

## Distribution Of Organic Compounds (PAHs and BTEX) And Heavy Metals (Pb, Zn, Fe, Cd) in An Oil Impacted Soils, Rivers State Nigeria.

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**Abstract:** This paper deals with the distributions of organic compounds (PAHs and BTEX) and heavy metals (Pb, Zn, Fe, Cd) concentrations in an oil impacted soils of Rivers State, Nigeria. The concentrations of organic compounds ranged from  $597.340 \pm 0.02$  -  $896.784 \pm 0.011$  Mg/Kg, total PAHs;  $0.030 \pm 0.006$  -  $0.057 \pm 0.003$  Mg/Kg, BTEX and heavy metals ranged from  $2.700 \pm 0.002$  -  $3.960 \pm 0.006$  Mg/Kg, Pb;  $0.460 \pm 0.003$  -  $0.730 \pm 0.007$  Mg/Kg, Cd;  $3.060 \pm 0.003$  -  $3.92 \pm 0.004$  Mg/Kg, Zn and  $92.040 \pm 0.013$  -  $129.400 \pm 0.031$  Mg/Kg, Fe. Soil samples from Bonny had the highest total PAHs concentration ( $773.213 \pm 0.004$  -  $896.784 \pm 0.011$  Mg/Kg). The BTEX concentrations were of smaller values due to the time of crude oil spillage. Total PAHs concentrations increases as depth of the soil increases and distributions of the heavy metals in the various depth has no regular pattern.

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**Key words:** Oil spillage, PAHs, BTEX, Heavy metals and soils.

### 1. Introduction

Environmental contaminants are widely distributed in our environment, therefore, will have an effect on the tropic chain. Soil may contain many organic compounds and heavy metals of natural as well as anthropogenic origin. The concentrations and toxicity of organic compounds (Mira, 2004) and heavy metals (Irha et al., 2003) present in such complicated mixtures range very widely and depend also on possible interactions among chemicals.

An oil spill is the release of a liquid petroleum hydrocarbon into the environment due to human activity, and is a form of pollution. The oil may be a variety of materials, including crude oil, refined petroleum products or by – product, ship's bunker, oily refuse or oil mixed in waste.

Polycyclic aromatic hydrocarbons (PAHs) is a chemical compound that contained more than one fused benzene ring e.g Naphthalene, Anthracene, Phenanthrene, benz(a) pyrene, benz (a) anthracene, Fluoranthene, pyrene, benz(a) Fluoranthene etc. The point sources of anthropogenic origin are: Coal gasification, heat and power generation, coke production, catalytic cracking, carbon – black production and use, Asphalt production and use, refining/distillation of crude oil, wood treatment and preservation, fuel operations, incineration and landfills/waste disposal (Alexander, 1985; Wilson and Jones, 1993; Lima et al., 2005; Boehm, 2006; Boehm and Tarek, 2008).

Because of the very low water solubility and high octanol – water partition coefficient ( $K_{ow}$ ) values, they will tend to be sorbed to the organic matter in the soil in stead of being solubilized in the infiltrating water and through this, it will be transported downwards to the groundwater reservoirs (Zhang et al., 1998). It has been observed that a slow sorption following the initial rapid and reversible sorption lead to a chemical fraction that is very resistant to desorption (Hatzinger and Alexander, 1995). This phenomenon is called aging, and the existence of such a desorption-resistant residues may increase the time as the compound stay in the soil.

Carcinogenic PAHs are found in all surface soils (Menzie et al., 1992), only the following are considered as possible human or animal carcinogens; benz(a) anthracene, benzo(K) fluoranthene, Chrysene dibenz(a,h) anthracene, indeno (1,2,3)pyrene (ATSDR, 1990). The general population may be exposed to these compounds by inhalation of the compounds in tobacco smoke and contaminated air, as well as ingestion of contaminated food.

Values in the order 1000 – 3000  $\mu\text{g/Kg}$  are regarded as being in the upper range. Smokers consuming one pack of nonfiltered cigarettes per day had an estimated additional intake of 1 – 5  $\mu\text{g/day}$  (Menzie et al., 1992).

BTEX is an acronym for benzene, toluene, ethylbenzene, and xylene. BTEX have in recent years attracted much attention, since they constitute one of

the most common and serious threats to groundwater reservoirs and indoor climate deriving from contaminated sites. This is mainly due to the potential effects of benzene, which is considered a strong carcinogen, and is highly mobile in the soil and groundwater environment (Salanitro et al., 1997). Benzene cannot be degraded with nitrogen as terminal electron acceptor (Schreiber and Bahr, 2002). The release of BTEX's to the environment is influenced by their fate and transport mechanisms. The remediation of BTEX in soil is affected by volatilization, dissolution, sorption and degradation by microorganism. The nature bacterial flora in soil has an ability to aerobically degrade the BTEX. This degradation will reduce the concentration in soil and groundwater (Bedient, 1994).

Organic contaminants and heavy metals correlates significantly with the corresponding levels in soil (Bakker et al., 2000; Irha, 2003; Dahle et al., 2003) and may provide important information on

In this study, the level of soil contamination by PAHs, BTEX and heavy metals in an oil impacted soils of Rivers State, Nigeria.

## 2. Materials And Methods

The study areas, Bonny, Ogoni and Egbema are of major concern because of numerous crude oil fields. The soil samples were collected from three different towns; Bonny, Ogoni and Egbema at different depths (0 – 10 cm, 10 – 20 cm and 20 – 30 cm) using soil auger in September, 2010. The samples were labeled Aa, Ab, Ac, Ba, Bb, Bc, Ca, Cb, and Cc. Where A, B, and C represent the study areas; Ogoni, Bonny and Egbema respectively and a, b, c represent the various depth; 0 – 10 cm, 10 – 20 cm and 20 – 30 cm respectively.

### Soil PAH and BTEX Analysis:

The organic compound extraction was performed by the US EPA 3540 C and 3630 C method. The extraction was carried out by a soxhlet apparatus in the following manner: Soil samples were extracted with 100 ml methylene chloride for 24 hours. The extract was purified on a silica gel column where the compounds were eluted with 25 ml of methylene pentane mixture (2:3), reduced till dry and dissolved for analysis in acetonitrile. The acetonitrile extract was analysed by gas chromatography (HP 5890).

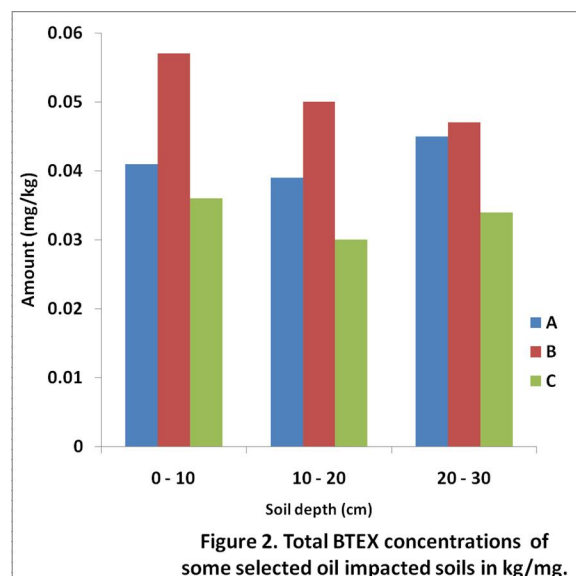
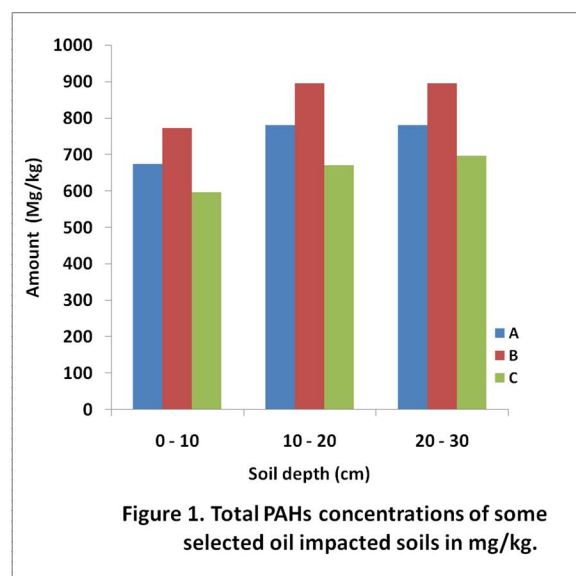
### Heavy metal analysis:

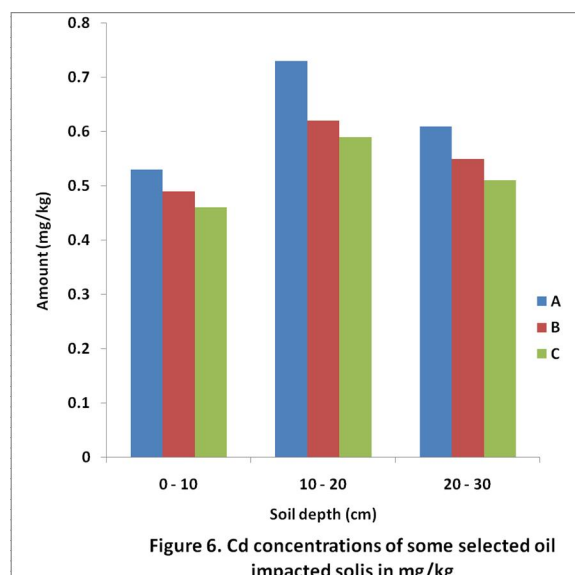
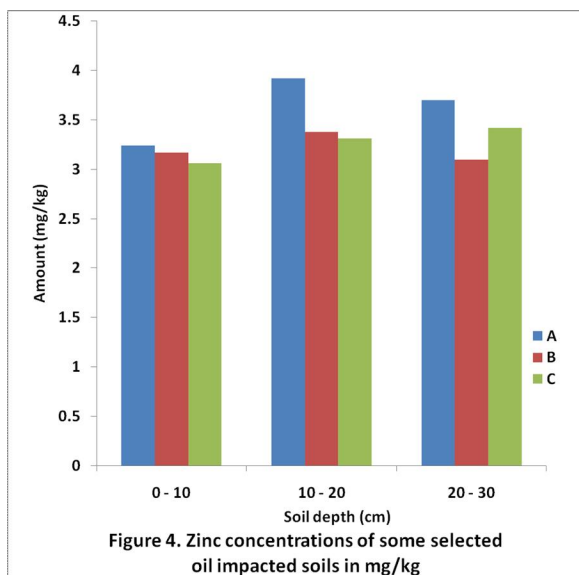
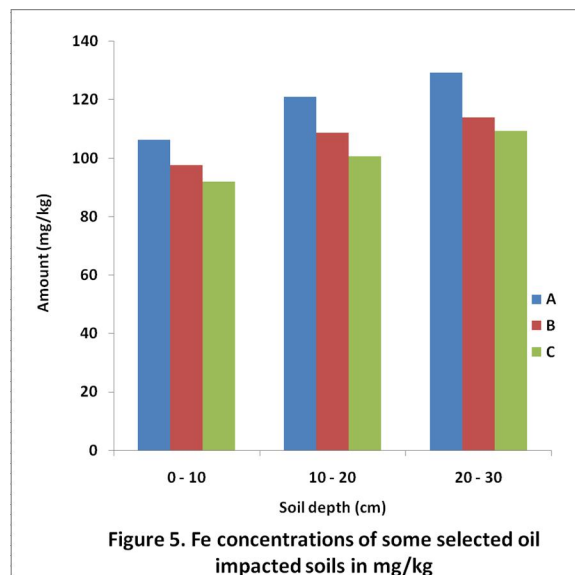
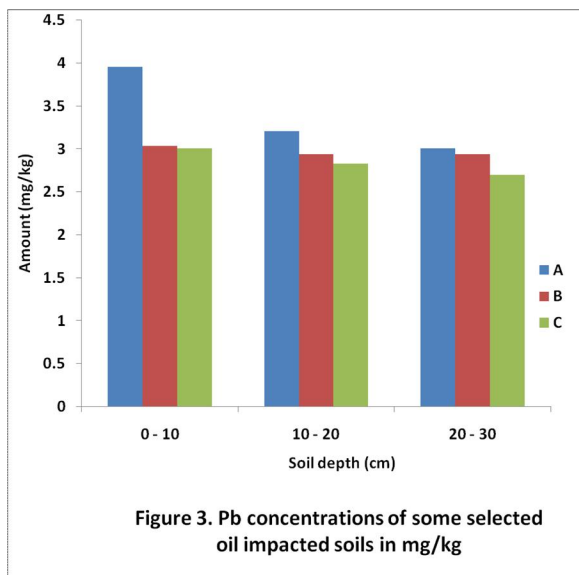
The digestion method proposed by the ministry of Agriculture, Fisheries and Food (MAFF, 1981) with slight modifications was used. One gram of dried and homogenized soil was weighed into a beaker (100 ml) and 10 ml nitric acid was added.

This was then heated until dryness. Thereafter, 10 ml  $\text{HNO}_3$  and 3 ml  $\text{HClO}_4$  was added and the solution was heated until fuming. The sample solution obtained by processing the residue with hot 6 M HCl (4ml) and then filtered and diluted with water to 50 ml. The solution was used for atomic absorption spectrophotometer (UNICAM SOIAAR 32) analysis for heavy metal determination.

## 3. Results

The results are shown in the following figures.





**4. Discussion.**

Distribution of the total PAHs at various soil depths is shown in figure 1. The total concentration ranged from  $597.340 \pm 0.021 - 896.784 \pm 0.011$  mg/kg. the total PAHs concentration in soil from B ( $773.213 \pm 0.004 - 896.784 \pm 0.011$  mg/kg) was higher than the corresponding data from other sampling sites. This was attributed to the influence of the level of oil activities that is been carried out including oil spillage and the time it was dumped. The lowest concentration ( $597.340 \pm 0.021 - 697.013$

$\pm 0.081$  mg/kg) of the total PAHs was found in soil sample C.

Soil samples collected from these areas were contaminated in varying degrees with respect to the depths of the soil by the organic compound. The total concentration of PAHs increases as the depth of the soil increases from 0 – 30 cm for all soil samples. Because of the very low water solubility, PAH will tend to be sorbed to the organic matter in the soil instead of being solubilized in the infiltrating water and through this, it will be transported downwards to the groundwater reservoirs. The sorption process is therefore counteractive to efficient biodegradation since it will decrease bioavailability due to sorption, the compounds will be located in micro porous areas of the soil making it inaccessible to the bacteria, and the biodegradation will thus be controlled by the slow desorptive and diffusive mass transfer into the biologically active areas (Zhang et al., 1998). It has been reported that a slow sorption following the initial rapid and reversible sorption lead to a chemical fraction that is very resistant to desorption (Hatzinger and Alexander, 1995). This phenomenon is called aging and the existence of such a desorption – resistant residues may increase the time as the compound stay in the soil dramatically. PAHs have also been shown to be partitioned or incorporated more or less reversibly into the humic substances of the soil after partial degradation and thereby be even more immobilized in the soil (Kastner et al., 1999; Ressler et al. 1999).

PAHs show very low aerobic degradability depending on the environmental conditions and the available concentration. Very low concentrations have a strong influence on the biodegradation of such hydrophobic compounds, and some studies have indicated that the process stops below a certain threshold concentration (Alexander, 1985). Only two and three – ringed compounds have been shown to be degraded under anaerobic conditions with nitrate or sulfate as the terminal electron acceptor (Mihelic and Luthy, 1998; Coates et al., 1996). The low mobility and high persistence means that they can stay in the soil for decades.

The results of this study showed that the soils are highly contaminated with PAHs which have harmful health effects and are considerably higher compared to the range of  $0.601 \pm 0.001 - 3.678 \pm 0.036$  mg/kg reported by Osu and Asuoha (2010). PAHs concentrations in uncontaminated and contaminated soils have been reported (Zou et al., 2003; Olajire and Brack, 2005; Mira and Petar, 2004; Udoetok and Osuji, 2008; Beg et al., 2003).

From figure 2, it was found that the concentrations of BTEX ranged from  $0.030 \pm 0.006 - 0.057 \pm 0.003$  mg/kg. Sample B had the highest value

( $0.057 \pm 0.003$  mg/kg) while sample C had the lowest concentration value ( $0.036 \pm 0.006$  mg/kg). The values were very small. This is due to volatilization, dissolution, sorption, biodegradation. These factors depend on the time the soils were impacted with crude oil. These values were lower than the concentrations ( $< 0.001 - 0.013 \pm 0.003$  mg/kg) reported by Osu and Asuoha, (2010).

The concentrations of heavy metals found in the contaminated soils studied, ranged from  $2.70 \pm 0.002 - 3.96 \pm 0.006$  mg/kg, Pb;  $3.06 \pm 0.003 - 3.92 \pm 0.004$  mg/kg, Zn;  $92.040 \pm 0.013 - 129.40 \pm 0.031$  mg/kg, Fe and  $0.490 \pm 0.001 - 0.730 \pm 0.007$  mg/kg, Cd (Table 3 – 6). Iron had the highest concentration while cadmium had the lowest concentration in all the soil samples. There was no regular vertical pattern of distribution of these heavy metals along the depths in all the samples studied. The result showed significant lower values of cadmium and lead contents than the results reported by Osu and Okereke, (2010) and similar with the values reported by Nwoko and Egunjobi, (2002).

The concentrations level of PAHs and heavy metals obtained in this study were above permissible level for soils as recommended by USEPA, (1986) and ATSDR, (1995). This raises a lot of environmental concern.

#### **Conclusion:**

The usual improper dumping of crude oil on the soil either through bunker or transportation now demands attention in order to protect the soil for agricultural purposes. High concentrations of total PAHs and heavy metals were found in all the soil samples. These was as result of crude oil spillage in the areas, which is the most common source of these contaminants. The BTEX concentrations was found to range from  $0.030 \pm 0.006 - 0.057 \pm 0.003$  mg/kg. the concentration of BTEX decreases as time increases due to evaporation, volatilization, adsorption and other factors.

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**References**

1. Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological profile for polycyclic aromatic hydrocarbon (PAHs). Atlanta GA: U.S. Department of health and Human services, Public Health Service, 1995.
2. Alexander, M. (1985). Biodegradation of organic chemical. *Environ. Sci. Technol.* 18, 108 – 111.
3. Bakker, M. I., Casado, B., Koerselman, J. W., Tolls, J. and Kolloffel C. Polycyclic aromatic hydrocarbons in soil and plant samples from the vicinity of an oil refinery. *Sci. Total Environ.*, 263, 91 – 100.
4. Beg, M. U., Saeed, T., Al-Muzaini, S., Beg, K.R., and Al – Bahloul, M. Distribution of petroleum hydrocarbon in sediment from coastal area receiving industrial effluent in Kuwait. *Ecotoxicology and Environmental safety* 2003; 54: 47 – 55.
5. Bedient, Philip B. Groundwater contamination, Transport and Remediationul-Ghaffar. Removal and stabilization of chromium metal ions from industrial effluents. *EJEAFICHE*, 2006; 5 (2): 1286-1295.
6. Boehm, P.D. Polycyclic aromatic hydrocarbons (PAHs). Chapter 15. In: *Environmental Forensics, Contaminant specific Guide*. R. Morrison and B. Murphy (eds.) Academic Press.
7. Coates, J.D., Anderson, R.T., Lovley, D.R. Oxidation of polycyclic aromatic hydrocarbons under sulfate – reducing conditions. *Appl. Environ. Microbiol.* 1996; 62: 1099 – 1101.
8. Dahle, S., Savinov, V.M., Matishov, G.G., Evenet, A. and Naes K. Polycyclic aromatic hydrocarbons (PAHs) in bottom sediments of the Kara sea shelf, Gulf of Ob and Yenisei Bay. *Sci. Total Environ.*, 306, 57 – 71.
9. Hatzinger, P.B., Alexander, M. Effect of aging of chemicals in soil on their biodegradability and extractability. *Environ. Sci. Technol.* 29, 537 – 545.
10. Kastner, M., Streibich, S., Beyrer, M., Richavid, H.H., Fritsche, W. Formation of bound residues during microbial. 1999; 65(5), 1834 – 1842.
11. Lima, A.C., J.W. Farrington, and C.M. Reddy. Combustion – derived polycyclic aromatic hydrocarbon in the environment- a review. *Environ. Foren.*
12. Maliszewska – Kordybach B., Smerczak B. The content of polycyclic aromatic hydrocarbons (PAH) in agricultural Soils in Lublin district. *Roczniki Gleboznawcze. T. XL VIII(1- 2)*, 95.
13. Menzie, C.A. et al., Exposure to carcinogenic PAHs in the environment. *Environmental Science and Technology*, 26: 1278 – 1284.
14. Mira, M. Pucarevic, Petar D. Sekulic. Polycyclic Aromatic Hydrocarbons and Pesticides in Soil of Vojvodina. *Proc. Nat. Sci.*, No. 107, 93 – 100.
15. Mihelic, J.R., Luthy, R.G. Microbial degradation of acenaphthene and naphthalene under dinitrification conditions in soil – water systems. *Appl. Environ. Microbiol.* 1988; 54: 1188 – 1198.
16. Natalya Irha, Jorgen Slet, Walter Petersell. Effect of heavy metals and PAH on soil assessed via dehydrogenase assay. *Environmental International* 28, 779 – 782.
17. Nwoko, C.O. and J.K Egunjobi. Lead contamination of soil and vegetation in an abandoned battery factory in Ibadan , Nigeria. *Sustain. Agric. Environment* 2002: 4(1): 91 - 96
18. Olajire, Abbas, A. and W. Brack. Polycyclic aromatic hydrocarbons in Niger Delta Soil: Contamination Sources and profiles. *Int. J. Environ. Sci. Tech.* 2(4): 343 – 352.
19. Osu, Charles I. and Okereke Victor C. Heavy metals contamination in relation to Microbial counts in soils of automobile mechanic workshops, Port- Harcourt Metropolis, Rivers state, Nigeria. *Journal of American Science.* 2010; 6(9): 236 – 241.
20. Osu, Charles I. and Asuoha Adaku N. Polycyclic aromatic hydrocarbons (PAHs) and Benzene, Toluene, Ethylbenzene and Xylene (BTEX) contamination of soils in automobile mechanic workshops in Port-Harcourt metropolis, Rivers State, Nigeria. *Journal of American Science.* 2010; 6(9): 242 – 246.
21. Paul Boehm and Tarek Saba. Identification and Allocation of polycyclic aromatic hydrocarbons (PAHs). *Environmental Forensic, Exponent vol. 4*; 1 – 4.
22. Ressler, B.P., Kneifel, H., Winter, J. Bioavailability of polycyclic aromatic hydrocarbons and formation of humic acid – like residues during bacterial PAH degradation. *Appl. Microbiol. Biotechnol.* 1999; 53(1): 85 – 91.
23. Salanitro, J.P., Dorn, P. B., Huesemann, M. H., Moore, K. O., Rhodes, I. A., Rice, J. L. M., Vipond, T.E., Western, M. M., Wisniewski, H. L. Crude oil hydrocarbon and soil ecotoxicity assessment. *Environ. Sci. Technol.* 31, 1769 – 1776.
24. Schreiber, M.E., Bahr, J.M. Nitrate enhanced bioremediation of BTEX-contaminated groundwater. Parameter estimation from natural gradient tracer experiments tracers. *J.contam.. Hydrol.* 2002; 55: 29 - 56.

25. Udoetok, I.A. and Osuji Leo C. Gas Chromatographic fingerprinting of crude oil from Idu-Ekpeye Oil spillage site in Niger Delta, Nigeria. *Environ. Monit. Assess.* 2008; 141: 359 - 364.
26. United States Environmental Protection Agency. Test methods of evaluation of soil waste. USEPA, Washington, D.C. USEPA S/W-1986: 846.
27. Wcislo. E. Soil Contamination with polycyclic Aromatic Hydrocarbons (PAHs) in Poland. *Polish journal of Environmental studies*, 1998; 7(5): 267 - 272.
28. Wilson, S.S., Jones, K.C. Bioremediation of soil contaminated with polynuclear aromatic hydrocarbons( PAHs) : A review . *Environ. Pollut.* 1993; 81: 229 – 249
29. Zhang, W., Bouwer, E.J., Ball, W.P . Bioavailability of hydrophobic organic contaminants. Effects and implications of sorption-related mass transfer on bioremediation. *GWMR winter*, 1998; 126 - 138.
30. Zou, Y. L., Zhan,W., Atkinson, S. The characterization of polycyclic aromatic hydrocarbons emission from burning of different firewood species in Australia, *Environmental pollution*, 2003: 124: 283 - 589.

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