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CARBON–NITROGEN DYNAMICS IN ORGANIC WASTES AMENDED – CRUDE OIL POLLUTED WETLAND SOIL

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ABSTRACT

The study assessed the potentials of organic wastes for enhanced biodegradation of crude oil in sandy clay loam soil from lower Niger River wetland. The organic wastes used were poultry droppings (PD) and cassava peels (CP) and mixture of PD + CP. One week after polluting the soil with crude oil at the rate of 50 t/ha (0.06667 kg /3 kg soil), these amendments were mixed thoroughly with 3 kg of potted crude oil – polluted soil at the rates of 0 kg/3 kg soil (control), 0.06667 kg/3 kg soil and 0.1333 kg/3 kg soil, equivalent to 0 t/ha, 50 t/ha and 100 t/ha. Each amendment was replicated three times. The soils were watered to saturation once in a week, while soil samples were taken from the pots at five different times (namely, 14, 46, 76, 131 and 201 days) for the determination of the content of organic carbon, nitrogen and total hydrocarbon. The carbon/nitrogen ratio and the level of petroleum hydrocarbon were the parameters used to assess biodegradation and hence soil fertility restoration. The result showed that the application of crude oil increased the level of organic carbon (OC) and total hydrocarbon (THC) contents of the soil. The treatments, poultry droppings (PD), cassava peels (CP) and mixture of PD + CP significantly (P = 0.05) decreased the level of OC and THC contents. When the rates of biodegradation of these treatments were compared, adopting the C:N ratio, the order of reduction in the level of OC and THC in the soil was PD > mixture of PD + CP > CP. The highest concentration of OC and THC was recorded in the control. Thus, the application of C:N ratio index seems a suitable criterion for evaluating microbial degradation of crude oil pollution in soil. The implication for agriculture and environment is discussed.

Keywords: Crude oil pollution, organic waste amendments, biodegradation, C/N ratio, soil fertility restoration.

INTRODUCTION

Environmental degradation associated with oil exploitation is a major problem confronting oil-producing countries. The array of environmental degradation has multiple dimensions, which are dependent upon the composition and the quantity of the pollutants, and the configuration of the receiving media. In soils, petroleum hydrocarbon creates conditions which lead to the unavailability of essential plant nutrients, such as nitrogen, and the availability of some toxic elements such as arsenic (As), lead (Pb) and iron (Fe) to plants. Roane and Kellogg (1996) reported that sites polluted with organic compounds often contain metals, such as As, Hg, Pb and Zn. The soil may remain unsuitable for crop growth for months or years until oil is degraded to tolerable level (Odu, 1981). The response of crops to oil contamination depends upon the level of contamination. While crop leaves become gradually withered under slight contamination, heavy contamination results to total shading of leaves. In both conditions, total crop failure occurs. Only nitrogen fixing-plants can survive under this condition.

There are many physical, chemical and biological technologies available for treating sites contaminated with petroleum hydrocarbon. However, the treatment selected depends upon the contaminant and site characteristics, regulatory requirements, cost and time constraints (Ram *et al.*, 1993). Although relatively slow (Zobell *et al.*, 1973) and complex (Kasthuri *et al.*, 1993) in natural ecosystem, biodegradation of petroleum hydrocarbon has been widely accepted as environmentally friendly and an economic approach to the remediation of polluted soils. This method is based on the provision of optimal condition for the proliferation and growth of petroleum hydrocarbon degrading microorganisms. Although climatic conditions are optimal for biodegradation process to occur in the tropical region (Prado- Jata *et al.*, 1993), information on the biodegradation of petroleum hydrocarbon in organic manure-amended soils and actual field applications in Nigeria have been limited, despite the occurrence of numerous oil pipe line bursts and spillages which constantly pollute the environment and threaten agriculture. The objective of this greenhouse investigation was to evaluate the rate of biodegradation of crude

Table 1: Physical Properties of Soil Samples from Atani

Soil Depth (cm)	Clay (%)	Silt (%)	F.S. (%)	C.S (%)	T.S (%)	T.C	Bulk Density (g/cm^3)	Total Porosity (%)	Water Retention (%)	Hydraulic Conductivity (cm/hr)
0 – 18	24	20	32	24	56	SCL	1.62	38	33.90	8.41
18 – 40	44	20	12	24	36	C	1.56	41	35.07	1.72
40 – 71	24	20	20	36	56	SCL	1.79	32	32.26	2.67
71 – 190	14	14	26	45	72	SL	1.61	39	36.08	3.25

Where: F.S = Fine sand; C.S = Coarse sand; T.S = Textural class; S.C.L = Sandy clay loam; C = Clay; and S.L = Sandy loam.

Table 2: Chemical Characteristics of the Non-polluted and Polluted Soil Samples from Atani

Sample	pH	OC	Total N	C/N	Exchangeable Base (Meq/100g Soil)					EA (Meq/100g Soil)		Av. P	THC
Depth (cm)	H_20	(%)	(%)	Ratio	Ca^{2+}	Mg^{2+}	Na^+	K^+	CEC	H^+	Al^{3+}	(PPM)	(PPM)
0 – 18	5.4	0.41	0.032	13:1	1.8	1.0	0.209	0.050	8.23	0.4	2.8	4	<0.010
18 – 40	4.9	0.36	0.029	12:1	1.8	0.8	0.214	0.030	16.0	0.6	3.2	ND	ND
40 - 71	5.1	0.22	0.019	12:1	1.6	0.8	0.214	0.024	7.00	0.4	2.5	1	ND
71 - 190	5.3	0.08	0.007	11:1	1.6	0.4	0.214	0.023	6.56	0.2	2.2	ND	ND
Polluted													
Atani (0 – 15)	5.0	3.82	0.129	30:1	2.9	0.6	0.050	0.198	11.2	0.6	3.2	12	3951

Where ND = Not detected; and THC = Total hydrocarbon

Table 3: Chemical Characteristics of the Amendments

Amendments	OC (%)	Total N (%)	C/N Ratio	Exchangeable Base (cmol/kg soil)				P (ppm)
				Ca	Mg	K	Na	
Poultry Droppings (PD)	13.60	3.80	4:1	8.00	1.92	0.46	0.76	7.16
Cassava Peels (CP)	51.50	0.36	143:1	1.20	0.72	0.70	0.28	0.88
PD + CP (1:1)	36.10	0.60	60:1	1.36	0.96	1.20	0.45	0.166

oil-polluted soil, amended with organic wastes, poultry droppings and cassava peels. The parameters for the evaluation were C:N ratio and the level of petroleum hydrocarbon in the soil.

MATERIALS AND METHODS

Location of Sample Material

This study was carried out at the University of Nigeria, Nsukka, using a sandy clay loam topsoil from soil profile pit sited at the wetland area of the lower Niger River at Atani, Ogbaru LGA, Anambra State. Atani is located between Latitudes 05^0 52′ N and 06^0 30′ N and Longitudes 06^0 49′ E and 6^0 42′ E. It is characterized by bimodal rainfall pattern. The dry season lasts from November to February, with the driest month recording 28.85 mm of rainfall and the wet season lasts from March to October, with total annual rainfall ranging from 1875 mm to more than 2500 mm (Inyang, 1975). The soil profile was characterized to provide information that will enhance the understanding of the characteristics of the soils and enable extrapolations to be made. The lower Niger River wetland is ecologically similar to locations in the Niger delta areas where petroleum spillages leading to environmental pollution occur most regularly.

Greenhouse Study

The topsoil (0-15 cm) collected from the soil profile, poultry droppings (PD) and cassava peels (CP) were air-dried, ground and sieved to pass through 2 mm sieve. The soil was polluted with crude oil at the rate of 0.06667 kg /3 kg soil (equivalent to 50 tonnes crude oil/ ha). The polluted soil, CP, and PD were characterized. The amendments were applied in single form (50 tonnes PD/ha, 100 tonnes PD/ha, 50 tonnes CP/ha and 100 tonnes CP/ha) and combined form (25 tonnes PD/ha + 25 tonnes CP/ha, and 50 tonnes PD/ha + 50 tonnes CP/ ha), with the control 0 tonnes/ha. The organic amendments were mixed thoroughly with 3 kg of the polluted soils. Each amendment was applied after one week contamination and replicated three times. The soils were placed in ceramic pots with drainage holes at the base, plugged with cotton wool to retain the soil. The pots were arranged in a completely randomized design in the greenhouse and watered to saturation once in a week, with soil samples taken from the surface of the pots on five different times (namely, 14, 45, 76, 131 and 201 days).

Laboratory Analyses

Soil properties which were thought to influence the biodegradation of petroleum hydrocarbon were determined after the soil samples were air-dried, ground and sieved to pass 2 mm sieve. These included the following: organic carbon by Walkley and Black analytical method as described by Nelson and Sommes (1982); total nitrogen by macro Kjeldahl method as described by Bremner and Mulvaney (1982); available phosphorus by Bray II method as described Bray and Kutz (1945); total hydrocarbon, using Infrared Spectrophotometer; and hydrocarbon utilizing bacteria, using mineral salt agar. Other parameters determined were particle size distribution, using hydrometer method as described by Bouyoucos (1951), and bulk density, using Blake and Hartge (1986). Total porosity was calculated from the bulk density at an assumed particle density of 2.65 g/cm3, using f = 100(1 – Dry bulk density/Particle density), where f = Total porosity. This method was described by Vomocil (1965). Hydraulic conductivity was determined at saturation, and water retention at 60 cm tension, using tension Table.

RESULTS AND DISCUSSION

Physical and Chemical Properties of the Atani Soil

The Atani sandy clay loam soil profile has bulk density ranging from 1.56 g/cm^3 to 1.79 g/cm^3 (Table 1), with moderately low total porosity (32 – 41 %) and very low hydraulic conductivity (1.78 – 8.4 cm/hr). The moderately low total porosity and the loamy texture of the subsoil may account for the low hydraulic conductivity recorded for the soil profile, which suggests slow rate of vertical distribution of water in the soil profile. The water retention at saturation in all the identified pedogenic horizons ranged from 32.3 – 36.1 %, indicating that the internal drainage is restricted thereby causing perched hydromorphism of the soil.

The soil was strongly to moderately acidic, with low organic carbon and total nitrogen (Table 2). The C/N ratios ranged from 11:1 to 13:1. The cation exchange site was dominated by calcium, while the exchangeable acidity showed a dominance of Al^{3+} over H^+ ion. The CEC ranged from low to moderately high. The available P and THC were very low.

Table 4: Changes in Organic Carbon and Total Hydrocarbon in Polluted Soil

Amendments	14 Days	45 Days	76 Days	131 Days	201 Days	14 Days	45 Days	76 Days	131 Days	201 Days
	Orgaic Carbon (%)					Total Hydrocarbon (ppm)				
A0 (0 t, Control)	3.41	3.34	3.22	3.17	3.03	3711	3681	3640	3583	3516
A1 (50 t CP)	3.23	3.06	2.81	2.81	2.57	3740	3645	3560	3385	3315
A2 (100 t CP)	3.27	3.25	3.07	3.02	2.90	3748	3726	3562	3426	3386
A3 (50 t PD)	3.21	3.17	3.10	2.78	2.40	3928	3664	3411	3341	3124
A4 (100 t PD)	3.21	3.02	2.60	2.58	2.22	3695	3426	3279	3106	3085
A5 (25 t CP + 25 t PD)	3.00	2.80	2.41	2.60	2.30	3692	3645	3425	3367	3227
A6 (50 t CP + 50 t PD)	3.22	3.05	3.01	2.48	2.59	3622	3492	3541	3325	3213

Table 5: Changes in Total Nitrogen and Total Heterotrophic Bacteria in Polluted Soil

Amendments	14 Days	45 Days	76 Days	131 Days	201 Days	14 Days	45 Days	76 Days	131 Days	201 Days
	Total Nitrogen (%)					Total Heterotrophic Bacteria (cfu/g Soil)				
A0 (0 t, Control)	0.127	0.094	0.087	0.097	0.097	1.11×10^7	1.13×10^7	2.6×10^7	6.5×10^7	1.06×10^8
A1 (50 t CP)	0.167	0.170	0.154	0.121	0.112	1.15×10^7	1.4×10^7	2.8×10^7	6.3×10	6.9×10^7
A2 (100 t CP)	0.182	0.190	0.154	0.142	0.124	1.3×10^7	1.66×0^7	5.5×10^7	6.6×10^7	6.6×10^7
A3 (50 t PD)	0.196	0.204	0.183	0.154	0.143	2.42×10^7	1.71×10^7	7.0×10^7	7.5×10^7	5.1×10^7
A4 (100 t PD)	0.224	0.252	0.236	0.215	0.166	2.74×10^7	1.85×10^7	2.13×10^7	7.7×10^7	5.4×10^7
A5 (25 t CP + 25 t PD)	0.155	0.168	0.167	0.191	0.126	2.15×10^7	1.7×10^7	5.9×10^7	5.05×10^7	5.5×10^7
A6 (50 t CP + 50 t PD)	0.213	0.197	0.183	0.197	0.155	2.7×10^7	1.7×10^7	6.0×10^7	5.7×10^7	5.9×10^7

Table 6: Changes in Carbon/Nitrogen Ratio in Polluted Soil

Amendments	14 Days	45 Days	76 Days	131 Days	201 Days
A0 (0 t, Control)	27:1	36:1	37:1	33:1	31:1
A1 (50 t CP)	19:1	18:1	18:1	23:1	23:1
A2 (100 t CP)	18:1	17:1	20:1	21:1	23:1
A3 (50 t PD)	16:1	16:1	17:1	18:1	17:1
A4 (100 t PD)	14:1	12:1	11:1	12:1	13:1
A5 (25 t CP + 25 t PD)	19:1	17:1	14:1	14:1	18:1
A6 (50 t CP + 50 t PD)	15:1	15:1	16:1	13:1	17:1

Chemical Properties of the Crude Oil Polluted Soils

A comparison of the polluted and non-polluted soils of Atani showed slight increase in soil acidity (pH 5.0) and exchangeable acidity, a moderately high increase in percent organic carbon (% OC), percent total nitrogen, and a wider C/N ratio for the polluted than the non-polluted soil (Table 2). Similarly, while the cation exchange site of the polluted soil was dominated by divalent cations, especially calcium, the CEC, available P and total hydrocarbon (THC) were higher in the polluted than non-polluted soil. These changes in the chemical properties of the polluted soil could be attributed to the presence of the crude oil in the soil.

Chemical Properties of the Amendments

The organic carbon was 13.60 %, 51.50 % and 36.10 % in poultry droppings (PD), cassava peels (CP) and mixture of PD and CP, respectively (Table 3). The total nitrogen content of the amendments varied in the order, PD > mixture of CP and PD > CP. The C/N ratio also in the order CP, > PD + CP > PD. The exchangeable Ca, Mg and Na of the amendments varied in the order, PD > PD + CP > CP, while K varied in the order, PD + CP > CP > PD. The values of available phosphorus were 7.16, 0.88 and 0.17 ppm in PD, CP and PD + CP, respectively and this indicates that PD contributed most of the exchangeable bases and available phosphorus to the soil.

The Fertility Status of the Organic Waste-Amended Soil

This study revealed that the application of amendments to polluted soil played a great role in the degradation of the crude oil and restoration of the soil fertility. There was significant (P = 0.05) effect of the amendments on the parameters studied at all the stages of the study. The percent organic carbon (% OC) and total hydrocarbon (THC) concentrations of the soil, which decreased with time, were significantly affected by the amendments (Table 5). Shimp and Pfaender (1984) reported that naturally occurring organic materials could influence the ability of microorganisms to degrade pollutants. The high cation exchange capacity and high density of reactive functional groups of organic matter help to bind both organic and inorganic compounds (Riser-Roberts, 1998), hence allowing more time for biodegradation of the compounds.

The highest concentration of OC during the study was in the control (Fig. 1), while the least concentration was in the poultry droppings-amended soil at 201 days after application (DAA). The order of OC concentration at the end of the study was, control > CP > mixture of CP + PD > PD. Similarly, the control generally recorded the highest concentration of THC, especially after 14 DAA (Fig. 2), suggesting relatively slow degradation of THC, probably due to the absence of the contribution of soil amendments. However, the sole application of poultry droppings gave the least concentration of THC at the end of the investigation, probably due to the comparatively quick net nitrogen minerlization of poultry droppings. Miller and Donahue (1992) reported that organic matter with C:N ratios wider than 30:1 decomposes slowly because they lack sufficient nitrogen for the microorganisms to increase their number. This results in the use of nitrogen already in the soil. By the end of the study, the OC and THC concentrations in the soils treated with PD (C/N ratio of 4:1) were significantly (P = 0.05) low compared with the OC and THC concentration in soils amended with the mixture of PD + CP and cassava peels (with C/N ratio of 60:1 and 143:1 respectively) which are not suitable for quick mineralization of nitrogen. Thus, while the least concentration of OC and THC in poultry droppings-amended soil can be attributed to the easily decomposable nature of poultry droppings, with consequent release of nitrogen, which is an essential nutrient element for biodegradation of pollutants in soil, the higher concentration of OC and THC observed in CP-amended soil can be accounted for by the low decomposable nature of CP due to its wide C/N ratio.

An increase in nitrogen content of the amended soils was observed within the first two months after application, with the poultry droppings-amended soil giving the highest concentration during the study (Table 6). Nitrogen concentration was higher in the soil treated with PD + CP than in soil amended with CP. Agbim (1985) had a similar result and reported that, incorporating PD with CP enhanced the potentials of CP as soil amendment. The low concentration of nitrogen and consequent wider C/N ratio (30: 1) (Fig. 3) in the control (0 t/ha) reflect the absence of the contribution of soil amendments (Table 7). Routson and Wildung, (1970) suggested that C:N ratio of < 25 leads to mineralization of nitrogen and a C:N ratio of >38 leads to depletion of mineral nitrogen. At C:N ratio >30, nitrogen limits microbial proliferation (Miller and Donahue, 1992), hence leading to the fixation of N already in the soil. Thus, poultry droppings-amended soil, with relatively low C/N ratio was more suitable for microbial prolifera-

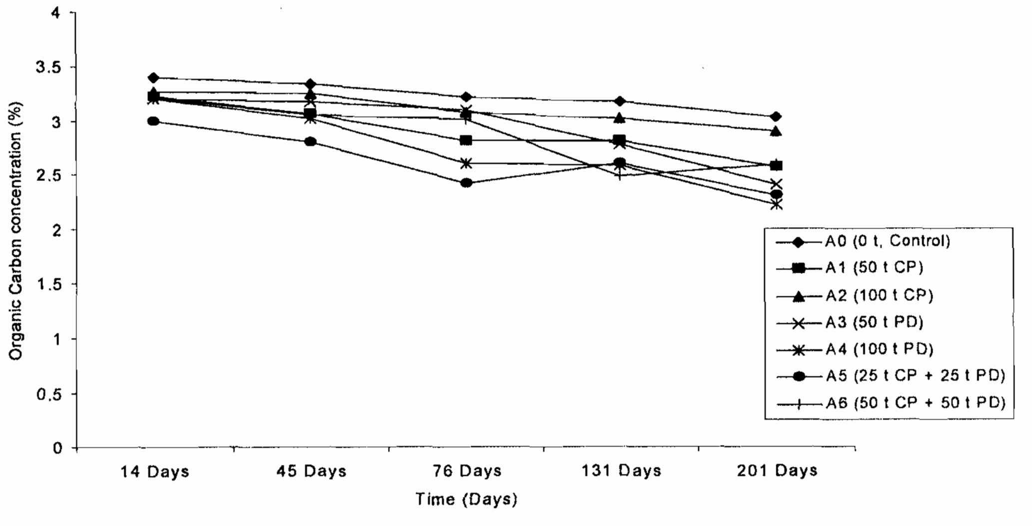

Figure 1: Changes in oganic carbon concentration

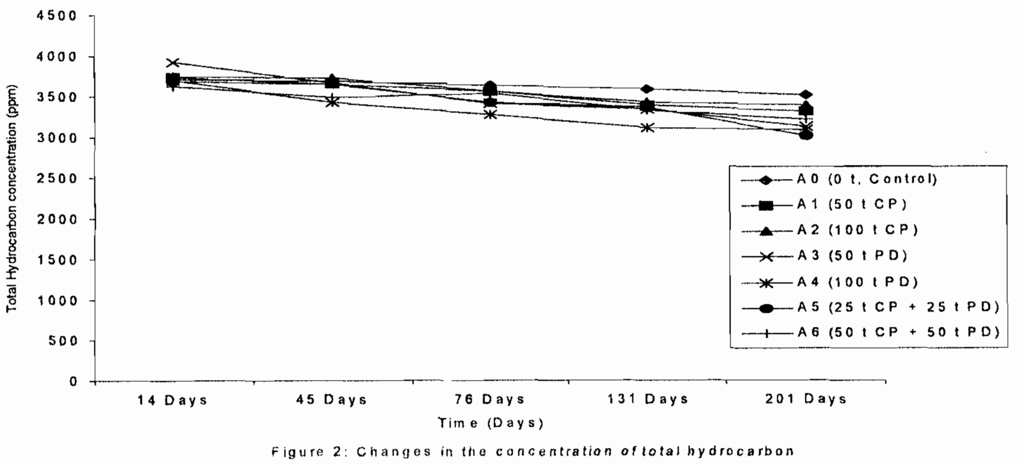

Figure 2: Changes in the concentration of total hydrocarbon

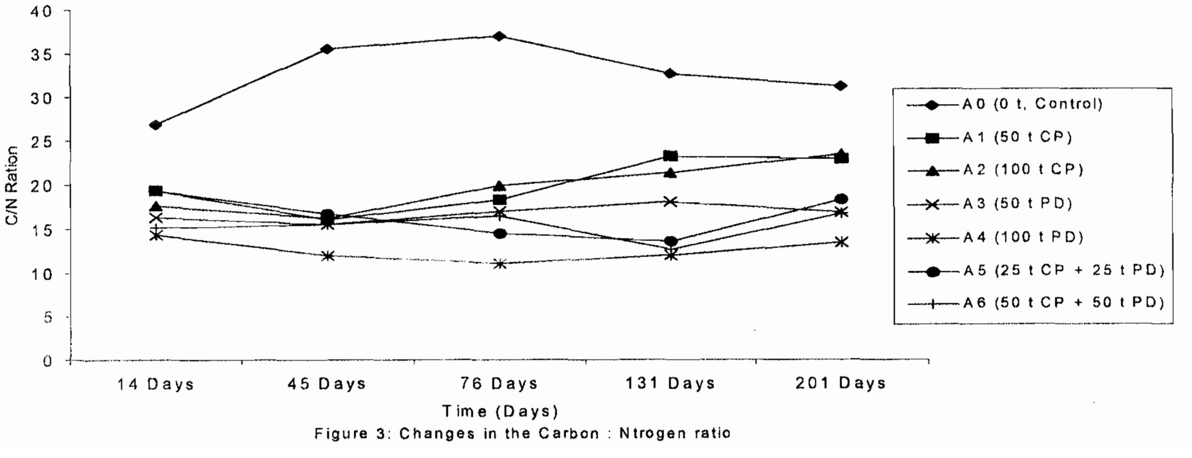

Figure 3: Changes in the Carbon : Ntrogen ratio

tion and degradation of THC in the soil than others. However, the higher microbial population recorded in the control (without amendment) at 201 DAA (Table 6) may be probably due to the comparatively higher concentration of THC, which serves as a source of energy for the microorganisms.

CONCLUSION

The degradation of crude oil and a probable restoration of the soil fertility were enhanced by the application of organic waste to polluted sandy clay loam soil of a wetland area. The study indicated that the use of C:N ratio and level of THC in the polluted soil were appropriate and suitable method of evaluating the rate of biodegradation of polluted environment. The study also revealed that the addition of organic wastes to crude oil polluted-soil was capable of restoring or reclaiming the soil. The organic waste PD performed best but because of non-availability of PD, a mixture of PD and CP is recommended. The implication of these results is that when this technology is extended to the field, it would benefit agriculture and the environment.

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