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Polycyclic Aromatic Hydrocarbons Profiles of Spent Drilling Fluids Deposited at Emu-Uno, Delta State, Nigeria

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Abstract The concentrations and profiles of polycyclic aromatic hydrocarbons were determined in spent drilling fluid deposited at Emu-Uno, Delta State of Nigeria. The total concentrations of polycyclic aromatic hydrocarbons in the spent drilling fluid deposits ranged between 40 and 770 μg kg^{-1}. The PAHs profile were predominantly 2- and 3-rings with acenaphthalene, phenanthrene, fluorene being the predominant PAHs. The prevalence of 2- and 3-rings PAHs in the spent drilling fluid deposits indicate contamination of the drilling fluids with crude oil during drilling. Incorporation of spent drilling fluids into the soil has serious implication for soil, surface water and groundwater quality.

Keywords Spent drilling fluids · Polycyclic aromatic hydrocarbons · Soil contamination

During drilling of oil and gas wells, special fluids are pumped down into the borehole to lubricate and cool the bits, float out cuttings, seal porous rock strata and apply hydrostatic pressure, prevent the borehole from filling with water. Upon completion of a gas or oil well, the spent drilling fluids and cuttings are normal incorporated into soil adjacent to well site or allowed to dewater in a pit and thereafter covered with soils.

Land disposal of spent drilling fluids/cuttngs is a common practice in the Niger Delta region of Nigeria. In most times, waste contractors collect these wastes from drilling sites and dispose off these wastes at some communities far away from the drilling sites without any prior assessment. This activity has hitherto heightened environmental activism, youth restiveness and host communities versus oil companies' conflicts in the Niger Delta. Recently, concerns have been raised on the composition of these wastes, long and short term effects of land disposal of drilling cuttings. Plant yields, groundwater and surface water quality may be adversely affected by incorporation of drill cuttings into soil due to its alkalinity, salinity and trace metals or petroleum hydrocarbons contents of these wastes. Drilling wastes in any form requires characterization before land disposal in order to ascertain the types and quantity of contaminants that have been added into agricultural lands and its adverse environmental impact.

Polycyclic aromatic hydrocarbons (PAHs) were ranked as the 9th most threatening compounds to human in 2001 (King et al. 2002; Samimi et al. 2009). Polycyclic aromatic hydrocarbons are class complex organic chemicals, which includes carbon and hydrogen with fused structure containing at least two benzene rings. PAHs may also contain additional rings that are not six-sided (Ravindra et al. 2008). Considering the increasing evidence of the ubiquitous presence of PAHs and health risk associated with exposure, studies on the profiles and levels in environmental matrices have attracted substantial research interest because many of these compounds are carcinogenic and mutagenic causing irreversible changes in structures and functioning of living organisms (Marynowski et al. 2004). PAHs are derived from both natural and anthropic sources. Small amounts have been found in geological formations such as hard coal, brown coal, crude oil and bituminous shales (e.g. Bojakowska and Sokolowska 2001a, b, c; Lavric and Spangerberg 2002).

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Data on the polycyclic hydrocarbons composition and profiles drilling cutting is grossly limited. The objective of the present study was to determine the concentrations and profiles of some polycyclic aromatic hydrocarbons in drilling cuttings deposited at Emu-Uno with a view of providing information on risk associated with such land disposal practices.

Materials and Methods

The study area (Emu-Uno) lies on longitude 6°14′E and latitude 5° 37′N. A total of six composite samples were collected from six dumps at Emu-Uno. The samples were sieved to pass through 2 mm mesh, and stored at 4°C prior to analysis. Total organic matter was determined by wet dichromate oxidation methods of Walkley and Black procedure and pH was determined (1:2.5 m/v) using a Jenway digital pH meter (Abollino et al. 2002). The conductivity was measured using a conductivity meter. Five g of the waste samples was extracted with hexane (90%) and dichloromethane (99.8% analar grade BDH, Poole, England) in an accelerated solvent extractor (ASE 200, Dionex, Sunnyvale, CA). Extraction cells were filled with solvent, pressurized to 14 MPa and heated to 120°C for 6 min. Pressure and temperature was held constant for extraction time of 5 min and cells were rinsed with cold solvent (60% of cell volume) and purged with argon for 150 s. The static extraction and purge step were performed twice for each sample and the extracts were combined (Wickel et al. 2005; Pie et al. 2007). The extracts were evaporated to 1 mL and purified by solid phase extraction with 2 g of aluminium oxide (5% deactivated upper part) and 2 g of silica gel (5% deactivated lower part). The PAHs were subsequently eluted with 15 mL of hexane, 5 mL of hexane and dichloromethane (9:1) and 20 mL of hexane and dichloromethane (4:1). The eluted fractions were combined and evaporated to approximately 0.5 mL. Eight deuterated PAHs (NAP-D_8, ACE-D_{10}, FLU-D_{10}, PYR-D_{10}, CHR-D_{12}, PYR-D_{12}, BGH-D_{12}) as internal standards, to check the recovery of the internal standards FLT-D_{10} was added to extract before injection into gas chromatography. The mean recoveries were greater than 94.8%. PAHs were detected with gas chromatography (HP 6890 Palo Alto, CA) equipped with a HP5 (cross linked PHME siloxane) (0.25 μm film thickness, 0.25 mm × 30 m) and flame ionization detector (FID). The carrier gas was helium with a flow rate of linear velocity 30 cm/s. Initial temperature of 100°C and increased finally to 310°C at a rate of 4°C/min. one μL of each sample was injected in splitless mode. The detection limit for the PAHs is 1 μg kg^{-1}. All results were calculated at dry weight basis.

Results and Discussion

Table 1 present the results of some physiochemical characteristics of spent drilling fluid dumps in Emu-Uno. The pH of the drilling muds ranged from 8.19 to 10.17. This indicates that these wastes are alkaline in nature. However, studies have shown that Niger Delta soils are usually acidic to near neutral in nature (Iwegbue et al. 2006; Iwegbue et al. 2009). Incorporation of wastes with soil high pH values will result to an increase in the soil pH. Similarly, the conductivity of the spent drilling mud ranged between 3,250 and 11,400 μS cm^{-1}. This is outrageously high compared to conductivity levels reported for Niger Delta soils (Iwegbue et al. 2006). Incorporation of spent drilling mud with such high pH and conductivity values could change microbial ecology, enzymes activities and availability of plant nutrients.

Table 2 present the results of the total petroleum hydrocarbons composition of spent drilling mud. The aliphatic fractions consist of 57.7%–99.4% of the total petroleum hydrocarbons content while the aromatic fraction consists of 0.6%–42.8%. E_4 has the highest aromatic hydrocarbon fractions.

The aliphatic hydrocarbons profile varied from one dump to another (Table 3). In dumps E_1 and E_3, the C_{10} (decane) shows predominance over all the forms of aliphatic hydrocarbons. The concentrations of decane in dumps E_1 and E_3 which constitutes 98.9% and 65.8% of total aliphatic hydrocarbons content of dumps E_1 and E_3 respectively. However, in the other dumps, the predominant form of aliphatic hydrocarbons is dodecane (C_{12}). The concentrations dodecane in the samples spanned between 109 and 14,597 μg kg^{-1}. The highest dodecane content was observed at dump E_6. Nonadecane (C_{19}) is the only odd carbon number aliphatic hydrocarbon detected in the spent drilling mud deposits. The concentrations of C_{19} ranged

Table 1 Some physicochemical characteristics of the spent drilling fluids

	E_1	E_2	E_3	E_4	E_5	E_6
Ph	10.17	10.57	8.82	9.24	8.19	9.17
Electrical conductivity (μS cm^{-1})	9,660	10,490	11,400	3,250	7,400	8,950
TOC %	1.66	2.40	1.54	0.64	1.79	2.03

Table 2 Total petroleum hydrocarbons ($\mu g\ kg^{-1}$) composition of spent drilling fluids

	Total PHC	Aliphatic	Aromatic
E_1	29,920	29,510 (98.62%)	430 (1.37%)
E_2	12,440	11,670 (93.81%)	770 (6.19%)
E_3	11,500	10,920 (47.78%)	230 (2.22%)
E_4	104	60 (57.62%)	40 (42.38%)
E_5	10,250	9,940 (96.98%)	310 (3.02%)
E_6	44,660	44,390 (99.39%)	270 (0.60%)
Mean			

from not detected at dump E_4 to 33 $\mu g\ kg^{-1}$ at dump E. In this study, the concentrations n-alkanes with an even number (especially C_{10}, C_{12}, C_{14}, C_{16}, C_{18}, C_{20}, C_{22}, and C_{24}) showed predominance over odd number carbon atoms. This is a characteristic feature of mature terrestrial organic matter (Tissot and Welte 1984; Marynowski et al. 1984).

The polycyclic aromatic hydrocarbons profiles of spent drilling muds are presented in Table 4. The concentrations of total polycyclic aromatic hydrocarbons spanned from 44 $\mu g\ kg^{-1}$ at E_4 to 771 $\mu g\ kg^{-1}$ at E_2. According to Danish standards, the PAHs concentrations of unpolluted mineral soils is 20–50 $\mu g\ kg^{-1}$ (Van Brummelen et al. 1996) and a total concentrations of 200 $ng\ g^{-1}$ is regarded as the upper limits of natural occurrence (Kabata-Pendias et al. 1995).

The Danish government has adopted an intervention value of 4,000 $ng\ g^{-1}$, although such levels typically occur in urban and industrial soils (Van Brummelen et al. 1996). The concentrations of polycyclic aromatic hydrocarbons in spent drilling mud deposits exceeded the levels that are found in natural unpolluted soils and upper limits of natural occurrence except for dump E_4. Incorporations of waste which such high contents of polycyclic aromatic hydrocarbons will no doubt increase the PAHs contents of the receiving soils. In this study, low molecular weight PAHs (<4 rings) showed predominance over higher molecular weight PAHs (>4 rings). No 4 rings to 6 ring PAHs was detected in the various spent drilling mud deposits.

Typical combustion PAHs (pyrogenic) fluorene, pyrene, and benzo[g h i] perylene were not found. However, lower molecular (PAHs) and substituted PAHs are typical components of petroleum and coals (petrogenic) (Stout et al. 2002). The predominant species of PAHs were acenaphthalene, fluorene and phenanthrene. The concentrations of acenapthalene, ranged from 11 $\mu g\ kg^{-1}$ at dump E_4 to 576 $\mu g\ kg^{-1}$ at dump E_2 which constitute approximately 25%–74% of the total PAHs content. The other predominant PAHs are fluorene and phenanthrene which constitutes 6.8%–33.0% and 3.76%–56.8% respectively of the total concentrations of polycyclic aromatic hydrocarbons. Similarly, the contents of PAHs determined in crude oils in Poland varied from 22.85 to 332.45 ppm. Of the polycyclic aromatic hydrocarbon compounds determined, the largest share was occupied by 3 rings PAHs (an average of 72%) and 4 rings (about 24%), whereas the content of 5– and 6–rings PAHs did not exceed 3%. Phenanthrene and fluorene were the prevailing polycyclic aromatic hydrocarbon compounds (Bojakowska and Sokolowska 2001a). Based on the proportions of different PAHs, most studies aimed at distinguishing PAHs of petrogenic sources from those of pyrolytic origins. The PAHs of petrogenic origin, prevalent in coals and crude oils are formed from digenesis of sedimentary organic material under low and moderate

Table 3 Concentrations of aliphatic hydrocarbons ($\mu g\ kg^{-1}$) in the spent drilling fluid deposits

Aliphatic hydrocarbons	E_1	E_2	E_3	E_4	E_5	E_6
Nonane C_9	50	nd	nd	nd	nd	nd
Decane C_{10}	9,660	10,490	11,400	3,250	7,400	8,950
Dodecane C_{12}	109	11,510	10,792	18	9,857	14,597
Tetradecane C_{14}	55	83	23	7	7	434
Hexadecane C_{16}	30	13	23	9	19	39
Octadecane C_{18}	19	6	12	10	9	3
Nonadecane C_{19}	24	28	9	0	7	33
Eicosane C_{20}	21	nd	13	17	6	39
Docosane C_{22}	14	nd	23	nd	14	39
Tetracosane C_{24}	nd	nd	nd	nd	nd	09
Hexacosane C_{26}	nd	nd	nd	nd	nd	nd
Octasane C_{28}	nd	nd	nd	nd	nd	nd
Triacontane C_{30}	nd	nd	nd	nd	nd	nd
Hexatriacontane C_{36}	nd	nd	nd	nd	nd	nd
Total	29,514	11,665	10,918	60	9,944	44,387

nd not detected

Table 4 Concentrations of polycyclic aromatic hydrocarbons (μg kg^{-1}) in the spent drilling fluids deposits

PAHs	Acronyms	E_1	E_2	E_3	E_4	E_5	E_6	Mean ± SD	CV %
Naphthalene	NAP	6	10	2	4	2	43	11.6 ± 15.9	142
2-methylnapthalene	2MNAP	4	3	16	0	15	13	8.5 ± 6.9	81.7
Acenaphthalene	ACY	219	576	164	11	142	80	210.6 ± 201.8	95.8
Acenaphathene	ACE	7	nd	nd	3	6	6	3.7 ± 3.1	85.7
Fluorine	FLU	73	143	40	25	36	59	62.7 ± 42.9	68.5
Phenanthrene	PHE	13	29	9	nd	103	73	37.8 ± 41.1	108.6
Anthrancene	ANT	5	9	nd	nd	5	3	3.7 ± 3.4	93.9
Flouranthene	FLT	nd	nd	nd	nd	nd	nd	nd	–
Pyrene	PYR	nd	nd	nd	nd	nd	nd	nd	–
Benzo(a)anthrancene	BAA	nd	nd	nd	nd	nd	nd	nd	–
Chrysene	CHR	nd	nd	nd	nd	nd	nd	nd	–
Benzo(b)flouranthrene	BBF	nd	nd	nd	nd	nd	nd	nd	–
Benzo(a)pyrene	BAP	nd	nd	nd	nd	nd	nd	nd	–
Benzo(k)flouranthrene	BKF	nd	nd	nd	nd	nd	nd	nd	–
Indeno(1,2,3)perylene	IND	nd	nd	nd	nd	nd	nd	nd	–
Dibenzo(a,h)anthracene	DAH	nd	nd	nd	nd	nd	nd	nd	–
Benzo(g,h,i)perylene	BGP	nd	nd	nd	nd	nd	nd	nd	–
ΣPAH		403	771	233	44	310	277	339.6 ± 234.3	71.3%

nd not detected

temperature and tend to consist of low molecular weight PAHs with two to three rings (Pathiratne et al. 2007). The dominance of 2 and 3 rings PAHs in this study indicates that the PAHs in the spent drilling fluid was petrogenic arising from contamination of the drilling mud with crude oil during drilling.

Land disposal of spent drilling fluids containing reasonable concentrations of polycyclic aromatic hydrocarbons have serious implications for soil, surface and groundwater qualities. Therefore, spent drilling fluids required some forms of remediation before incorporation into agricultural lands.

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