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ORIGINAL RESEARCH

Seasonal variation of nutrient composition in an oil spill contaminated soil: a case of Rumuolukwu, Eneka, Port Harcourt, Nigeria

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ABSTRACT

This study assessed the nutrient composition (including sulphate, nitrate and phosphate) and electrical conductivity in an oil spill contaminated soil along Shell Petroleum Development Company Right of way in Rumuolukwu, Eneka, Port Harcourt. Oil spill contaminated soil and control samples (50 m away from the contaminated site) were collected at different depth i.e. 0- 15cm, 15 - 30 cm, 30 – 45 cm and 45 – 60 cm across a period of 6 months i.e. August to October, 2013 (Wet season) and November 2013 to January 2014 (dry season). The samples were prepared and analyzed using standard procedures. The mean result at various depth for wet and dry season was 18.2 and 41.7 $\mu\text{S}/\text{cm}$ (electrical conductivity), 1.5 and 1.9 mg/kg (nitrate), 4.2 and 4.7 mg/kg (sulphate), 0.62 and 0.68 mg/kg (phosphate) respectively. The electrical conductivity and nutrient concentration in an oil spill contaminated soil were lower than the control soil. Also the concentration during the wet season was lower than the findings during the dry season. As such season affects nutrient concentration in an oil spill contaminated soil.

KEY WORDS: *Nutrient composition, Oil spill, Pipeline, Right of way*

Introduction

Crude oil exploration and production is a major source of earning to Nigeria following oil boom of 1970's. According to Ohimain (2013a,b), approximately 90% and 85% of Nigeria export and earning respectively are provided by petroleum. Oyem and Oyem (2013) also noted that crude oil is the main sources of foreign exchange and energy for several industries. As such Nigeria loss her place in commercial agriculture, where major cash crops such as cocoa, rubber and oil palm are main exports.

The exploration of crude oil and its processing into several products has led to several environmental pollution. For instance, dredging and canalization activities prior to

exploration in offshore leads environmental impacts (Ohimain, 2012) including heavy metal contamination (Ohimain et al., 2011, 2009; Ohimain, 2010), changes in water quality (Ohimain et al., 2008a,b), zooplankton (Ohimain et al., 2002). Oil spill when there is a leakage in the pipeline conveying it to another destination. Oil spill is caused by vandalism and or rupture oil facilities, Oil spill in various value chain of crude oil production have an impact on the ecosystem and its biota. For instance, on aquatic ecosystem it could impact on surface water and its biota including fisheries (fin and shelled fish), macrophytes and other aquatic plants. It could also contaminate ground water resources. Also during crude oil and natural gas

exploration, excess gas is flared into the ecosystem affecting soil fertility, crop yield (Ozabor and Obisesan, 2015; Olisemauche and Avwersuoghene, 2015), soil physicochemical parameters such as pH, temperature, soil moisture, soil microbial population (Ubani and Onyejekwe, 2013), phytochemical in plant (Ifemeje, 2015; Ujowundu et al., 2013), water quality (Dami et al., 2012, 2013; Mogborukor, 2014; Ubani and Onyejekwe, 2013; Ezenwaji, Okoye and Otti, 2013; Emumejaye, 2012), infrastructure (Iyorakpo and Odibikuma, 2015), human health (Nriagu et al., 2016; Donwa et al., 2015; Egwurugwu et al., 2013a, b; Egwurugwu and Nwafor, 2013).

Specifically, crude oil spilled into the environment could affect soil and its properties including general physicochemical, heavy metal, hydrocarbon and nutrient content. Variation in the soil characteristics could lead to changes in the composition of soil microflora. Typically, soil microflora play essential role in the soil including degradation of compounds and materials in addition to their role in biogeochemical cycles and rhizosphere depending on the microbial species.

According to Mussa et al. (2009), soil is a weathered superficial layer of the earth's crust which is made up decomposed and or decomposing parent rock material which associated with organic matter. The authors furthered reported that plant in the soil absorbs water and solutes essential for growth. Soil is also a platform through which plants and other infrastructures are anchored on.

Soil fertility is determined based on the nutrient composition. The soil nutrient composition includes anions (such phosphate, nitrate, nitrite, sulphate, carbonate, bicarbonate, etc) and cations (potassium, magnesium, calcium, sodium). Each of the nutrient play essential roles in the soil and under unfavourable conditions could affect the physiology and growth mechanism of plant that utilizes them. In addition, some anions assist in reducing the disease incidence in roots and leaves of plant could also be affected (Edeogu, 2007). Again, The affinity for adsorption of some of anions commonly present in soil is in the order: nitrate< chloride< sulphate< phosphate, as such anions easily adsorbed are lost by leaching processes (Mussa et al., 2009)

Therefore, this present studies aimed at determining nutrient (phosphate, sulphate and nitrate) and electrical conductivity

in a pipeline oil spill soil in Rumuolukwu, Eneka, Port Harcourt, Nigeria

Materials and Methods

Study area

Rumuolukwu community is within Eneka district in Port Harcourt metropolis. Rumuolukwu is located in Obio/Akpor Local Government Area of Rivers State. Like other region in the Niger Delta, two predominant climatic conditions is found in the area including dry season (November to March of the following years) and wet season (April to October). The region is characterized by relative humidity and temperature of 50 – 95% and 30 ± 7 respectively all year round. Shell Petroleum Development Company (SPDC) right of way passes through the community. The study was carried out in SPDC damage of the pipeline that led an oil spill within the right of way.

Sampling collection and preparation

The oil impacted site was mapped out such as to cover the spill area, as the plot was about 20 meters from point source of oil contamination (faulty oil pipeline). The total sampling area was measured to be about 100 m x 50 m area. Soil was collected at four (4) different depths at the plot centre of oil spill site (0 - 15 cm, 15 - 30 cm, 30 - 45 cm and 45 - 60 cm). Sampling covers a period of six months between August 2013 and January 2014 covering 3 month wet season (August – October) and 3 months dry season (October – January of the following year i.e. 2014). Prior to sample collection, a petroleum or oil sheen test as recommended by the Minnesota Pollution Control Agency (MPCA, 2008) was carried out to ascertain that the site under study was actually saturated or contaminated with crude oil. Soil samples collected were air dried under ambient temperature. The dried samples were homogenized, grounded and filtered by passing through a 2 mm mesh size.

Experimental Methods

Determination of Soil Electrical Conductivity

The electrical conductivity measurements of the soil samples were measured electrometrically using a conductivity meter. The conductivity meter was switched on. The electrode was rinsed with distilled water severally as the meter was calibrated using a 0.01 M potassium chloride (KCl) standard

solution, this standard reference solution at 25°C has an electrical conductivity of 1413 $\mu\text{S}/\text{cm}$. About 20 g of air-dried soil (crushed and passed through a 2-mm mesh size sieve) was weighed into a 50 ml beaker and 20 ml of distilled water was added so that a 1:1 soil to water ratio was attained; this soil-water mixture was allowed to stand for 30 minutes and stirred occasionally with a glass rod. The electrode of the conductivity meter was inserted into the partly settled suspension or supernatant after which the electrical conductivity was measured whilst avoiding the stirring of suspension during measurement and ensuring that the electrodes were rinsed with distilled water intermittently between readings before being wiped dry with a clean tissue or filter paper after each reading.

Nitrate determination

Soil nitrate were determined using Na-acetate Extraction Method:

Extraction procedure –About 5.0 g of soil was transferred into a shaking bottle and 1/4 teaspoon (about 0.25 g) of activated carbon and 20 ml of extracting solution (100 g Na-acetate + 30ml of 99.58% acetic acid, diluted to 1 liter) was agitated for 1 minute before filtration.

Test Procedure - A 1 ml aliquot of the soil extract was transferred to a sample vial and mixed. 0.5 ml of the brucine reagent (2.5 g brucine sulphate in 100 ml glacial acetic acid) was added, followed rapidly by the addition of 2 ml sulphuric acid. This solution was mixed for about 30 seconds and allowed to stand for 5 minutes. Solution was mixed again before 2 ml distilled water was added with continuous mixing for about 30 seconds. Afterwards, water was added to make solution up to the 10 ml mark of the sample vial. Vials were stood, while leaving them to be air-cooled for about 15 minutes (to allow the test solution form a brownish color) (Greweling and Peech, 1965), this was read as ppm nitrate (NO_3^-), at an absorbance measured at 400 nm using the HACH DR 890 colorimeter.

Sulphate determination

Extraction/Test Procedure–Extraction was carried out using KH_2PO_4 Extraction Method. About 5 g of soil sample (air-dried, 2 mm mesh size sieved) was weighed into a centrifuge tube and 25 ml of extracting solution (KH_2PO_4 solution containing 500 ppm P) was added. The soil solution was

agitated for 30 minutes on a mechanical shaker before the suspension was filtered through a Whatman filter paper (Ensminger, 1954). 10 ml of sample aliquot was pipetted into a 25 ml volumetric flask and made up to volume with distilled water; 1 ml of a gelatin- BaCl_2 reagent (0.6 g gelatin in 200 ml hot distilled water + 2 g BaCl_2 , refrigerated solution) was added, making the volume up to mark with thorough mixing, after which, the content was left to stand for 30 minutes (the test solution formed a whitish precipitate) and was measured at 420 nm (Tabatabai, 1974) using a HACH DR 890 colorimeter.

Phosphate determination

Phosphate in the soil samples was determined using Bray No. 1 Method.

Test Procedure–About 1 g of air-dried soil sample (passed through a 2 mm sieve) was weighed into a 15 ml centrifuge tube and 7 ml of extracting solution (15 ml, 1.0 N NH_4F + 25 ml, 0.5 N HCl + 460 ml distilled water) was added. The suspension was agitated on a mechanical shaker for 1 minute, after which it was centrifuged at 2,000 rpm for 15 minutes. 2 ml of clear supernatant was pipetted into a 20 ml test tube while, 5 ml of distilled water and 2 ml of ammonium molybdate was added. Content was mixed properly, followed by the addition of stannous chloride dilute solution (1 ml SnCl_2 stock solution (10 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 25 ml of conc. HCl) + 333 ml distilled water). A 10-minute reaction time was allowed and a bluish colour indicating the presence of phosphate ion was developed and read at a wavelength of 840 nm (Bray and Kurtz, 1945) using a HACH DR 890 colorimeter. A blank, consisting of distilled water and every other reagent as applicable to the test sample extract was mixed and used to zero the equipment. The concentration of PO_4^{3-} present in test sample was read as ppm $\text{PO}_4\text{-P}$.

Results and Discussion

Electrical conductivity and nutrient composition in soil contaminated by pipeline oil spill in Rumuolukwu, Eneka is presented in Table 1. The concentration of electrical conductivity and nutrients (nitrate, sulphate and phosphate) is lesser in contaminated soil compared to the control. This suggests that oil spill reduces nutrient composition in soil. Also the findings of this study also suggest that oil spill decreases the ability of the soil to convey electrical current.

Table 2 presents the seasonal variation in electrical conductivity and nutrients composition in oil spill contaminated soil at 0 - 30 cm depth. At August to October 2013 (wet season) for 0 – 30 cm depth, the mean electrical conductivity was 18.2 $\mu\text{S}/\text{cm}$ in contaminated soil and 26.8 $\mu\text{S}/\text{cm}$ in the control. Similarly during the dry season (November 2013 to January 2014) for 0 – 30 cm depth, the mean electrical conductivity was 41.7 $\mu\text{S}/\text{cm}$ (contaminated soil) and 71.8 $\mu\text{S}/\text{cm}$ (non- contaminated soil) Again the electrical conductivity soil at both season decreases with depth during both dry and wet seasons. This was similar to the findings of Benka-Coker and Ekundayo (1995), Oyem and Oyem (2013), Agbogidi et al. (2007) who reported lower electrical conductivity in oil contaminated soil compared to control. However in August 2013 of this study apparent lower conductivity was observed in the control compared to the contaminated soil. This could have arisen from the effect of soil topography, soil drainage conditions, heavy rainfall and occasional flooding which may have led to the erosion of organic-rich residues and transportation of leached nutrients from surrounding farmlands, thereby leading to enhanced soil nutrients of the oil contaminated soil. To this effect previous study in an oil spill contaminated soil at Owaza in Abia State suggests that there was positive correlation between soil Electrical conductivity and drainage conditions (Osuji and Nwoye, 2007).

Based on Table 2, the nitrate concentration at August to October 2013 (wet season) for 0 – 30cm depth, 1.5 mg/kg contaminated soil and 4.3 mg/kg in the control. Furthermore during the dry season (November 2013 to January 2014) for 0 – 15 cm depth, 1.9 mg/kg in contaminated soil and 5.1 mg/kg in non-contaminated soil. The observed trend in this study conformed with the earlier findings of Benka-Coker and Ekundayo (1995), Agbogidi et al. (2007). The low Nitrate levels in the oil contaminated soil could have resulted from the effect of oil contained in the soil which might have induced acidification of the soil (McKenzie, 2003). However, there was a steady rise in Nitrate levels for both the contaminated and control plots during the dry season, the comparatively lower levels of Nitrate in the oil contaminated soil during the dry season could have been as a result of the slow microbial nitrification of ammonium into Nitrates, leaving only crops which can absorb ammonium with access to

nitrogen (McKenzie, 2003)

Furthermore, the comparatively lower Nitrate levels during the rainy season conformed with earlier findings of McKenzie (2003), Osuji and Nwoye (2007) that suggested that in low CEC soil, the soil particles cannot bind strongly to the Nitrate ions, as a result, upon heavy rain, the Nitrates leach away into ground water or surface water and is washed away making them unavailable to crops. In water logged soil, Nitrates can be converted into N_2 and N_2O gases, which are then lost to the atmosphere. The effect of rainfall and flooding during this study period may similarly be attributed to nutrient loss in oil contaminated soil. The lower levels of Nitrate could also have been an indication that the oil contaminated soil structure and water retention capacity might have been destroyed, leading to the denitrification process (Hodges, 1996).

At August to October 2013 (wet season) for 0 – 15 cm depth, the mean sulphate was 4.2 mg/kg for crude oil contaminated soil and 13.4 mg/kg for control. Furthermore, during the dry season (November 2013 to January 2014) for 0 – 15 cm depth, the mean sulphate was 4.7 mg/kg for contaminated soil and 16.5 mg/kg for non-contaminated soil. The findings of this study are comparable to other study on crude oil contaminated soil. Benka-Coker and Ekundayo (1995) reported that soil nutrients in oil contaminated soil are generally lower in comparison to control soil. The lower sulphate level of the oil contaminated plot may have resulted from the similar effect of oil contained in soil which might have induced acidification of the soil.

At August to October 2013 (wet season) for 0 – 15 cm depth, the mean was 0.62 mg/kg for crude oil contaminated soil and 1.70 mg/kg for control. However, during the dry season (November 2013 to January 2014) for 0 – 15 cm depth, the mean phosphate was 0.68 mg/kg for contaminated soil and 1.84 mg/kg for non-contaminated soil. Like sulphate, lower phosphate levels may have resulted from the effect of oil contained in the soil which might have induced acidification of the soil. The trend of this study is comparable to the work of Benka-Coker and Ekundayo (1995) who reported that soil nutrients in oil contaminated soil are generally lower compared to non-contaminated soil.

Table 1: Electrical conductivity and nutrient composition in oil spill contaminated soil

Month	Parameter(s)	CPS (0-15)	CPS (15-30)	CPS (30-45)	CPS (45-60)	COMPS (0-15)	COMPS (15- 30)	Mean	CCS (0-15)	CCS (15-30)	CCS (30-45)	CCS (45-60)	COMCS (0-15)	COMCS (15- 30)	Mean
Aug 2013	Nitrate(mg/kg)	2.0	1.6	1.3	1.0	1.7	1.3	1.48	5.1	3.4	2.8	1.5	4.6	4.0	3.57
	Sulphate(mg/kg)	8.0	2.3	2.0	1.4	3.2	1.9	3.13	16.1	14.5	10.6	7.3	13.7	10.2	12.07
	Phosphate(mg/kg)	0.89	0.76	0.62	0.50	0.48	0.35	0.6	1.67	1.53	0.88	0.55	2.14	1.96	1.46
	EC(μ S/cm)	26	28	11	6	19	14	17.33	20	7	9	13	36	13	16.33
Sept 2013	Nitrate(mg/kg)	1.5	1.3	0.8	0.6	1.4	1.0	1.20	3.9	2.7	2.1	1.2	3.4	2.8	2.68
	Sulphate(mg/kg)	5.3	1.6	1.2	0.9	2.5	1.6	2.18	13.7	11.3	8.7	4.9	10.1	7.8	9.42
	Phosphate(mg/kg)	0.82	0.71	0.45	0.28	0.43	0.27	0.49	1.33	1.20	0.75	0.43	1.64	1.49	1.14
	EC(μ S/cm)	9	5	9	2	3	5	5.50	22	7	3	4	29	11	12.67
Oct 2013	Nitrate(mg/kg)	1.3	1.2	0.7	0.4	1.3	0.8	0.95	NM	NM	NM	NM	NM	NM	NM
	Sulphate(mg/kg)	4.1	1.3	1.1	0.7	2.0	1.2	1.73	NM	NM	NM	NM	NM	NM	NM
	Phosphate(mg/kg)	0.70	0.67	0.41	0.22	0.37	0.24	0.435	NM	NM	NM	NM	NM	NM	NM
	EC(μ S/cm)	30	11	22	25	22	25	22.5	NM	NM	NM	NM	NM	NM	NM
Nov 2013	Nitrate(mg/kg)	1.6	1.4	0.9	0.6	1.2	1.0	1.12	NM	NM	NM	NM	NM	NM	NM
	Sulphate(mg/kg)	4.0	1.5	1.2	0.7	1.7	1.4	1.75	NM	NM	NM	NM	NM	NM	NM
	Phosphate(mg/kg)	0.79	0.71	0.53	0.29	0.40	0.28	0.5	NM	NM	NM	NM	NM	NM	NM
	EC(μ S/cm)	21	17	11	23	11	19	17	NM	NM	NM	NM	NM	NM	NM
Dec 2013	Nitrate(mg/kg)	1.9	1.4	1.2	1.0	1.6	1.1	1.35	4.6	3.0	2.8	1.8	4.2	3.5	3.32
	Sulphate(mg/kg)	7.2	1.9	1.8	1.1	2.4	1.7	2.68	15.8	12.4	9.2	6.7	12.8	10.0	11.15
	Phosphate(mg/kg)	0.93	0.80	0.60	0.42	0.42	0.33	0.58	1.58	1.36	0.90	0.61	1.85	1.57	1.31
	EC(μ S/cm)	28	22	20	26	26	25	24.50	29	27	24	26	36	26	28.00
Jan 2014	Nitrate(mg/kg)	2.7	2.0	1.5	1.1	2.2	1.4	1.77	6.3	4.8	3.6	2.2	5.4	4.4	4.45
	Sulphate(mg/kg)	10.0	2.6	2.2	1.3	2.8	2.1	3.50	22.0	17.8	14.4	9.3	15.4	12.6	15.25
	Phosphate(mg/kg)	1.04	0.91	0.76	0.48	0.51	0.39	0.68	1.87	1.61	1.12	0.68	2.06	1.79	1.52
	EC(μ S/cm)	62	72	50	50	102	38	62.33	88	124	146	116	134	172	130.00

CPS - Centre of polluted Site, COMPS - Composite of polluted site, CCS - Centre of control site, COMCS - Composite of control site; NM-Not monitored

Table 2: Seasonal variation in electrical conductivity and nutrient composition in oil spill contaminated soil at 0-15cm and 15-30cm depth

Sampling Site	Rainy season (August - October 2013)			Dry season (November 2013 - January 2014)			
	Range	Mean	Standard deviation	Range	Mean	Standard deviation	
Electrical Conductivity Values ($\mu\text{S}/\text{cm}$)							
Oil Contaminated	(0-15cm)	3 - 30	18.2	10.3	11 – 102	41.7	34.2
	(15-30cm)	5 - 28	14.7	9.9	17 – 72	32.2	20.9
Control	(0-15cm)	20 - 36	26.8	7.3	29 – 134	71.8	49.1
	(15-30cm)	7 - 13	9.5	3.0	26 – 172	87.3	72.8
Nitrate Concentrations (mg/kg)							
Oil Contaminated	(0-15cm)	1.3 - 2.0	1.5	0.3	1.2 - 2.7	1.9	0.5
	(15-30cm)	0.8 - 1.6	1.2	0.3	1.0 - 2.0	1.4	0.3
Control	(0-15cm)	3.4 - 5.1	4.3	0.8	4.2 - 6.3	5.1	0.9
	(15-30cm)	2.7 - 4.0	3.2	0.6	3.0 - 4.8	3.9	0.8
Sulphate Concentrations (mg/kg)							
Oil Contaminated	(0-15cm)	2.0 - 8.0	4.2	2.2	1.7 - 10.0	4.7	3.2
	(15-30cm)	1.2 - 2.3	1.7	0.4	1.4 - 2.6	1.9	0.4
Control	(0-15cm)	10.1 - 16.1	13.4	2.5	12.8 - 22.0	16.5	3.9
	(15-30cm)	7.8 - 14.5	11.0	2.8	10.0 - 17.8	13.2	3.3
Phosphate Concentrations (mg/kg)							
Oil Contaminated	(0-15cm)	0.37 - 0.89	0.62	0.22	0.40 - 1.04	0.68	0.28
	(15-30cm)	0.24 - 0.76	0.50	0.24	0.28 - 0.91	0.57	0.27
Control	(0-15cm)	1.33 - 2.14	1.70	0.33	1.58 - 2.06	1.84	0.20
	(15-30cm)	1.20 - 1.96	1.55	0.31	1.36 - 1.79	1.58	0.18

In all the nutrient compositions, the top soil of both the oil contaminated and control soils retained more sulphate, phosphate and nitrate than the sub soils, as nutrients concentrations characteristically decreased with further depth. This may have resulted from nutrient demand by crops within the root zone and the predominance of sand presence of higher sandy soil compositions in both the contaminated and control soil and the predominance of sandy clay loam soils which may have led to a higher nutrient retention at the top soil, as higher clay contents of the bottom soil may have reduced the penetration of nutrients to further depths. This observation has been previously reported by Hodges (1996) suggesting that clay soils tend to retain more soil nutrients.

Conclusion

In this study, the nutrient (sulphate, nitrate and phosphate) and electrical conductivity in pipeline oil spill contaminated soil in Rumuolukwu, Eneka, Port Harcourt. Results show that the soils samples around crude oil contaminated soil decreases in nutrient and electrical conductivity concentration compared to control. This is an indication that crude oil in spoil alters soil chemical parameters which could affect plant growth and yield in the environment. The study also found that season affect soil nutrient, with high concentration observed during the dry season at various depth as compared wet season in both oil spill contaminated soil and control.

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