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Petroleum Products Spillage and Its Effect on Soil at Mbalim Gwer East Benue State Nigeria

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ABSTRACT

Soil samples were studied to provide information on the level of damage (if any) done as petroleum products were spilled from vandalized pipelines 10 years after . Petroleum products are volatile and evaporate in a short time, it is very difficult to determine their presence on soil after some time , instead the soil was analyzed in order to determine the quantity of essential elements still present in the soil after the spill Therefore five (5) locations (around Mbalim- at the immediate point of spill, one kilometer north, one kilometer South, one kilometer East and one kilometer West) were chosen. Basic elements of soil fertility - pH of the Soil , phosphorus , Nitrogen , Potassium , Organic Carbon and Manganese were determined The soil samples were heavy , hardly absorbed water, displayed acidity of 6.26 , 3.8% nitrogen , 6.6%phosphorus ,5.2% potassium and the texture loamy and sandy. Agricultural use of this land was considered a hard task except the process of remediation is applied. Aeration of the soil at the contaminated site was already sufficient , thermal remediation to raise subsurface temperatures to volatize chemical contaminants out of the soil was equally going on as the site was exposed to enough sunlight. Bioremediation including landfarming, biostimulation and bioaugmentating soil biota is recommended. In areas of intensive farming like Benue State where crops are harvested at least once a year and no animals browse the fields, human intervention in the form of traditional fertilizer, animal manure or muck, made from the straw bedding of cattle that has fermented for a period is also recommended.

Keywords Vandalization , Petroleum products, Spillage , Soil , Bioremediation

INTRODUCTION .

There is concern over soil contamination as direct contact with the contaminants and secondary contamination of water supplies within and underlying the soil causes radical changes which arise from the presence of many hazardous chemicals even at low concentrations US EPA and Snyder C (2005). The contaminant species manifest in the alteration of metabolism of endemic microorganisms and arthropods resident in a given soil environment. The result can be virtual eradication of some of the primary food chain, which in turn could have major consequences for predator or consumer species. According to Walter Mertz (87), Plants require inorganic salts which they absorb from the soil surrounding their roots; these include the elements phosphorus (in the form of phosphate), chlorine (as the chloride ion), nitrogen, in the form of nitrate (NO_3^-) or ammonium (NH_4^+) ions. potassium, sulfur, calcium, magnesium, iron, manganese, boron, copper, and zinc.These nutrients found in soil result in part from the gradual breakdown of the rocky material on the Earth's surface as a result of rain and, in some areas, freezing. Primarily composed of alumina and silica, rocks also contain smaller amounts of all the mineral elements needed by plants. Another source of soil nutrients is the decomposition of dead plants and animals and their waste products , two groups of bacteria fix atmospheric nitrogen—that is, they are able to incorporate this relatively inert element into nitrate ions. Bacteria of the genus Azobacter live freely in soil, while those of the genus Rhizobium live sheltered in the roots of leguminous plants such as peas and beans. Cyanobacteria (blue-green algae) also can fix nitrogen and are important for growing rice in the flooded paddy fields of Southeast Asia. Petroleum products are derived from crude oil processed in oil refineries. According to Walther W. Irion, Otto S. Neuwirth,(2005) the largest share of oil products is used as "energy carriers", i.e. various grades of fuel oil and gasoline. These fuels can be blended to give gasoline, jet fuel, diesel fuel, heating oil, and heavier fuel oils. Heavier (less volatile) fractions can also be used to produce asphalt, tar, paraffin wax, lubricating and other heavy oils. Refineries also produce other chemicals, some of which are used in chemical processes to produce plastics and other useful materials. Since petroleum often contains a few percent sulfur-containing molecules, elemental sulfur is also often produced as a petroleum product . Representative petrochemicals are ethylene and benzene-toluene-xylenes ("BTX").

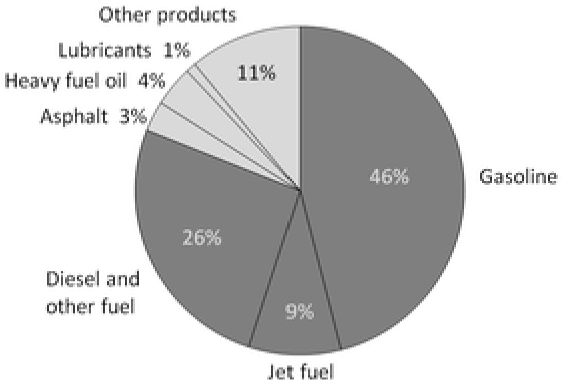

Figure 1 Pie chart distribution of petroleum products curtesy Encyclopedia of Industrial Chemistry 2005,

1.0 PETROLEUM PRODUCTS SPILL

The most efficient mode of bulk transport for petroleum products is the network of pipelines that are now found all over the country and indeed the world . Despite the efficiency and ease of making these products available to end users , criminals vandalize these pipelines in order to divert the products for illegal sales. A large quantity gets spilled on the ground and the sorrounding area . At Mbalim a similar vandalization took place and the spill made up of kerosine, premium motor spirit PMS and gasoline covered over 20 hectars of land which over 10 years has been laid bare and unproductive. Records Of Exxon Valdez Spill (2010) describes an oil spill as the release of a liquid petroleum hydrocarbon into the environment, especially marine areas, due to human activity, and is a form of pollution. The term is usually applied to marine oil spills, where oil is released into the ocean or coastal waters, but spills may also occur on land. Oil spills may be due to releases of crude oil from tankers, offshore platforms, drilling rigs and wells, as well as spills of refined petroleum products (such as gasoline, diesel) and their by-products, heavier fuels used by large ships such as bunker fuel, or the spill of any oily refuse or waste oil.

2.0 SOIL CHARACTERISTICS

Figure 2 Cross-Section of Soil curtesy Kenneth W.Frik Photo Researchers, Inc.

Soil forms over many thousands of years from weathered rock fragments and the decaying remains of living organisms. As soil develops, it forms distinct layers, known as horizons. Each horizon has a specific color, texture, and mineral content, as seen in the vertical cross-section of soil above. The number and type of horizons in a particular soil vary, but in general the uppermost horizon of soil forms the nutrient-rich topsoil. Beneath the topsoil lies the subsoil, which contains minerals that have trickled down from the topsoil. Rock fragments reside below the subsoil, and the horizon forming the foundation of soil consists of unweathered parent rock.

Soil chemical characteristics particularly the clays, measure of the ability of an insoluble material to undergo displacement of ions previously attached and loosely incorporated into its structure by oppositely charged ions present in the surrounding solution. Zeolite minerals used in water softening, for example, have a large capacity to exchange sodium ions (Na^+) for calcium ions (Ca^{2+}) of hard water. High cation-exchange capacities are characteristic of clay minerals and numerous other natural and synthetic substances possessing ion-exchanging properties. Clay minerals are able to adsorb certain cations and anions and retain them around the outside of the structural unit in an exchangeable state, generally without affecting the basic silicate structure. These adsorbed ions are easily exchanged by other ions. The exchange reaction differs from simple sorption because it has a quantitative relationship between reacting ions. calcium, magnesium, and potassium become attached to the soil particles, in a process known as cation exchange The chemical reactions in cation exchange make it possible for calcium and the other elements to be changed into water-soluble forms that plants can use for food. Therefore, a soil's cation exchange capacity is an important measure of its fertility.

Another important chemical measure is soil pH, which refers to the soil's acidity or alkalinity. This property hinges on the concentration of hydrogen ions in solution. A greater concentration of hydrogen results in a lower pH, meaning greater acidity. Scientists consider pure water, with a pH of 7, neutral. The pH of a soil will often determine whether certain plants can be grown successfully. Blueberry plants, for example, require acidic soils with a pH of roughly 4 to 4.5. Alfalfa and many grasses, on the other hand, require a neutral or slightly alkaline soil. In agriculture, farmers add limestone to acid soils to neutralize them .Encyclopædia Britannica. (2010).

2.1 SOIL USE

Figure 3 Plowing Turns Up Soil curtesy Rob Crandal/ Boston Inc.

Growing farm crops is one of the most important uses of soil. Crops grow in the topsoil, the nutrient-rich upper layer of soil. Farmers plow soil prior to planting to improve soil structure, helping it to retain water, and to improve the distribution of the soil’s nutrients. To prevent soil erosion, farmers plow across the face of a slope of land instead of up and down the slope.
Rob Crandall/Stock Boston Inc.

2.2 SOIL CONTAMINATION.

Soil contamination can be caused by application of pesticides and fertilizers, oil and fuel dumping , disposal of coal ash, leaching from landfills , drainage of contaminated surface water into the soil and discharging urine and faeces in the open . The effects of petroleum products: Petroleum Motor Spirit (petrol, PMS), Automobile Gas

Oil (diesel. AGO), Dual Purpose Kero (kerosene, DPK), were investigated on the chlorophyll accumulation in Barbula lambarenensis. . Petroleum products were discovered to have damaged the chlorophyll of the plant Fatoba Olorunmaiye and Ogunlade (2010) . Contaminants typically alter plant metabolism, often causing a reduction in crop yields. This has a secondary effect upon soil conservation, since the languishing crops cannot shield the Earth's soil from erosion. Many if not all petroleum products on long term exposure induce liver changes, kidney changes and depression of the central nervous system. Not unexpectedly, soil contaminants can have significant deleterious consequences for ecosystems. There are radical soil chemistry changes which can arise from the presence of many hazardous chemicals even at low concentration of the contaminant species. These changes can manifest in the alteration of metabolism of endemic microorganisms and arthropods resident in a given soil environment. The result can be virtual eradication of some of the primary food chain, which in turn could have major consequences for predator or consumer species. Even if the chemical effect on lower life forms is small, the lower pyramid levels of the food chain may ingest alien chemicals, which normally become more concentrated for each consuming rung of the food chain. Many of these effects are now well known, such as the concentration of persistent DDT materials for avian consumers, leading to weakening of egg shells, increased chick mortality and potential extinction of species.

Table 1 Toxicity Characteristic (TC) Rule Hazardous Waste Regulatory Levels for Toxicity Characteristic established by U.S. Environmental Protection Agency March 29, 1990.

Constituent	Regulatory Level (mg/L)
Benzene	0.5*
Carbon tetrachloride	0.5*
Chlordane	0.03*
Chlorobenzene	100.0*
o-Cresol	200.0*
m-Cresol	200.0*
Cresol (Total)	200.0*
2,4-D	10.0
1,4-Dichlorobenzene	7.5*
1,2-Dichloroethane	0.5*
1,1-Dichloroethylene	0.7*
2,4-Dinitrotoluene	0.13*
Hexachlorobenzene	0.13*
Hexachloro-1,3butadience	0.5*
Hexachloroethane	3.0*
Lead	5.0*
Nitrobenzene	2.0*
2,4,5-Trichlorophenol	400.0*
2,4,6-Trichlorophenol	2.0*

*New Toxicity Characteristics Effective 9/25/90

3. 0 METHODOLOGY

3.1 MATERIALS

The materials used for the analysis were volumetric flask, weighing balance, stirrer, pH meter, beakers, mortar, hydrometers, thermometer,sieve (2mm) conical flask (5mm) and Test tube (20ml) .

Reagents Potassium dichromate (K_2CrO_7), Sodium hydroxide (NaOH), Hydrochloric Acid (HCL), Ammonium Fluoride (NH_4F), Mixed boric Acid Indicator, Magnesium oxide (MgO), Potassium sulphate (K_2SO_4), Ammonium Acetate , Ferrous Sulphate ($FeSO_4$), O-Phenanthroline indicator, Sodium hexametaphosphate, Mercury catalyst, Ammonium molybdate $(NH_4)_6$ $MO_2O_{24,}$ distilled water, Phenolphthalein,

. 3.2 SOIL SAMPLING

The soil samples were collected in five (5) different areas north, south, East and west axis and at the immediate point of the occurrence (spilled) the depth of the samples collected was 45cm deep in each of the 5 areas and the distance was 1km in each axis. The soil sample collected was spread on flat trays to air dried at room temperature, keeping their identity unchanged in all stages for 3 days , the soil samples were crushed with a mechanical grinder and sieved through a 2mm sieve

3.3 PREPARATION FOR ANALYSIS

On the arrival of the soil samples in the laboratory, each soil samples were given laboratories numbers which was as follows:

Table 2

	SAMPLE	LAB. NO
A	(at the immediate point)	01
B	(North axis)	02
C	(South axis)	03
D	(East axis)	04
E	(West axis)	05

3.4 DETERMINATIONS

3.41 PARTICLE SIZE

51.0g each of the soil samples from the five (5) location were weighted and poured into a container, 50ml of sodium hexameta phosphate was added, and the soil mixture was shaken with the aid of mechanical shaker machine for 30 minutes the resultant solution was poured into a 1000ml cylinder and distilled H_2O was added up to the 1000ml mark. The cylinder was kept inverted until all the soil was in suspension. The temperature and the hydrometer reading were measured and the following textural class was obtained together with their amount in percentage.

The percentage was calculated using this formula

$$\frac{\text{Weight of extract}}{} \times 100 = \text{Weight of Sample}$$

3.4.2 pH

10g each of the air-dried soil samples collected in the 5 location were weighed on a weighing balance and put into a 50ml Beaker 10ml of distilled water was added, and stirred thoroughly the soil solution in the beaker was allowed to stand tor 30 mins and the pH meter into the settled suspension of the sample and reading was noted.

3.4.3 PHOSPHORUS

2g each of the air-dried soil samples from the 5 location were weighed into a 50ml beaker and 7ml of extracting solution was shaken for 10 minutes using mechanical shaker and allow to settle.

2ml of ammonium molybdate solution was added and mixed properly. 1ml of dilute $SnCl_2$. $2H_2O$ solution was then added up and mixed again. The mark of the test tube was made up with distilled H_2O and allows the colour to develop for 15 minutes and then measured as percentage transmittance on the electrophotometer at 660nm wavelength.

3. 4.4 Total Nitrogen

1g each of the soil sample from the 5 location was weighed into a 500ml macro-Kjedahi flask, 5ml of distilled water was added and stirred for 2 mins and allow to stand for 30 mins 1 tablet of mercury catalyst and 10g of K_2SO_4 was added with 30ml of conc. H_2SO_4 through an automatic pipe. The flast was continuously headed at low heat on the digestion stand. The flask was later cooled and about 100ml of the distilled water was added. The resulting solution was transferred into another clean macro-kjadahi flask (750ml) and the soil residue was washed with 50ml distilled water four times and the aquitos was transferred into a small flask.

50ml boric acid indicator (H_3BO_3) solution was added into a 500ml flask and was placed under condenser of the distillating apparatus.

750 kjedahi flask was attached to the distillation apparatus and about 150ml of NaOH was poured into the flask through the distillation flask opening.

The funnel stop clock commence distillation. The condenser was kept to cool at a temperature of 30^oC allowing sufficient cold water to flow through the regulated heat to minimize floating and sucking back. 150ml distillate was collected and the distillation was stopped. NH_4Cl in the distillate was determine by filtrating with 0.01m standard HCL of H_2SO_4 using a 25ml burette. The end point colour changes was from green to pink which according to Mckerizic and Wallace (1954) found this result as insufficient quantity of nitrogen.

3.4.5 POTASSIUM

5g each of the air-dried soil sample from the 5 locations were put into a $25cm^3$ beakers and shaken for 5 minutes and filtered. $1cm^3$ of the filtrate was mixed with a solution of formaldehyde and ethlylenecliamine tetraacetic acid (EDTA) in a $10cm^3$ volumetric flask after which $1cm^3$of the alkaline was forcibly injected with a hyperdomic needle after standing and diluting, the turbidity of the solution was measured using spectrometer set at a wavelength of 525nm. The purpose of injecting the reagent was to standardized the rates of its addition and hence of reaction.

3.4.6 ORGANIC CARBON

1g each of the air-dried soil from all the 5 location were weighted and put into a 250ml flask 10ml of conc. $KrCr_2O_7$ was added and then 20ml of conc. H2SO4 was added the solution was left to cool for 30 minutes after which 100ml of distilled water was added up to each of the sample 3 drops of 0-phenanthroline indicator was added to each of the soil sample and was shaken thoroughly 0.5m $FeSO_4$ was titrated against the content of the flask and the result of the titration was shaken.

The colour change was from orange to blue which is a clear indication of insufficient organic carbon.

3.4.7 MANGANESE

The soil samples from all the five (5) location were each wetted with nitric acid and hydrochloric acid (HCL) and was diluted to $100cm^3$ volumetric flasks. It was allow evaporate to dryness in a $150cm^3$ beaker to the residue left $10cm^3$ of conc. Nitric acid and $2cm^3$ of perchloric acid was added. The $150cm^3$ beaker was covered with a watch glass and evaporates on a hot plate until dense white fumes appear it was then cooled and take up in H_2O containing $2cm^3$ phosphoric acid 0.5g of sodium periodate was added. The solution was then diluted to $1000cm^3$ flask and the transmittance was read at 54nm.

4.0 RESULTS .

Table 3 Percentage values of Total nitrogen, Phosphorus and Potassium

A.	0.60	5.36	5.20
B.	0.70	6.50	6.15
C.	0.65	7.75	7.0
D.	0.70	7.25	5.60
E.	0.75	5.60	6.25

A -At the immediate point of spilled B -North axis (1Km) C - South(1Km) D
East(1Km) E - West(1Km)

Table 4 Particles Sizes Distribution

SAMPLE	% Sand	% Clay	% Loamy	% Silt	Textural class
A.	98.0	12.4	12.5	19.2	Sandy
B.	90.4	2.4	2.8	7.2	Loam
C.	96.4	2.4	2.5	1.2	Sandy
D.	94.4	2.4	2.5	1.2	Sandy loam
E.	58.4	20.4	20.4	21.2	loam

Table 5 The pH

SAMPLE	PH VALUES
A.	5.50
B.	6.51
C.	6.35
D.	6.43
E.	6.60

5 .0 DISCUSSION

The percentage of sand was high ranging from 58.4 – 98.4, silt varies from 1.2% - 2.12% clay ranges from 2.4 - 20.4%

The total nitrogen in all the 5 locations around the spilled area was low 0.60% - 0.7%. lowest at the immediate point (Sample A) and highest in D (East axis) of the area, 5.36 – 7.75%. of available phosphorus is highest in sample C (South axis) of the area which is about 7.75% and is lowest in Sample A (at the immediate point of spill) which is about 5.36%. , the potassium content in the soil sample is highest in C (South axis) of the spilled area which is about 7.0% and lowest in A (at the immediate point) 5.20% .Manganese present in the soil sample collected in the 5 different location around the spilled area shows a range of 4.0% and 6.% .

Organic carbon is highest in B (north axis) of the area about 8.6% and lowest in A (at the immediate point of spilled) about 6.50%. hence organic carbon plays an important role in the growth of plant its insufficient in the soil will cause infertility of the soil which lead to poor growth of plants.

All the 5 locations around the spilled area has fairly low level of calcium (Ca) from the data given in table 2 shows that, the available calcium in the sample of the spilled soil is lowest in A (at immediate point of occurrence) and highest in E (West axis) about 4.50% and 7.25% respectively.

The pH ranges from 5.50 – 6.60 the pH is low in E (West axis). This shows that, the response of crops to these areas will be very slow.

6.0 CONCLUSION

The soil samples collected from all the five (5) locations around the spilled area in Mbalim serves to be the baseline study that will provide information for soil management and environment which has been spilled with petroleum products.

Based on the properties determined the textural class of soil at the spilled soil at Mbalim area is sandy and loamy with pH unfavourable to most crops and does not meet any requirement for crop production and effective growth of plants.

Most of the soils samples studied in these areas were highly acidic. Other elements such as nitrogen (N), phosphorus (P) Potassium (K) Manganese (Mn) and organic matter contents were found to be slightly lower than expectation.

7 0 RECOMMENDATIONS

The following recommendations are possible remediation of this spillage area .

Bioremediation, involving microbial digestion of certain organic chemicals. Techniques used in bioremediation include landfarming, biostimulation and bioaugmentating planting of Hibiscus cannabinus an animal herbaceous plant can be used to absorb spilled petroleum products as well as introducing microfloral organism which has the ability to break down the spilled oil and, thus reducing its toxicity. Aeration of soils at the contaminated site which is still on. Thermal remediation by introduction of heat to raise subsurface temperatures sufficiently high to volatize chemical contaminants out of the soil for vapour extraction. Phytoremediation, or using plants (such as willow) to extract heavy metals
and quantity of leaf crops.

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