should be discouraged. Also, the increase in the level of heavy metals such as zinc, copper and variations in the level of chromium in chronic kerosene contaminated soil samples encouraged bioaccumulationin plant and dependent animal population and result in ground and surface water pollution. Thus, chronic kerosene contamination posses a threat to agriculture and public health, hence, the need for admendment of kerosene contaminated soil.

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TABLE 1

Physico-chemical properties of pristine and chronic kerosene contaminated soil samples

			Samples		
Parameters	**PC**	**A**	**B**	**C**	**D**
pH	4.75[d] ±0.03	5.30[b] ±0.1	4.96[c] ±0.07	6.40[a] ±0.03	6.38[a] ±0.03
Organic C %	3.40[c] ±0.04	7.99[b] ±0.11	7.63[b] ±0.04	9.92[a] ±0.02	9.76[a] ±0.07
Total N %	0.22[a] ±0.02	0.14[b] ±0.03	0.16[b] ±0.02	0.06[c] ±0.02	0.11[b] ±0.01
C:N Ratio	15.46	57.07	47.69	165.33	88.73
Available P (mg/kg)	40[a] ±0.6	29.34[a] ±0.2	39.61[a] ±0.4	25.06[a] ±0.1	32.06[a] ±0.08
Calcium (cmol/kg)	5.22[c] ±0.03	5.53[b] ±0.07	5.08[d] ±0.11	6.56[a] ±0.05	5.24[c] ±0.07
Magnesium (cmol/kg)	2.3[a] ±0.21	2.9[a] ±0.5	2.6[a] ±0.21	3.8[a] ±0.3	2.7[a] ±0.31
Sodium (cmol/kg)	0.13[a] ±0.02	0.21[a] ±0.03	0.19[a] ±0.03	0.61[a] ±0.03	0.32[a] ±0.02
Potassium (cmol/kg)	0.27[a] ±0.02	0.18[a] ±0.04	0.21[b] ±0.03	0.05[a] ±0.02	0.18[a] ±0.04
Exchangeable acidity (EA) (cmol/kg)	1.13[a] ±0.02	1.06[a] ±0.02	1.08[a] ±0.01	1.11[a] ±0.03	1.09[a] ±0.02
ECEC (cmol/kg)	9.22[a] ±0.05	9.88[a] ±0.08	9.16[a] ±0.06	12.13[a] ±0.06	9.53[a] ±0.03
BS %	87.74[a] ±0.2	89.27[a] ±0.16	88.20[a] ±0.03	90.84[a] ±0.07	85.56[a] ±0.07
TPH (mg/kg)	40[e] ±0.6	975[c] ±3.1	358[d] ±2.5	2330[a] ±4.7	1530[b] ±2.0

Data were expressed in mean and standard error (X + S.E) in triplicates. * Mean followed with the same case letter along horizontal row shows no significant difference ($p \leq 0.05$)

TABLE 2

Heavy metal content of pristine and chronic kerosene contaminated soil samples

Soil samples **Heavy metals**	**PC (ppm)**	**A (ppm)**	**B (ppm)**	**C (ppm)**	**D (ppm)**
Lead (Pb)	0.546[a] ±0.01	0.321[b] ± 0.01	0.307[c] ± 0.01	0.375[c] ± 0.01	0.323[c] ± 0.19
Chromium (Cr)	2.601[c] ±0.01	2.542[d] ± 0.00	2.350[e] ± 0.01	3.001[a] ± 0.01	2.620[b] ± 0.01
Zinc (Zn)	0.384[b] ±0.01	0.451[a] ± 0.00	0.436[a] ± 0.01	0.465[a] ± 0.02	0.456[a] ± 0.01
Copper (Cu)	0.071[a] ±0.00	0.065[b] ± 0.00	0.046[a] ± 0.00	0.072[a] ± 0.00	0.066[a] ± 0.01
Nickel (Ni)	0.290[a] ±0.00	0.197[b] ± 0.01	0.157[b] ± 0.00	0.216[b] ± 0.01	0.200[b] ± 0.01
Manganese (Mn)	5.571[a] ±0.00	2.82[c] ± 0.05	2.63[d] ± 0.04	2.95[c] ± 0.06	3.74[b] ± 0.08
Cadmium (Cd)	ND	ND	ND	ND	ND
Cobalt (Co)	ND	ND	ND	ND	ND
Iron (Fe)	96.077[a] ±0.01	100.099[a] ± 0.03	96.082[a] ± 0.01	100.06[a] ± 0.01	100.102[a] ± 0.01

Data were expressed in mean and standard error (X + S.E) in triplicates. * Mean followed with the same case letter along horizontal row shows no significant difference ($p \leq 0.05$)

KEY:

PC	=	Pristine soil sample
A	=	Chronic kerosene-contaminated soil sample
B	=	Chronic kerosene-contaminated soil sample
C	=	Chronic kerosene-contaminated soil sample
D	=	Chronic kerosene-contaminated soil sample
ND	-	Not detectable
ppm	-	Parts per million