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Petroleum Contamination of Sombreiro River in Akuku-Toru Local Government Area Rivers State, Nigeria, revealed by Chemical Fingerprinting of Aliphatic Hydrocarbons

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ABSTRACT: Water samples were collected from the lower section of Sombreiro River in Akuku Toru local government area (L.G.A.) of Rivers State, Nigeria and analyzed for aliphatic hydrocarbons using gas chromatography-flame ionization detector (GC-FID) after extraction and clean up. GC identified well resolved aliphatic hydrocarbons from C_9 to C_{40} which showed similar bimodal *n*-alkane distributions and unresolved complex mixtures (UCM). Pristane was observed as the most prominent aliphatic hydrocarbon and dominant over phytane in all the samples. Common aliphatic hydrocarbon diagnostic ratios used for fingerprinting and interpreting chemical data were determined. These include carbon preference index (CPI) from 0.70 to 0.82; Pr/Ph from 1.85 - 2.17; Pr/nC_{17} from 1.67 - 1.87; Ph/nC_{18} from 0.94 - 1.07 and cross plot.The results reveal the following: (1) crude oil contamination of the lower section of Sombreiro river in Akuku Toru L.G.A. of Rivers State; (2) the same crude oil spilled in the river; (3) the spilled oil is Niger Delta in origin, derived from mixed marine and terrigenous organic matter deposited in an oxic environment; (4) the spilled oil was slightly degraded, its chemical composition has not undergone significant alteration.

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Spills and leaks of crude oil and its refined products cause widespread contamination of the environment. It can occur due to accidents, from industrial releases, or by-products of commercial or domestic uses (Ou *et al*., 2004 and Mille *et al*., 2007). Crude oil is composed of a complex mixture of hydrocarbons classified in bulk groups of saturates, aromatics, resins and asphaltenes (Wang *et al*., 2006). The saturate include aliphatic and cycloalkanes which consist of hydrocarbons up to C_{40} (Rudzinski and Aminabhavi, 2000). Aliphatic hydrocarbons (AHCs), normal and isoalkanes, are the predominant class of chemical compounds in most crude oils and refined products (Tissot and Welte, 1984). Their distribution and compositionin petroleum is unique and used for chemical fingerprinting of petroleum spills (Wang *et al*., 2006). Chemical fingerprinting of the AHCs can provide information on the biological sources of organic matter which generated the petroleum, the condition of deposition at that time, the age of the petroleum source rock, the relative maturity, and the degree of microbial biodegradation (Osuji, 2011). They can also provide reliable environmental forensic information used for the determination of the source of unknown oil spilled, even for biodegraded oils, correlation, differentiation and subsequent monitoring of the affected ecosystems (Peters *et al*., 2005). Samples collected from contaminated environments are usually analyzed for the AHCs by gas chromatography (GC) and the composition data obtained are used for characterization by chemical fingerprinting techniques (Wang *et al.,* 1999; Sun *et al*., 2009). Diagnostic tools of AHCs generally employed for chemical fingerprinting related environmental forensic investigations include carbon preference index (CPI), ratios of pristane/phytane (Pr/Ph), pristane/*n*-heptadecane (Pr/nC_{17}) and phytane/*n*-octadecane (Ph/nC_{18}) (Wang *et al.,* 1999; Seki *et al*., 2006). Simoneit *et al.* (1990) used aliphatic ratios of nC_{15-35}/nC_{16}, $\Sigma nC_{15-20}/\Sigma nC_{21-35}$ and nC_{31}/nC_{19} for assessing petroleum contamination.The Niger Delta is located in Southern Nigeria, between longitude 5° - 9° E and latitude 4° - 6° N, on the Atlantic coast of West Africa. It is endowed with enormousnatural resources, especially hydrocarbons (crude oil) which is the mainstay of Nigeria's economy. River Niger splits into rivers, forming deltas, via which it drains into the Atlantic Ocean. Sombreiro river is one of the major rivers of the Niger Delta. The Sombreiro river flows from Egbema area of Imo State into Rivers State through a number of communities and empties into the Atlantic Ocean (Iyama *et al*., 2014).This study describes the chemical fingerprinting and data interpretation technique used to reveal hydrocarbon

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contamination of Sombreiro river within Akuku Toru local government area (L.G.A.) of Rivers State in Niger Delta, Nigeria. The study determined the composition, origin, fate, and correlation of aliphatic hydrocarbons in the waters of Sombreiro River.

MATERIALS AND METHODS

Study area: The study area is the lower section of Sombreiro River located in Akuku Toru local government area (L.G.A.) of Rivers State in Niger Delta, Nigeria. Akuku-Toru L.G.A. is typically riverine and endowed with abundant oil and gas reserves. Sombreiro River is one of the outlets through which the River Niger drains into the Atlantic Ocean. It is mainly freshwater and predominantly occupied by rural communities that depend on the water for drinking, bathing, washing of clothes and fisheries (UNDP Report, 2006). Other activities carried out in the river include washing and fermentation of cassava, defecation and the dumping of refuse and abattoir. These activities result in the discharge of various pollutants into the aquatic environment, threatening the health of the local dwellers and damaging the quality of the environment (Abowei and Sikoki, 2005).

Sampling: Water samples were collected from four (4) points of the lower section of the Sombreiro River located in Akuku Toru L.G.A. of Rivers State between longitude 6° 46′39.4″ E to 6° 48′ 28.2″ E and latitude 4°34′46.8″ to 4° 40′04.7″ N. The water samples, one (1) litre each, were collected using a dark glass bottle. The sample bottles were sealed, labelled appropriately, transported to the laboratory and stored in the refrigerator prior to analysis.

Sample extraction and cleanup: Petroleum hydrocarbons were extracted from the contaminated water samples according to the separatory funnel liquid-liquid extraction EPA Method 3510 (EPA, 1996). 50 ml each contaminated water sample was poured into a separatory funnel and equal volume of hexane added. The separatory funnel was agitated for 30 minutes with a mechanical shaker and the mixture left to stand for two hours to allow for maximum separation of the aqueous and organic phase. The organic phase was concentrated by evaporating hexane under a stream of nitrogen at 40 °C. Cleanup was achieved by transferring the concentrated extracts onto the top of a glass column (25 cm x 1 cm) packed with activated silica and plugged with glass wool at the bottom. *n*-hexane was poured into the column to elute the saturates, which contains the aliphatic hydrocarbons. The eluent was concentrated by evaporating the solvent at room temperature in the laboratory.

Gas Chromatography (GC) analysis: Detailed aliphatic hydrocarbon analysis was performed on each sample using an Agilent 7890B gas chromatography (GC) system equipped with a HP-5 silica capillary column 30 m x 320 µm ID and 0.25 µm film thickness, flame ionization detector (FID). The clean-up concentrates were dissolved in hexane and 1µL of each was injected into the GC capillary column with the aid of a G4513A automatic liquid sampler (ALS), using the splitless injection mode. Hydrogen was used as carrier gas at a linear velocity of 30ml/minand the oven temperature was programmed from 40 °C to 260 °C at 10 °C/min with a 5 mins hold at 40 °C and a 20 mins hold at 260 °C.

RESULTS AND DISCUSSION

Gas chromatography (GC) analysis of all the samples showed well-resolved peaks of aliphatic hydrocarbons from C_9 to C_{40} (Fig. 1). Petroleum oil and its refined products can be identified by their GC carbon range profile (Wang, 2009). The aliphatic hydrocarbon range of the water samples was considerably wider than that of refined petroleum products but similar to crude oils. This suggest the source of contamination of Sombreiro River in Akuku Toru L.G.A. was crude oil.

The GC profiles of the water samples showed bimodal *n*-alkane distributions (fig. 1). GC fingerprints characterized by the dominance of the C_{13} - C_{20} *n*-alkanes reflect marine sources for crude oils, while the dominance of the C_{25} - C_{35} *n*-alkanes are associated with terrestrial sources (Zhu *et al.*, 2005). All the water samples showed the abundance of *n*-alkane in the C_{13} - C_{20} and C_{25} - C_{35} range. These bimodal distributions suggest the spilled crude oil in Sombreiro River was derived from mixed marine and terrestrial sources. The rise above the baseline of the sample chromatograms, unresolved complex mixtures (UCM), was observed (fig. 1). UCM consist of hydrocarbons connected at one or more branched points which are not resolved into peaks during gas chromatography. It is a strong evidence for petroleum hydrocarbon contamination and degradation (Peters and Moldowan, 1993). Pristane (Pr) and phytane (Ph) are the most common isoprenoids in crude oils (Tissot and Welte, 1984). In Niger Delta crude oils, pristane is characteristically dominant over phytane (Stout *et al.*, 2007; Manilla and Onyema, 2008). From fig. 1, it was observed that pristane was the most prominent aliphatic hydrocarbon and was dominant over phytane in all the water samples (fig. 1). This suggest a similar crude oil of Niger Delta origin as the source of contamination of Sombreiro River. The carbon preference index (CPI) is the ratio of odd to even number *n*-alkanes between C_{23} and C_{34} and is used to indicate the source of aliphatic hydrocarbons (Didyk*et al*., 2000). CPI values close to 1 indicate crude oil source values below unity suggesting degraded crude oils (Maioli *et al*., 2010; Onyema *et al*., 2013). Higher CPI values represent oiled sediment with increased terrigenous input, while values from 4 to 10 indicate land plant sources (Kennicutt *et al*., 1987; Jeanneau *et al*, 2006). From table 1, the CPI values from 0.70 to 0.82 were below unity. This indicated the crude oil which contaminated the waters of Sombreiro river was degraded. *n*-heptadecane (nC_{17}), pristane (Pr), *n*-octadecane (nC_{18}) and phytane (Ph) are aliphatic hydrocarbons commonly used for characterization in oil spill studies. Each pair of compounds elute almost simultaneously from the gas chromatograph. Ratios derived from these hydrocarbons are Pr/Ph, Pr/nC_{17} and Ph/nC_{18} (Table 1). Pr/Ph ratio is a commonly used indicator of diagenetic condition during organic matter deposition. Values below 1 indicate anoxic deposition, between 1 and 3 reflect oxic deposition and above 3 indicate terrigenous source (ten Haven *et al*., 1988).

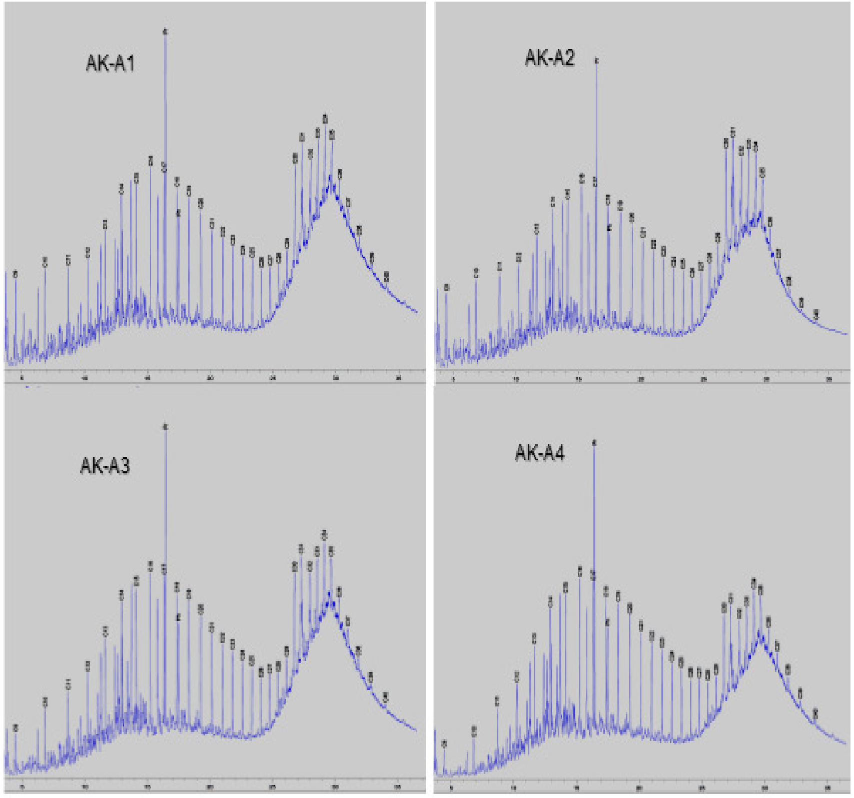

Fig 1: Gas chromatograms of the analyzed water samples from Sombreiro River in Akuku Toru L.G.A. showing the aliphatic hydrocarbon distributions

Table 1: Diagnostic ratios of aliphatic hydrocarbons

Sample Code	CPI	Pr/Ph	Pr/nC_{17}	Ph/nC_{18}
AK-A1	0.76	2.11	1.67	0.96
AK-A2	0.70	2.17	1.87	0.94
AK-A3	0.82	1.85	1.71	1.07
AK-A4	0.81	1.98	1.68	0.96

CPI = $(C_{23} + C_{25} + C_{27} + C_{29} + C_{31} + C_{33}) / (C_{24} + C_{26} + C_{28} + C_{30} + C_{32} + C_{34})$

From table 2, the calculated Pr/Ph ratios ranged from 1.85 - 2.17 and suggest the spilled oil was generated from organic matter deposited in an oxic environment, typical of Niger Delta crude oils. Pr/nC_{17} and Ph/nC_{18} ratios are used evaluating the degree of maturation and biodegradation of resolved hydrocarbons. Waples (1985) stated that with increasing maturity, *n*-alkanes are generated faster than isoprenoids, but during biodegradation, they are degraded faster than the isoprenoids leading to increased ratio values. Ratio values of Pr/nC_{17} and Ph/nC_{18} for Niger Delta crude oils are 1.35 and 0.66 but for significantly degraded oils 3.55 - 3.78 and 2.45 - 2.61 respectively (Onyema *et al*., 2013). For the water samples from Sombreiro river, ratio values of Pr/$nC_{17}$from 1.67 - 1.87 and Ph/nC_{18} from 0.94 - 1.07 suggest the spilled oil was slightly degraded. Shungunam (1985) used the cross plot of Pr/nC_{17} and Ph/nC_{18} ratios to provide information on source, diagenetic conditions, maturation and biodegradation (Fig. 2).

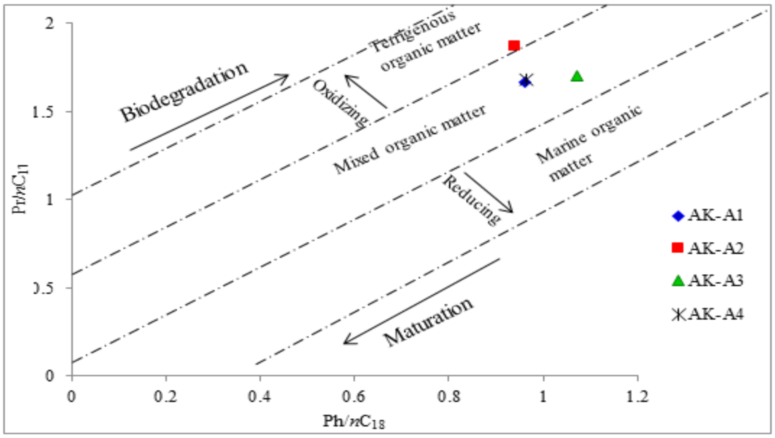

Fig 2: Cross plot of Pr/nC$_{17}$ versus Ph/nC$_{18}$ ratios for water samples from Sombreiro River

Figure 2 suggest the spilled oil which contaminated Sombreiro River was derived from mixed marine and terrigenous sources deposited in a suboxic to oxic environment. The cross plot also showed the spilled oil was degraded in the order: AK-A2> AK-A3> AK-A4 >AK-A1.

*Conclusion***:** Gas chromatography analyses of water samples from Sombreiro River in Akuku Toru L.G.A. of Rivers state identified aliphatic hydrocarbons from C$_9$ to C$_{40}$. Pristane was the most prominent aliphatic hydrocarbon and dominant over phytane. Bimodal *n*-alkane distributions, ratios of CPI, Pr/Ph, Pr/nC$_{17}$, and Ph/nC$_{18}$ suggest slightly degraded crude oil derived from mixed marine and terrigenous sources deposited in a suboxic to oxic environment. The results revealed a typical Niger Delta crude oil contaminated the Sombreiro River.

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