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Full Length Research Paper

Establishing Baseline PAH Levels in Rural Agricultural Wetlands of the Niger Delta Prior to Oil Well Reactivation

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The concentration and distribution of 17 polycyclic aromatic hydrocarbons (PAHs) in some rural agricultural wetland soils of the Niger delta region, Nigeria was determined. There were measurable amounts of naphthalene, acenaphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene and benzo(b)fluoranthene. Benzo(a)pyrene, benzo(k)fluoranthene, indeno(1,2,3)perylene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene were not detected in the soils. There were also significant correlations between the occurrences of some of the PAHs. However, the concentrations of the PAHs obtained were within the background levels expected for rural agricultural soils. The PAHs levels obtained in this study would act as baseline levels of these persistent organic pollutants in this environment with about 50 abandoned oil wells that are now been reactivated for completion and production.

Key words: Polycyclic aromatic hydrocarbons, wetland soils.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a group of chemicals that are formed during the incomplete burning of coal, oil, gas, wood, garbage, or other organic substances, such as tobacco and charbroiled meat (UDHHS, 1995). PAHs are ubiquitous in soil and because anthropogenic combustion processes are a major source of PAHs in soils. Soil concentrations of PAHs have tended to increase over the last 100-150 years, especially in urban areas (Jones et al., 1989a,b). There have also been elevated concentrations of PAHs at contaminated sites.

In a 1988 study at a hazardous wasteland treatment site for refinery process wastes, which has been operated since 1958, average PAHs concentrations in surface soils (0-30 cm) ranged from not detected for acenaphthene, anthracene, benzo(a)anthracene, and benzo(k)flouranthene to 340 mg/kg dry weight for dibenzo(a,h) anthraxcene (Loer, 1993). PAH concentrations decreased with increasing depth and the majority of PAHs were not detected at depths below 60 cm. At depth 90-135 cm, only phenanthrene (1.4 mg/kg), pyrene (4.0 mg/kg), chrysene (0.9 mg/kg) and dibenzo(a,h)anthracene (0.8 mg/kg) were found.

The rate and extent of distribution and/or accumulation of PAHs in soils are affected by environmental factors such as the organic content, structure and particle size of the soil, characteristics of the microbial population, the presence of contaminants such as metals and cyanides that are toxic to micro-organisms, and the physical and chemical properties of the PAHs (Wilson and Jones, 1993).

Wetlands have been variously defined (Addriesses, 1986; Ojanuga et al., 2003) and the definition of Ojanuga et al. (2003) which is in conformity with the United States Fish and Wildlife Services (USFWS) described them as “lands where water table is at or near or above the land surface long enough to promote the formation of hydric soils or to support the growth of hydrophytes”. Wetlands abound in various parts of the world and have different uses. A survey of the oil concession map of Nigeria shows that virtually all lands in the Niger delta region

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have been conceded to various oil prospecting activities. According to Nigerian National Petroleum Corporation (NNPC, 1985), “the objectives of exploratory and exploittative activities are to locate oil and gas if they exist and to acquire vital geological information about major sedimentary basins. However, if gas and oil do not exist and therefore not located the land ought to revert as soon as possible to its pre-exploration or other highest and best use”. Unfortunately, abandoned wells and associated lands abound in many oil-producing communities.

Udo (2001) working in the Niger delta zone of Nigeria recognized the following agricultural uses of the wetland soils in the delta region: (i) Traditional gathering of forest products such as oil palm, raffia palm, medicinal plants, firewood and building materials. (ii) Cultivation of yams which are grown in large mounds or heaps made during the dry season. (iii) Dry season vegetation production. (iv) Rain-fed lowland rice, and (v) mangrove rice cultivation.

The agricultural quality of a land can be judged by the physico-chemical properties of its soils which provide anchorage, water and nutrients to the plants. Moreover, agricultural soils must be devoid of environmental contaminants and pollutants such as PAHs. Considering the unique uses and diversity of wetland soils ecosystem in the Niger delta, it is therefore imperative to maintain the present levels of petroleum production and consumption with some controls on land for agricultural production.

In order to sustain the cultivation of both tree and arable crops in this area with about 50 abandoned marginal oil fields, it is essential to establish the base-line levels of soil contaminants such as PAHs. It is envisaged that information and data gathered from this study will be invaluable to government and policy makers in making better-informed decision on how best these wetlands can be used sustainably, especially when these oil wells abandoned since the 60s are now been reactivated for completion and production.

MATERIALS AND METHODS

Study area

The soils were collected from Kwale area of Delta State, Nigeria. The entire land mass is flat with significant presence of both arable and tree crops, such as *Elaeis guineensis Jacq* and *Raphia hookeri spp*. Farming is the main occupation of the rural populace in the area. There are equally about 50 marginal oil wells abandoned in the 60s in this community, which implies that soils in this area would have been exposed to a high level of organic contaminants from oil exploration and exploitative activities.

Soils were collected at geo-referenced (with Garmin’s GPSMAP 76S) spots with the aid of a stainless soil sugar. Soils collected for the determination of their physicochemical properties were transferred into the polyethylene bags while soils for the evaluation of the polycyclic aromatic hydrocarbons (PAHs) were placed in cleaned 1 litre glass jars with Teflon lined screw cap, cooled to about 4°C in ice jackets for further processing and analysis. The soils were sampled at 0-15, 13-30 and 30-45 cm.

Soil preparation and analysis

Soils for the determination of physico-chemical properties were dried at ambient temperature (22-2°C), crushed in a porcelain mortar and sieved through 2 mm (10 mesh) stainless sieve. The <2 mm fraction was used for the various determinations. Soil pH was determined according to Folson et al. (1981). The soil solution ratio was 1:2. Total soil organic carbon was determined by the Walkey- Blacke rapid dichromate oxidation technique (Nelson and Sommers, 1982) with the use of correction factor 1.3 to account for the incomplete oxidation of organic carbon. Particle size analysis was achieved according to the method of Bouyoucos (1962).

Determination of the PAHs

The soils were dried by mixing 10 g of the soil samples with 10 g anhydrous Na_2SO_4 and placed in an extraction thimble. Thereafter, 10 ml of 1:1 (v/v) mixture of analytical grade dichloromethane and acetone were added and the samples were sonicated for 30 min. The sample was collected and filtered using a glass wool plurged into a glass funnel with 1 g anhydrous Na_2SO_4 into a 250 litre conical flask. The extraction was then repeated. Concentration of the extract was done using the rotary evaporator and the extract was concentrated to 10 ml at 60°C, after which 10 ml of hexane was added and further concentrated to about 2 ml at 60°C. The extract was made to undergo cleanup and fractionation using silica gel permeation chromatography. The final extract was packed in a 2 ml gas chromatogram (GC Perkin-Elmer/Clarius 500) vials and analyzed for the polycyclic aromatic hydrocarbons (US Environ- mental Protection Agency, 1984). The mean and standard deviations of selected soil physiochemical properties and the PAHs were determined using SPSS version 10.0. Also, the correlation between any two of the ten prevalent PAHs was evaluated.

RESULTS AND DISCUSSION

The pH of the soils and other selected physico-chemical properties are shown (Table 1). The soils generally had pH ranging from 3.49 to 8.14. The mean soil pH of the entire area was 4.42 with a standard deviation of 1.15 indicating that there were little differences in the pH irrespective of the location. There was however no consistent trend in the variation of the pH with soil depth. Low or acidic soil pH is associated with wetland soils due to the reducing (lack of oxygen) conditions experienced in these soils (Ojanuga, 2005). Total organic carbon was low (0.19-1.77%) with a mean value of 0.94% (Table 3). Low organic carbon content in soil is suggestive of increasing weathering activities (photochemical oxidation) and leaching of water-soluble organic matter (Larson and Weber, 1994) and/or exhaustive tillage and cropping of the soil (Ojeniyi, 1990). Soil texture was predominantly loamy sand and sandy loam with variable clay and silt content (Table 1).

Table 2 shows that there were detectable and measurable amounts of naphthalene, 2-methyl naphthalene, acenaphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene and benzo(b)fluoranthene, while benzo(a)pyrene, benzo(k)fluoranthene, indeno(1,2,3) perylene, dibenzo(a,h)anthracene and benzo(g,h,i)pery-

Table 1. Physicochemical properties of the soils.

LOCATION	Depth (cm)	pH	TOC (%)	Sand (%)	Silt (%)	Clay (%)	Texture
UMTW$_1$ Umutu	0 - 15	7.28	1.30	59.76	19.09	21.15	Sandy loam
0.5° 54.308'N	15 - 30	8.14	1.20	64.34	6.79	28.86	Sandy loam
06° 13. 068'E	30 - 45	7.59	0.70	48.68	21.42	29.91	Loam
UMT$_1$WB Umutu	0 - 15	3.69	1.34	46.66	19.81	33.53	Loam
05° 54.912'N	15 - 30	3.89	0.79	85.27	1.21	13.49	Loamy Sand
06° 13.125'E	30 – 45	3.76	0.79	87.03	8.22	4.75	Loamy Sand
UMT$_1$C Umutu	0 - 15	3.51	0.84	47.12	45.39	7.49	Sandy Clay
05° 54.109'N	15 - 30	3.73	1.01	51.37	18.23	30.39	Sandy Loam
06° 13.137'E	30 – 45	3.66	1.05	68.58	11.51	19.96	Sandy loam
UMT$_1$ Umutu	0 - 15	3.54	0.62	50.47	26.28	23.21	Sandy Clay loam
05° 54.613'N	15 - 30	3.72	0.19	79.84	1.39	18.81	Loamy sand
06° 13. 347^{1}E	30 – 45	3.49	0.64	79.84	1.34	18.63	Loamy sand
Umds Ogbe	0 - 15	3.92	1.68	83.53	2.35	14.08	Loamy sand
05° 42.791'N	15 - 30	5.70	1.54	83.85	4.04	12.01	Loamy sand
06° 25.429'E	30 – 45	6.04	1.23	75.66	2.85	21.48	Loamy sand
L$_3$W Amorji	0 - 15	4.43	0.47	69.88	20.98	9.14	Sandy loam
05° 46.662'N	15 - 30	4.01	0.57	85.15	3.73	11.08	Loamy sand
06° 24.93'N	30 – 45	3.98	0.49	86.25	5.81	7.94	Loamy sand
L$_3$WC Amorji	0 - 15	3.98	0.82	84.08	5.08	10.83	Loamy sand
05° 45.769'N	15 - 30	3.70	0.79	84.49	4.85	10.66	Loamy sand
06° 26.369'E	30 – 45	4.34	0.84	81.87	5.18	12.95	Loamy sand
L$_2$ Egeme Unor	0 - 15	3.94	0.87	79.68	2.01	18.30	Loamy sand
05° 01.128'N	15 - 30	3.78	0.55	61.79	24.02	14.18	Sandy clay loam
06° 22.031'E	30 – 45	3.90	0.37	48.95	42.12	8.93	Sandy clay
L$_7$ Obodeti	0 - 15	3.80	0.94	64.58	19.97	15.43	Sandy loam
05° 39.123'N	15 - 30	3.69	1.09	77.47	18.61	15.49	Sandy loam
06° 19.313'E	30 – 45	3.55	0.43	69.75	16.07	14.18	Sandy loam
L$_8$ Ozoro	0 - 15	4.29	0.89	85.00	5.84	9.15	Loamy sand
05° 34.471'N	15 - 30	4.69	0.84	85.61	9.32	5.06	Loamy sand
06° 13.153'E	30 – 45	4.50	0.68	76.55	15.29	8.15	Sandy loam
PNT Utuagba	0 - 15	5.07	1.77	75.64	14.32	10.03	Sandy loam
Ogbe	15 - 30	5.03	1.72	73.18	14.44	12.376	Sandy loam
05° 40.834'N	30 – 45	4.48	0.76	78.38	7.97	13.66	Loamy sand
06° 26.043^{1}E							
IgK Igbwku	0 - 15	4.09	1.44	66.84	6.63	26.52	Sandy loam
05° 36.539'N	15 - 30	4.17	1.50	67.62	9.24	23.12	Sandy loam
06°24. 678'E	30 – 45	4.22	1.33	61.46	12.88	25.88	Sandy loam

Table 3. Mean concentration and standard deviation of the PAHs and physicochemical properties of the soils.

Properties	Mean	Standard deviation
pH	4.420	1.154
TOC (%)	0.944	0.405
Clay (%)	16.140	7.636
Naphthalene (mg/kg)	0.005	0.005
2 – Methylnaphthalene (mg/kg)	0.006	0.018
Acenaphthalene (mg/kg)	0.001	0.003
Acenaphthene (mg/kg)	0.007	0.032
Flourene (mg/kg)	0.115	0.118
Phenanthrene (mg/kg)	0.014	0.025
Anthracene (mg/kg)	0.084	0.266
Flouroanthrene (mg/kg)	0.029	0.125
Pyrene (mg/kg)	0.012	0.046
Benzo(a)anthracene (mg/kg)	0.111	0.209

Table 2. Concentration (mg/kg) of the PAHs in the soils.

Coordinate	Soil depth (cm)	Naphthalene	2-methyl Naphthalene	Acenapthalene	Acenaphthene	Florene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benzo(a) Anthracene	Chrysene	Benzo(b) Fluoranthrene	Benzo(a) Pyrene	Benzo(k) Fluoranthrene	Indeno(1,2,3) Perylene	Dibenzo (a,h) Anthracene	Benzo (g,h,i) Perylene
UMTW1 Umutu	0 - 15	ND	0.012	ND	ND	ND	0.147	0.160	ND	ND	1.094	ND	0.065	ND	ND	ND	ND	ND
	15 – 30	ND	ND	ND	ND	ND	0.17	0.077	ND	ND	0.224	ND	ND	ND	ND	ND	ND	ND
	30 – 45	ND	ND	ND	ND	ND	0.021	0.090	ND	ND	0.292	ND	ND	ND	ND	ND	ND	ND
UMTIB Umutu	0 – 15	ND	ND	ND	ND	ND	0.035	0.151	ND	ND	0.306	ND	ND	ND	ND	ND	ND	ND
	15 – 30	ND	ND	ND	ND	ND	0.020	0.085	ND	ND	0.234	ND	ND	ND	ND	ND	ND	ND
	30 - 45	ND	ND	ND	ND	0.025	0.008	0.302	ND	ND	0.368	ND	ND	ND	ND	ND	ND	ND
UMT$_I$C Umutu	0 - 15	ND	ND	ND	ND	ND	0.019	0.069	ND	ND	0.163	ND	ND	ND	ND	ND	ND	ND
	15 – 30	ND	ND	ND	ND	ND	0.29	0.122	ND	ND	0.267	ND	ND	ND	ND	ND	ND	ND
	30 - 45	ND	0.008	ND	ND	ND	0.026	0.089	ND	ND	0.271	ND	ND	ND	ND	ND	ND	ND
UMT$_I$ Umutu	0 - 15	ND	ND	ND	ND	0.010	0.025	0.089	ND	ND	0.328	ND	ND	ND	ND	ND	ND	ND
	15 – 30	ND	ND	ND	ND	ND	0.18	0.060	ND	ND	0.175	ND	ND	ND	ND	ND	ND	ND
	30 - 45	ND	ND	ND	ND	ND	0.014	0.047	ND	ND	0.095	ND	ND	ND	ND	ND	ND	ND
Umds Ogbe	0-15	ND	ND	ND	ND	ND	0.028	0.093	ND	ND	0.205	ND	ND	ND	ND	ND	ND	ND
	15-30	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	30-45	0.007	0.110	0.021	ND	0.009	0.010	ND	ND	0.267	ND	ND	ND	ND	ND	ND	ND	ND
Amorji L$_3$W	0-15	0.007	0.007	ND	ND	0.171	0.010	ND	0.008	ND	ND	ND	ND	ND	ND	ND	ND	ND
	15-30	0.009	0.007	ND	0.006	0.231	0.014	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	30-45	0.010	0.012	0.005	0.005	0.318	0.010	ND	0.044	0.014	ND	0.086	ND	ND	ND	ND	ND	ND

Table 2. contd.

Amorji L_3Wc	0-15	0.008	0.008	0.006	0.005	0.346	0.008	ND	0.083	0.015	ND	0.085	ND	ND	ND	ND	ND	ND
	15-30	0.011	0.007	ND	0.005	0.200	0.015	ND	0.015	0.070	ND	ND	ND	ND	ND	ND	ND	ND
	30-45	0.009	0.007	ND	0.005	0.210	0.004	0.606	0.010	0.020	ND	ND	ND	ND	ND	ND	ND	ND
Ejeme Umor	0-15	0.014	0.006	0.005	0.190	ND	ND	1.589	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	15-30	0.008	0.006	ND	ND	0.163	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	30-45	0.010	0.008	0.004	0.004	0.262	0.003	ND	0.012	ND	ND	ND	ND	ND	ND	ND	ND	ND
Obodeti	0-15	0.007	ND	ND	ND	0.141	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	15-30	0.007	ND	ND	ND	0.77	ND	ND	0.012	ND	ND	ND	ND	ND	ND	ND	ND	ND
	30-45	0.006	ND	ND	ND	0.132	ND	ND	0.028	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ozoro	0-15	0.007	0.018	ND	ND	0.159	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	15-30	0.009	ND	ND	0.005	0.221	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	30-45	0.007	ND	ND	ND	0.237	ND	ND	ND	0.016	ND	ND	ND	ND	ND	ND	ND	ND
PNT Utuagba Ogbe	0-15	0.006	ND	ND	ND	0.192	ND	ND	ND	0.029	ND	ND	ND	ND	ND	ND	ND	ND
	15-30	0.017	0.005	0.005	0.012	0.370	0.005	0.005	0.006	0.014	0.016	ND	0.089	ND	ND	ND	ND	ND
	30-45	ND	ND	ND	ND	0.081	0.005	0.005	ND	0.026	0.035	ND	ND	ND	ND	ND	ND	ND
Igk Igbuku	0-15	0.016	ND	ND	ND	0.073	ND	ND	ND	0.750	ND	ND	ND	ND	ND	ND	ND	ND
	15-30	0.005	ND	ND	ND	0.128	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	30-45	0.011	0.005	0.005	0.009	0.272	0.003	0.003	0.005	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND = NOT Detected.

Table 4. Background soil concentrations of polycyclic aromatic hydrocarbons (PAHs).

Compound	Concentrations (x 10^{-3} mg/kg)		
	Rural soil	Agricultural soil	Urban Soil
Acenaphthene	1.7	6	NE
Acenaphthylene	NE	5	NE
Anthracene	NE	11 – 13	NE
Benzo(a) anthracene	5-20	56-110	169-59,000
Benzo(a)pyrene	2-1,300	4.6-900	165 – 220
Benzo(b)flouranthene	20-30	58-220	15, 000-62, 000
Benzo(e)perylene	NE	53-130	60-14, 000
Benzo(g,h,i)perylene	10-70	66	900-47,000
Benzo(k)fluoranthene	10-110	58-250	300-26,000
Chrysene	38.3	78-120	251-640
Fluoranthene	0.3-40	120-210	200-166,000
Flourene	NE	9.7	NE
Ideno (1,2,3-c,d) pyrene	10-15	63-100	8,000-61,000
Phenanthrene	30.0	48-140	NE
Pyrene	1-19.7	99-150	145-147,000

Source: Jones et al. (1987).
NE: Not established.

lene were not detected in the soils. There was equally no specific distribution pattern of the PAHs with respect to the increasing soil depth. Fluorene had the highest mean concentration (0.15 mg/kg) in the soils (Table 3). However, acenaphthene, phenanthrene, anthracene fluoranthene, pyrene and benzo(a)anthracene had higher standard deviations than their respective means. This implies that these PAHs were not uniformly distributed in the entire area.

It is important to emphasize that although abandoned marginal oil wells abound in the area, farming is the predominant occupation of this community. The incomplete burning of plant residues before planting or the cropping season seem to be the main source of the PAHs in these soils, hence their relatively low amounts.

Comparing the values obtained in the present work with background soil concentration of PAHs (Jones et al., 1987), it is evident that the PAHs in this study have low amounts especially with respect to rural and agricultural soils (Table 4). The correlation matrices between any two of the ten prevalent PAHs indicate that there were significant correlation between benzo(a)anthracene and phenanthrene (0.93), acenaphthene and fluoranthene (0.96), and acenaphthalene and pyrene (0.86). Similarly, 2-methyl naphthalene correlated significantly (0.90) with acenaphthene. Significant correlations between any two PAHs may be suggestive of the same source of the PAH.

In conclusion, the present study has shown that there are detectable, variable and non detectable amounts of the 17 PAHs profile investigated in the wetland soils. The concentrations and distributions of these PAHs were not consistent with increasing soil depth. All the PAHs obtained were within the background levels expected for rural and agricultural soils. This implies that both the farming and other scanty industrial or production activities so far, have sustainable impact on the PAH concentrations in these soils.

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