

Full Length Research Paper

Remediation of soil contaminated with polycyclic aromatic hydrocarbons from crude oil

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Accepted 27 December, 2010

The aim of this study was to determine ways of remediating soils contaminated with polycyclic aromatic hydrocarbons (PAHs) associated with crude oil. The study involves the use of planted cowpeas, mushrooms, algae, dead vegetable and live earthworm, and fire-heating of the contaminated garden soil collected from the Niger Delta area of Nigeria. The types and levels of the PAH in the soil before and after three weeks of contamination were determined using gas chromatography. Mushrooms and cowpeas proved to be very adequate phytoremediators. Fire heat was third, algae and dead vegetable with live earthworm showed the least reduction. This study thus recommends that the people of the Niger Delta should engage in planting of mushrooms and cowpeas to regenerate and ameliorate petroleum contaminated land for beneficial farming.

Key words: Crude oil, petroleum, contaminated soil, polycyclic aromatic hydrocarbons, mushrooms, cowpeas.

INTRODUCTION

Since commercial exploration of petroleum started in Nigeria in 1958 (Okoh, 2003), petroleum has been the main stay of the economy. There is likelihood of a legacy of environmental pollution (of land and water) and destruction. Agricultural lands have become less productive (Dabbs, 1996). Hence, there is much of civil unrests in the Niger Delta of Nigeria (Inoni et al., 2006). Continued study of remediation of the quality of the soil is of paramount importance. Of the trio: natural attenuation, engineering and biological remediation methods; biological techniques (such as phytoremediation and bioremediation) are currently evaluated to clean up and restore petroleum-contaminated sites.

Biological growth processes can accumulate and degrade petroleum hydrocarbons (Cunningham et al., 1996; Siciliano and Germida, 1998). Phytoremediation exploits the natural ability and content of the environment to regenerate it (Cunningham et al., 1996). For example, Gudin and Syrratt (1975) have shown that legumes occurring naturally in oil-contaminated areas have the potential

to clean up petroleum hydrocarbons. The aesthetic value is greater than that of other remediation techniques (Shrimp et al., 1993). There is also the advantage to culture various organisms in the same site to cooperate in rendering petroleum hydrocarbons less toxic and less persistent. Phytoremediation has attracted public support and least applicability (McIntyre and Lewis, 1997) in restoration of soil quality in view of soil structure, porosity, water infiltration (Schnoor et al., 1995; Cunningham et al., 1996) and soil stability (Simonich and Hites, 1994a,b).

The Niger Delta area of Nigeria had in the past witnessed many cases of severe crude oil spillage. These adverse situations not only affect the ecosystem adversely as plant and animals may not survive, the crude may also contain varying levels of polycyclic aromatic hydrocarbons (PAH's); many of these have been reported to have adverse consequences. Some studies have shown that heavy PAHs (those containing more than four benzene rings) can induce dioxin-like activity and weakened estrogenic responses (Villeneuve et al., 2002). The present study is a desired contributory solution to problems arising from severe petroleum spills. It is aimed [by determining the concentration of polycyclic aromatic hydrocarbons (PAHs) in soil, crude oil and

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petroleum-contaminated soils in which selected accumulators and degraders are grown in experiments] to discover additional means of regenerating crude oil-contaminated soil congenial for farming, especially remediating the polycyclic hydrocarbon content arising from severe oil spillage.

MATERIALS AND METHODS

This study was carried out in a biological garden in Ughelli, Delta State, Nigeria. The soil was sandy loamy. Soil samples were collected, air-dried and sieved to remove large particles and debris. The uncontaminated soil was analysed for its PAH content. Two portions (1 kg each) were measured into plastic bowls; fungi - mushroom (*Basidiomycetes*), algae (filamentous chlorophytes) were planted respectively in the bowls. The algae bowl was flooded with water.

A second portion of the soil sample was mixed with crude oil (1 L /5.0 kg) and allowed for three weeks to homogenize and to release volatile organic carbons (VOC) (Njoku et al., 2009). The contaminated soil was then shared into five plastic bowls. In bowl 1 was planted cowpea (bean) (*Vigna unguiculata*), mushroom (*Basidiomycetes*) in bowl 2, algae (*filamentous chlorophytes*) in bowl 3 which was flooded with water, dead vegetable cum live earthworm (*byodrilus*) in bowl 4 and bowl 5 was heated.. All the bowls were left for four weeks with periodic watering. At the end, the soil was analysed.

PAH determination

10 g of each soil sample was taken and 60 ml of mixture (1:1, v/v) of acetone and dichloromethane (DCM) was added. The mixture was warmed for 3 min at 30°C in a water bath. The extract was decanted into a clean dried round bottom flask and taken to the rotary evaporator to be concentrated to 3 ml. This was fractionated by a fractionating column of silica gel into aromatic portion using 60 ml DCM. The DCM fractionates were transferred to a rotary evaporator and re-concentrated to 3 ml, transferred to 3 ml gas chromatographic vials, corked and ultimately analysed with gas chromatography (6890 series).

RESULTS AND DISCUSSION

The concentrations of component of polycyclic aromatic hydrocarbons and the total PAH are shown in the Table 1. It was observed that the cowpea planted in the contaminated soil showed delayed sprouting and started to wither before the expiration of the observation period. It was also noted that the contaminated soil looked flooded in the first five days but this was less in the mushroom planted soil in this period than the others.

The results showed that all treatments formed, reduced the level of the PAH. The mushroom was most effective (98.93% reduction) than cowpea (97.90%), algae (97.07%), heat (97.81%) and the last dead vegetable cum live earthworms (89.99%). The reduction of PAHs in the contaminated soil with mushroom could also probably be hydrocarbon accumulation in the shoot and their absorption to the roots. Noteworthy is that, most PAH higher than naphthalene in molecular weight were almost com-

pletely removed. This is a mechanism of bioremediation of hydrocarbons (Cunningham et al., 1966). The result also showed that the mushroom seemed to have introduced some new PAHs to the uncontaminated soils as the soil showed the presence of phenanthrene, anthracene and fluoranthene with increased levels of acenaphthene and fluorene. This showed that while the fungi help to biodegrade the PAHs in situations of high concentration, in small amounts, there was seeming conversion to larger ring forms. This magnification of PAHs concentration (112.5%) in the uncontaminated soil may be due to conversion of one form of aromatics to another as fall-off in the metabolism process.

Benzo(a)anthracene was found in the soil enriched with decaying matter and earthworm. This may probably be from the decaying plant, or the waste from the earthworm. In the contaminated soil with dead vegetable and live earthworm, humification could have impeded hydrocarbon degradation, though the earthworm probably used hydrocarbon's carbon as source of energy to degrade polycyclic aromatic hydrocarbons. This combination of dead vegetation and earthworm was not as effective as fungi or cowpeas. However, since they could occur naturally in the soil, they would support application of fungi and cowpeas. They help to nourish the soil and offset nutrient deficiency. When microbes degrade hydrocarbons, available nutrients are used quickly (Kanaly et al., 1997; Xu and Johnson, 1997).

It is noteworthy that heating the soil significantly reduced the PAH content, but this may just have transferred the pollution to the air. Also, the plants in the contaminated soil showed delayed sprouting. This delay may be due to reduced levels of oxygen and this corroborates the report of Dibble and Bartha (1979) in their studies on germination of wheat and soybeans in kerosene contaminated soils. Notably, phytoremediation process is optimised by adequate oxygen, nutrients and water (Wright et al., 1997).

The flooded look of the contaminated soil may be attributed to low permeability and low infiltration of water in crude oil contaminated soils. This leads to artificial drought in the subsurface layer of soil. Thus, there is a likelihood of inadequate access to water and dissolved nutrients as the roots grow in size and tend to penetrate deeper into the soil. But growing roots could create pores and lacunae in the soil which might enhance water infiltration. This could be the reason why the oil-contaminated soil in which mushroom was planted, showed low moisture flooding. The planting of mushroom could therefore be applied to eliminate water logging in crude oil-polluted soil, to improve aeration of such soil, and achieve microbial degradation of petroleum spill.

It is noteworthy that the blend of crude oil was low in high molecular weight PAHs as their toxicity is reported to increase as molecular weight increases and with increase in alkyl substitution in the aromatic (Neff, 1979). However, the presence of PAH's like acenaphthene, pyrene and

Table 1. Levels of polycyclic aromatic hydrocarbon in soil samples (mg/kg).

Component	Uncontaminated soil	Uncontaminated soil + algae	Uncontaminated soil + mushroom	Soil + Crude oil	Contaminated soil + cowpea (% reduction)	Contaminated soil + heat (% reduction)	Contaminated soil + mushroom (% reduction)	Contaminated soil + dead vegetable and earthworm (% reduction)	Contaminated soil + algae (% reduction)
Naphthalene	0.008	0.004	0.000	3.489	0.067 (98.1)	0.019(99.4)	0.079(97.7)	0.076(97.8)	0.032(99.1)
2-methyl naphthalene	0.007	0.002	0.000	1.787	0.049(97.2)	0.029(98.4)	0.014(99.2)	0.074(95.9)	0.013(99.3)
Acenaphthalene	0.003	0.004*	0.029	0.594	0.050 (91.6)	0.056(90.6)	0.000(100)	0.011(98.1)	0.007(98.8)
Acenaphthene	0.003	0.002	0.056*	0.668	0.021 (96.8)	0.020(97.0)	0.003(99.6)	0.077(88.5)	0.013(98.1)
Fluorene	0.002	0.002	0.020*	0.176	0.000 (100)	0.036(79.5)	0.000(100)	0.120 (31.8)	0.003(98.3)
Phenathrene	0.000	0.003*	0.036*	1.339	0.000(100)	0.020(98.5)	0.000(100)	0.143(89.3)	0.092(93.1)
Anthracene	0.000	0.000	0.020*	0.311	0.000(100)	0.016(94.8)	0.000(100)	0.075(75.9)	0.042(96.1)
Fluoranthene	0.000	0.000	0.016*	0.409	0.000(100)	0.000(100)	0.000(100)	0.224 (45.2%)	0.060(86.5)
Pyrene	0.000	0.000	0.000	0.171	0.000(100)	0.000(100)	0.000(100)	0.005(97.1)	0.000(100)
Benzo(a)anthracene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.099*	0.000
Chrysene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Benzo(b)fluoranthrene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Benzo(a)pyrene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Benzo(k)fluoranthrene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Indeno(1,2,3)perylene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Dibenzo(g,h,i)perylene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Benzo(g,h,i)perylene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Total (mg/kg)	0.024	0.015 (37.5%)	0.051 (112.5%)	8.943	0.188 (97.90%)	0.196(97.81%)	0.096 (98.93%)	0.903 (89.99%)	0.262 (97.07%)

*Higher than initial soil level.

anthracene compounds known or suspected to increase the risk of various types of cancer in the crude oil, calls for a lot of monitoring of the Niger Delta environment.

Conclusion

This study has shown that mushrooms and cowpeas are very adequate phytoremediators for polycyclic aromatic hydrocarbons (PAHs) contaminated soils. Because cowpeas enrich the soil with nitrogen, it is advisable that the people of Niger Delta engage in planting of cowpeas and mushrooms to ameliorate the situation.

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