Proceedings of the Annual International Conference on Soils, Sediments, Water and Energy

Volume 17 Article 2

2012

Characteristics of Soils and Heavy Metal Content of Vegetation in Oil Spill Impacted Land in Nigeria

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PART I: Heavy Metals

Chapter 1

CHARACTERISTICS OF SOILS AND HEAVY METAL CONTENT OF VEGETATION IN OIL SPILL IMPACTED LAND IN NIGERIA

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ABSTRACT

This study examined the impact of an oil spill on soil characteristics and heavy metal content of vegetation. Soil and vegetation were sampled using a 1 metre square quadrant at distances of 1 m, 10 m, 20 m and 30 m from the oil spill. After vegetation identification, they were separated into leaves, stems and roots. Analysis of soil characteristics and heavy metals (Pb, Cd and Zn) content of the vegetation was carried out. The data were analyzed using descriptive statistics and ANOVA. *Calopogonium mucunoides, Axonopus compressus and Sida acuta* were identified. Leaves had higher heavy metals content followed by stems and roots. Concentrations of heavy metals in the soils with respect to distances were in the order of 1 m > 10 m > 20 m > 30 m. Soil organic carbon content ranged from 18.75 – 27. 30 g/kg. The soils heavy metal concentrations ranged from 0.10 – 0.18 mgCd/kg, 0.34 – 0.46 mgZn/kg and 0.28 – 0.44 mgPb/kg.

Key words: Soils characteristics; Vegetation; Heavy metals; Oil impacted land

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1. INTRODUCTION

The amount of oil produced and transported between points of production, processing and distribution, or export terminals, has greatly increased as the demand of and dependence on oil has increased. Although this increase in oil production level contributes to Nigeria's economic growth, it also presents increased potential for environmental pollution and degradation. Contamination of soils with crude oil and refinery products is becoming an ever-increasing problem especially in the light of several breakdowns of oil pipelines and wells and distribution of petroleum-based products (Song and Barhta, 1990; Amadi et al., 1996; Jorgensen et al., 2000). Nigerian crude oil is known to have about 0.003 – 42.31 mg/kg of transition metals (V, Cr, Mn, Fe, Co, Ni and Cu) (Nwachukwu et al., 1995); some of which can not be completely removed during the crude refining processes. Once they enter ecosystems, petroleum-based products initiate a series of processes, affecting both biotic and abiotic elements (Malachowska-Jutsz et al., 1997). Oil spills on land may lead to retardation of vegetation growth and causes infertility of soil for a long period of time until natural processes re-establish stability (Sparrow and Sparrow, 1988; Racine, 1993; Wyszkowska et al., 2001). Several studies have shown that metals, such as Pb, Cd, and Ni, are responsible for certain diseases of man and animals (Gustav, 1974). Thus, there is need to clean up oil contaminated soil. Conventional remedial methods include removal of the contaminated soil from the sites, covering the contaminated area with barren soils or impervious cover, remediation in situ to remove contaminants and remediation by reducing bioavailability. (Gleseler, 1987). Remediation by conventional technologies is very expensive (Salt et al., 1995). Therefore, comparatively cheaper and feasible sustainable methods of pollutant removal from soil are necessary. Phytoremediation has emerged as an alternative to the engineering-based methods. In this approach, plants are used to absorb contaminants from the soil and translocate them to the roots, stalk or shoot. The metal-rich plant material may be safely harvested and removed from the site without extensive excavation, disposal cost and loss of top soil associated with traditional remediation practices (Blaylock et al., 1997, Joner et al., 2004). Rock and Sayre (1998) estimated phytoremediation clean up costs of \$ 162 per m^3 compared to \$ 810 per m^3 for excavation and incineration. Identification of plants growing in oil spill impacted land is of prime importance in order to establish suitable plants for the clean up of such oil spills. The objective of this study was to examine the impact of oil spill on soil characteristics and heavy metal content of vegetation growing on the impacted land.

2. MATERIALS AND METHODS

2.1 Study area

This study was carried out at the Atlas Cove-Mosimi Pipeline Right of Way, Mosimi, Sagamu, Ogun State, Nigeria on latitude 6º 45' 18" N, longitude 3º 33' 5" E, at altitude of 77 m.

2.2 Soil and plant sampling

Plants growing along the pipeline were sampled using a 1 m square quadrant at distances of 1 m, 10 m, 20 m and 30 m away from the edge of the pipeline. Vegetation within the quadrant was identified and samples were uprooted for laboratory analysis. Each vegetation sample was replicated three times. The plant samples were kept in labeled polyethylene bags and taken to the laboratory for analysis. Composite soil samples were taken at similar distances (1 m, 10 m, 20 m and 30 m) away from the edge of the pipeline. Ten core samples randomly distributed around the observation points were taken with the aid of stainless steel Dutch auger and bulked. Sampling depths were 0 – 15 cm and 15 – 30 cm, which represent the main feeding zones of the plant roots. Each composite soil sample was replicated three times along each road and the samples were kept in labeled polyethylene bags.

2.3 Chemical analysis

Soil samples were air dried, crushed and passed through a 2 mm sieve. Soil pH was determined using a hand-held HANNA pH meter (Model number HI 98129, Hanna Instruments, California, USA) in distilled water according to Thomas (1996). Soil organic carbon was determined by the chromic acid digestion method of Walkley and Black as reported by Sparks (1996). The total N concentration was determined by the Macro-kjeldahl method according to Bremner (1996). Available P was determined by Bray-I method as described by Kuo (1996). Exchangeable Ca, Mg, K and Na were extracted with neutral normal ammonium acetate buffer according to Helmke and Sparks (1996). K and Na were determined using a Flame Photometer (Jenway, Gransmore Green, Felsted, Dunmow, Essex, CM6 3LB, England) and exchangeable Ca and Mg by Atomic Absorption Spectrophotometer (AAS, Varian SpectrAA-400plus, Varian Techtron Pty limited Mulgrave, Victoria, Australia). Flame Photometer was calibrated for each metal using standard solution of known concentrations (5 ppm, 10 ppm, 15 ppm and 20 ppm of sodium chloride and potassium chloride) while serial standard ranging from 0.03 ppm to 24 ppm were prepared from 1000 ppm industrially prepared standards and used to calibrate the AAS to get line of best fit before analysis. To determine soil heavy metals (Pb, Cd and Zn) content, one gram of the soil sample (< 2 mm fraction) was digested in 1:1 mixture of concentrated nitric and perchloric acids and the mixture was heated over a water bath in a fume cupboard. The solution was heated to dryness and the residue was re-dissolved in 5 ml of 2.0 M HCL as in Ure (1990). The mixture was finally filtered (Whatman No. 40). The resultant extracts were analyzed for the heavy metals using AAS (APHA - AWWA - WPCF, 1980).

The plant samples were placed under running tap to wash off soil particles and oven-dried at 80 ^{0}C for 48 hours. Each sample of the dried plant materials was ground to a fine powder using a laboratory stainless steel hammer mill in order to pass through 1 mm aperture screen. Ground plant samples were collected in polythene bags and kept in desiccator. For the determination of heavy metals, 2 g of each ground sample was accurately weighed into clean platinum crucibles, ashed at 450 °C and then cooled to room temperature in a desiccator. The ash was completely dissolved in 5 ml of 20 % HCl which was then made up to volume (50 ml) while 0.3 g was digested with 4 ml of concentrated sulphuric acid along with drops of hydrogen peroxide for the determination of exchangeable bases (Na, K, Ca and Mg) (Alloway, 1995). Analysis of the digest for the metals content was carried out using AAS.

2.4 Statistical analysis

Data were analyzed using descriptive statistics and Analysis of Variance (ANOVA). Test of significance of the means was by the Least Significant Difference (LSD).

3. RESULTS AND DISCUSSION

3.1 Plant identification at various distances from point of oil spill

Calopogonium mucunoides, *Axonopus compressus* and *Sida acuta* were identified in the oil spill impacted area. *Calopogonium mucunoides* was identified at every distance except 30 m away from the source of pollution (Table 1). These three plant species were able to tolerate the toxicity of oil spill. Prasad and Feitas (2003) identified *Fabaceae*, *Poaceae*, *Euphorbiaceae* and *Flacourtiaceae* as potential hyperaccumulators of heavy metals. Similarly, Bada and Raji (2010) observed that *Malvaceae* absorbed heavy metal from contaminated soil.

Table 1. Plant species encountered on the field

Distance (m)	Family	Plant species	Common name
1	Fabaceae	*Calopogonium mucunoides*	Calopo
	Poaceae	*Axonopus compressus*	Carpet grass
10	Fabaceae	*Calopogonium mucunoides*	Calopo
	Malvaceae	*Sida acuta*	Broom weed
20	Fabaceae	*Calopogonium mucunoides*	Calopo
30	Malvaceae	*Sida acuta*	Broom weed

3.2 Heavy metals and exchangeable cations in plant species

Calopogonium mucunoides at 1 m away from source of oil spill had the highest Cd, Zn and Pb followed by *Axonopus compressus* at 1 m and *Calopogonium mucunoides* at 10 m (Table 2). The levels of heavy metals in the plants decreased with distance away from the point of pollution, as reported by Amusan et al. (2003). This might be due to the proximity of the plants to the source of oil spill. Two basic strategies to explain heavy metal tolerance, metal exclusion and metal accumulator, have been identified (Baker, 1981; Steinborn and Breen, 1999; Yanqun et al., 2004). The excluders prevent metal uptake into roots, avoiding translocation and accumulation in shoots (De Voss et al., 1991). These plants have a low potential for metal extraction but could be used to stabilize the soil. Accumulators concentrate heavy metals in their shoots at both low and high soil metal concentrations and are utilized in extracting heavy metals from contaminated soils (Rotkittikhun et al., 2006). In plants that accumulate heavy metals, shoot/root quotients greater than 1 are commonly reported, while shoot/root quotients less than 1 characterize heavy metal excluders (Ogundiran and Osibanjo, 2008). *Calopogonium mucunoides*, *Axonopus compressus* and *Sida acuta* were potential Zn and Pb accumulators while *Calopogonium mucunoides* and *Axonopus compressus* were Cd accumulators (Table 3); shoot/root quotient greater than 1 (Ogundiran and Osibanjo, 2008). Significantly ($p < 0.05$) higher exchangeable bases (Na, K, Mg and Ca) were observed in the *Sida acuta* at 30 m away from the point of oil spill (Table 2). Significantly ($p < 0.05$) higher Na was observed in the roots, while leaves had higher concentrations of K, Mg and Ca. Contrary to heavy metals, concentration of exchangeable bases increased with distance away from the point of the oil spill. This might result from the degradation of the soil exchangeable bases close to the point of the oil spill. Oil spills on land may lead to infertility of soil for a long period of time until natural processes re-establish stability (Wyszkowska et al., 2001). *Calopogonium mucunoides* and *Axonopus compressus* were exchangeable bases accumulators while Sida *acuta* was a potential Na excluder (Table 3); shoot/root quotient less than 1 (Ogundiran and Osibanjo, 2008)

3.3 Effects of oil spill on soil characteristics

Soil acidity decreased with distance from the point of the oil spill. It also decreased with soil depth except at 30 m away (Table 4). The negative effect of oil on the soil pH can be attributed to the change in soil biochemistry (Atuanya, 1987). Atuanya (1987) confirmed that oil may alter soil biochemistry parameters such as pH, oxygen and nutrient availability. Also, the reduction in the soil pH might be attributed to the production of organic acids by microbial metabolism (Osuji and Nwoye, 2007). However, soil organic carbon content generally increased with distance and it decreased with soil depth (Table 4). Decrease in the organic carbon content close to the point of the oil spill might be due to reduced soil fertility. Oil spills on land may lead to infertility of soil for a long period of time until natural processes re-establish stability (Wyszkowska et al., 2001). Higher heavy metals contents were observed in the soil very close to the source of pollution and this decreased with soil depth (Table 4). The higher metal content might be due to proximity to the source of pollution. Nigerian crude oil contains heavy metals which are not completely removed during refining processes (Nwachukwu et al., 1995). Exchangeable bases increased with distance and decreased with soil depth (Table 4).

5. CONCLUSION

We demonstrate that an oil spill increased acidity and heavy metal content of the soil. It reduced soil organic carbon and exchangeable bases. *Calopogonium mucunoides*, *Axonopus compressus* and *Sida acuta* were identified from oil spill impacted land and contained Pb, Cd, Zn. Phytoremediation of heavy metal contaminated soil can be achieved by the use of these plants.

Table 2. Metals (mg/kg) contents of plant parts collected from oil impacted area

Distance (m)	Plant species	Plant parts	Cd	Zn	Pb	Na	K	Mg	Ca
1	*C. mucunoides*	Root	0.13	0.87	0.30	7.41	2.52	23.96	47.25
		Stem	0.15	1.00	0.37	4.91	2.69	24.30	54.15
		Leaf	0.21	1.44	0.39	4.23	2.69	27.02	56.75
	A. compressus	Root	0.12	0.71	0.28	4.18	1.79	7.80	38.90
		Stem	0.14	0.87	0.35	3.56	2.37	19.82	41.91
		Leaf	0.17	1.29	0.37	7.64	2.51	23.06	43.71
10	*C. mucunoides*	Root	nd	0.62	0.14	7.63	2.97	31.06	56.87
		Stem	0.10	0.63	0.22	5.05	3.00	33.26	61.90
		Leaf	0.12	0.69	0.27	5.44	3.18	33.88	63.44
	S. acuta	Root	nd	0.59	0.09	12.19	3.32	36.51	65.82
		Stem	0.01	0.62	0.22	4.57	3.50	39.07	80.40
		Leaf	0.11	0.63	0.25	4.75	3.77	44.09	82.44
20	*C. mucunoides*	Root	nd	0.44	0.02	9.31	3.94	47.78	84.39
		Stem	nd	0.48	0.05	5.98	4.29	50.10	99.12
		Leaf	nd	0.58	0.05	5.19	4.35	53.83	102.20
30	*S. acuta*	Root	nd	0.33	nd	49.86	6.36	56.71	107.26
		Stem	nd	0.41	0.01	4.41	8.09	69.84	163.08
		Leaf	nd	0.43	0.02	4.59	26.46	72.66	212.36
		LSD	0.05	0.53	0.11	2.68	1.50	22.85	60.26

nd = not detected

Table 3. Shoot/Root quotient of plants collected from oil contaminated area

Distance	Plant species	Cd	Zn	Pb	Na	K	Mg	Ca
1	*C. mucunoides*	2.79	2.80	2.53	1.23	2.13	2.14	2.35
	A. compressus	2.53	3.04	2.57	2.68	2.73	5.50	2.20
10	*C. mucunoides*	nd	2.13	3.50	1.37	2.08	2.16	2.20
	S. acuta	nd	2.12	5.22	0.76	2.19	2.28	2.47
20	*C. mucunoides*	nd	2.41	5.00	1.20	2.19	2.18	2.39
30	*S. acuta*	nd	2.55	nd	0.18	5.43	2.51	3.50

nd = not determined

Table 4. Selected soil characteristics in the oil impacted area

Distance (m)	Soil depths (cm)	pH	Organic carbon (g/kg)	Cd (mg/kg)	Zn (mg/kg)	Pb (mg/kg)	Na (cmol/kg)	K (cmol/kg)	Mg (cmol/kg)	Ca (cmol/kg)
1	0-15	5.38	21.20	0.18	0.46	0.44	2.42	1.22	4.96	13.52
	15-30	5.76	18.75	0.14	0.39	0.34	2.22	1.14	3.57	6.91
10	0-15	5.79	23.80	0.17	0.43	0.40	3.03	1.67	6.36	20.00
	15-30	5.79	23.60	0.13	0.38	0.33	2.73	1.38	5.36	14.10
20	0-15	5.96	25.30	0.16	0.40	0.39	3.06	1.71	6.70	24.76
	15-30	6.07	24.40	0.13	0.38	0.31	2.91	1.41	6.24	18.74
30	0-15	6.51	27.30	0.11	0.36	0.29	9.60	2.26	7.10	27.63
	15-30	6.31	25.90	0.10	0.34	0.28	2.97	1.52	6.28	19.71
	LSD	0.47	2.32	0.09	0.04	0.08	0.90	0.36	0.64	3.10

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