

# GLOBAL JOURNAL OF PURE AND APPLIED SCIENCES



Volume 2 No.2  
June, 1996

## COMPOSITION AND POTENTIAL SOURCE OF NIGERIAN BEACH TARS

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(Received 24 October, 1995; Revision accepted 15 January, 1996)

### ABSTRACT

Chemical composition of representative beach tars collected monthly over a two-year period (1989-1991) at two locations (Badagry and Ibeno), 800 km apart, on the Nigerian coastline and those of crude oil samples from offshore production wells have been determined as a basis for identifying the potential source of the beach tars. The concentration ratios of pristane/phytane and  $nC_{17}$ /background of the beach tars are discernibly different from those of the oil samples. The tars are characterized by enhanced long chain n-alkanes above  $nC_{25}$ , low pristane/phytane ratio (0.10-1.53), high V/Ni ratio (15-3000), and low methylphenanthrene index ratio (0.72-0.78). N-alkanes in the tar of more than 50% of the samples had a bimodal distribution, this being characteristic of tanker oil sludges. The observed compositional differences between the beach tars and crude oil samples suggest ballast waters to be the most likely source of the beach tars.

**KEY WORDS:** Beach tars, bimodal distribution, tanker oil sludges.

### INTRODUCTION

One of the environmental problems associated with exploration, exploitation, refining and transportation of crude oil in the marine environment is the pollution of beaches by tar balls (Golik 1982, Corredor et al. 1983). Tar particulates can also be found floating on

water (Wong et al. 1976), Balkas et al. 1982, Van Vleet et al. 1983) and on the sea bed (Balkas et al. 1982, Alcazar et al. 1989).

Several attempts at source identification of tarry residues have been reported world-wide, e.g. from Bermuda/Sargasso Sea (Ehrhardt and Blumer 1972), Mediterranean coast (Shekel



and Ravid 1977, Albaiges 1980, Baikas et al 1982), and from the Gulf of Mexico (Van Vleet et al. 1983, Van Vleet et al. 1984, Alcazar et al. 1989).

The use of pristane/phytane (Pr/Ph) ratio, trace metal ratios, especially V/Ni, and biomarker compounds

(steranes  $m/z$  217) as fingerprinting tools to identify the source of tars has been reported by Shekel and Ravid (1977), Albaiges (1980), Van Vleet et al. (1984) and Alcazar et al. (1989). Similarly, the concentration ratios of  $n_{C_{17}}^c/Pr$  and  $n_{C_{18}}^c/Ph$  have been utilized as diagnostic parameters to determine the extent of microbial degradation of weathered samples (Ehrhardt and

Blumer 1972, Ehrhardt and Derenbach 1977, Van Vleet et al. 1983).

Available reports show that pelagic tars are ubiquitous in the Nigerian marine environment (Enyenih and Antia 1985, Okonya and Ibe 1985, Asuquo 1991, Antia, 1993, Asuquo 1994). The beach tars are more abundant on the western segment (Badagry Beach) of the Nigerian coast than on the east coast (Ibena-Okposso Beach), even though there are no oil exploratory activities in the vicinity of the Badagry Beach (Asuquo 1994).

The main objective of the present study is to chemically characterize stranded

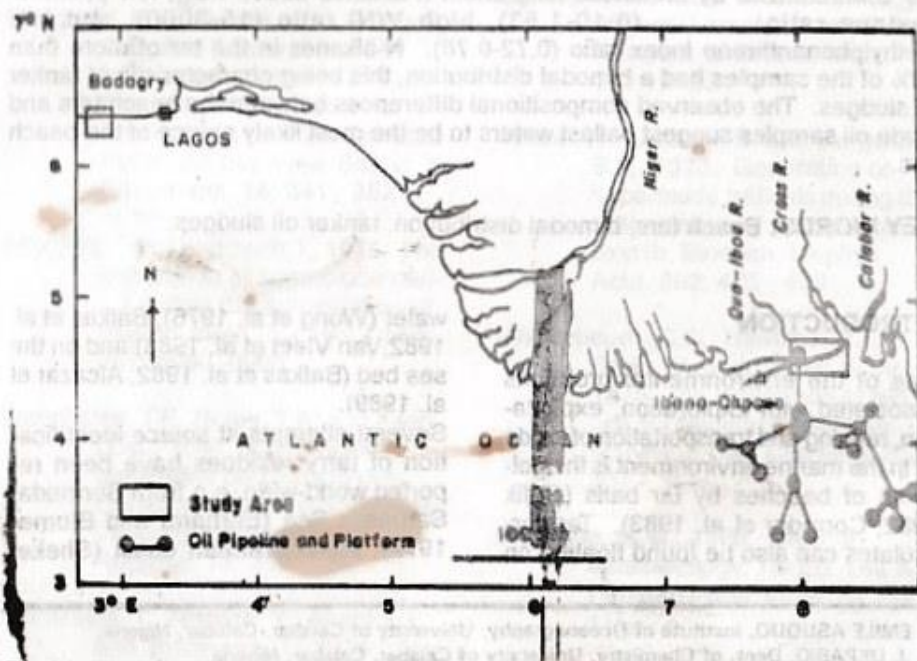


Fig. 1. Map of the Nigerian coastline showing the locations of the beaches where the tar samples were collected. Note locations of oil production installations in the vicinity and offshore of the Ibena-Okposso beach.

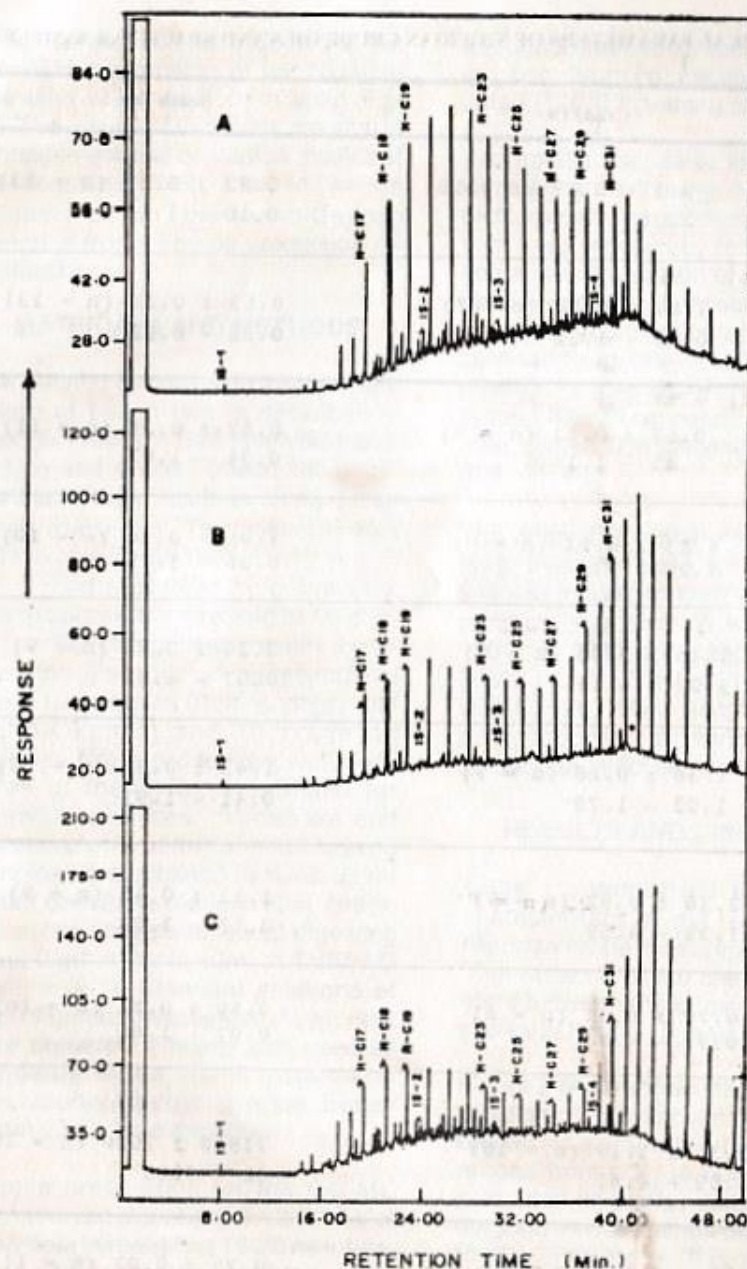


Fig. 2. The n-alkane distribution of the aliphatic fraction of - beach tar samples for the beaches (A - degraded tar, B and C - highly degraded tars).



TABLE 1. CHEMICAL PARAMETERS OF NIGERIAN CRUDE OILS AND BEACH TAR SAMPLES

Parameters	Crude Oil	Beach Tar
Pr/Ph		
mean	3.1 ± 0.49 (n = 10)	0.92 ± 0.39 (n = 13)
range	2.39 - 3.94	0.10 - 1.53
iso-C <sub>18</sub> /Ph		
mean	1.07 ± 0.08 (n = 7)	0.53 ± 0.16 (n = 13)
range	0.99 - 1.22	0.30 - 0.92
nC <sub>17</sub> /Pr		
mean	0.67 ± 0.13 (n = 9)	0.82 ± 0.26 (n = 11)
range	0.45 - 1.19	0.34 - 1.87
nC <sub>18</sub> /Ph		
mean	1.73 ± 0.21 (n = 11)	1.05 ± 0.30 (n = 10)
range	1.20 - 3.0	0.36 - 1.75
nC <sub>17</sub> /Bk		
mean	3.45 ± 0.93 (n = 8)	3.24 ± 0.79 (n = 9)
range	1.90 - 6.19	0.57 - 4.51
Ph/Bk		
mean	1.36 ± 0.28 (n = 9)	1.43 ± 0.23 (n = 10)
range	1.03 - 1.78	0.41 - 1.91
nC <sub>20</sub> /Bk		
mean	2.36 ± 0.92 (n = 9)	1.11 ± 0.45 (n = 9)
range	1.32 - 4.59	0.13 - 2.03
nC <sub>27</sub> /Bk		
mean	0.70 ± 0.31 (n = 8)	0.50 ± 0.22 (n = 10)
range	0.31 - 1.23	0.07 - 1.66
Si		
mean	3.30 ± 1.19 (n = 10)	719.0 ± 1020 (n = 10)
range	1.59 - 4.61	15 - 3000
MPI		
mean	1.00 ± 0.1 (n = 10)	0.75 ± 0.02 (n = 11)
range	1.06 - 1.12	0.72 - 0.78

beach tar particulates collected at the above two segments of the Nigerian coastline, which are 800 km apart (Fig. 1). The results of this study are vital in management and ecological studies of the coastline. Note that, unlike the Badagry beach, the Ibeno-Okposo Beach is fronted by oil production installations.

#### MATERIALS AND METHODS

The method of collection and quantification of beach tars is described in Asuquo (1991). This involved hand-picking and sieving (mesh 200 $\mu$ ) of available tarry residues along designated transects. The collected tars were washed, air-dried for 12 hours, and quantified by gravimetry. The results were expressed as tar density per beach length per month. However, for this study 13 representative beach tar samples (from Badagry and Ibeno-Okposo) and 10 crude oil samples (from production wells offshore of Ibeno) were selected for chemical analyses. Vanadium and nickel contents of the tar and crude oil samples were obtained by AAS, as reported elsewhere (Asuquo et al. 1995). The metal analysis involved digesting about 2 gm of tar in 10ml of THF/H<sub>2</sub>O mixture (9:1). Standard solutions of salts of metals investigated (V, Ni, etc.) were prepared similarly and used as standards in the atomic absorption spectrophotometric (Perkin Elmer model 2380) determinations.

Sample preparation for the GC-MS runs involved dissolving 0.12-0.26 g of tar sample in redistilled 10-20 ml n-hexane (dissolution aided by ultrasonification) and then filtering. About 100 ml of the filtrate was passed

through a chromatographic column (15 cm long, 3mm i.d) packed with reactivated (120°C in vacuo) silica gel.

Two fractions saturates and aromatics, were separated using n-hexane and dichloromethane as eluents. The eluents were reduced by rotary evaporation and with a stream of purified nitrogen (oxygen free, 5A<sup>o</sup> molecular sieve) to a volume of about 50 ml. The concentrated eluents were injected into Hewlett-Packard GC-MS model 5993c system with 25 cm quartz capillary column coated with silicone gum SE 54 (0.3 mm id).

The analytical conditions were as follows: injection was carried out in the splitless mode (0.5 min) at 40°C. Temperature programming was from 40 to 100°C at 20°C min<sup>-1</sup> and from 60 to 300°C min<sup>-1</sup>. The hold time at 300°C was 5 min. Data acquisition of the mass spectrometer started 6.5 min after sample injection.

#### RESULTS AND DISCUSSION

Table 1 summarizes the chemical characteristics of the beach tars and Nigerian crude oil samples analyzed. The variation of the chemical parameters between the oil and the tars are shown in Figs. 2, 3, and 4.

Figure 2 (A-C) shows the n-alkane distribution of the aliphatic fraction of the beach tar samples. The n-alkanes ranged from nC<sub>15</sub> to nC<sub>30</sub>. This suggests that all the tar samples had undergone environmental degradation up to nC<sub>14</sub> homologs. It is, however, observed that few tar samples still retained their original fingerprints (Fig. 2a), as indicated by the full range of



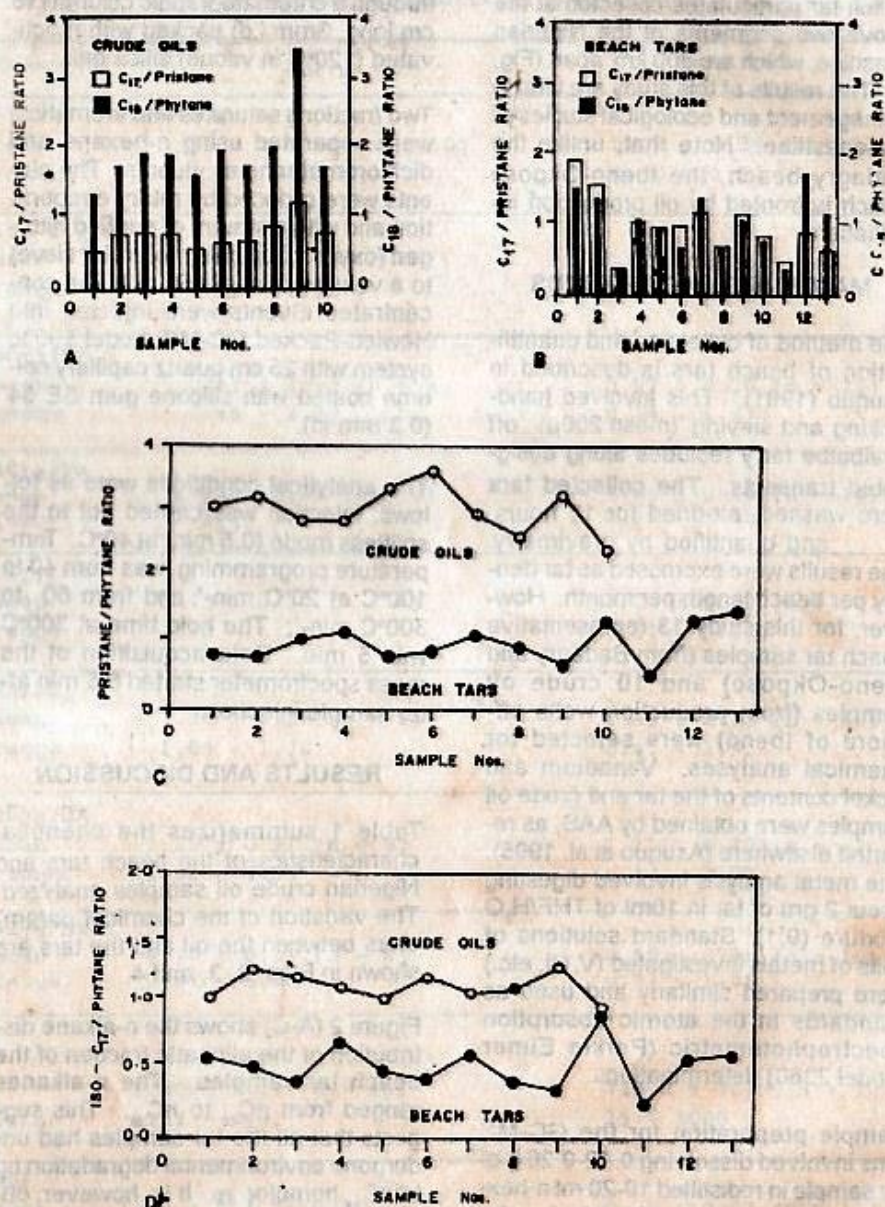


Fig. 3. The ratios of  $nC_{17}/\text{Pr}$ ,  $nC_{18}/\text{Ph}$ ,  $\text{Pr}/\text{Ph}$  and  $\text{iso-}nC_{17}/\text{Ph}$  for some of the Nigerian crude oils and beach tar samples analyzed.

the aliphatic component in the gas chromatograms. This agrees with the suggestion that tar balls can retain their characteristic molecular component ratios for several months after their initial weathering losses (Bulter et al, 1973).

Based on the degree of degradation, two classes of tars can be distinguished: degraded (Fig 2a) and highly degraded tars (Fig. 2b and c). The highly degraded tars showed a typical bimodal n-alkane distribution, with maxima at  $nC_{20}$  and  $nC_{32}$ . A similar characteristic has been found in tars from Bermuda (Bulter et al. 1973) and Gulf of Mexico (Van Vleet et al. 1983, Van Vleet and Pauly 1989), where they are related to crude oil sludge (tanker ballast waters).

Based on the above reports, the first n-alkane maximum occurred at approximately  $nC_{17}$ , and the second at approximately  $nC_{29}$ . More than 50% of the beach tar samples analyzed in this study exhibited a bimodal distribution with n-alkane maxima within the ranges of  $C_{20}$  to  $C_{22}$  and  $C_{32}$  to  $C_{34}$ . This observation is not surprising since the Nigerian coast lies in the main tanker route stretching from the 'Middle East through the horn of Africa to Europe and America. Available pelagic tars may have been transported to shore by strong south-west trade winds, especially during the storm season, and by the Benguela and Guinea currents.

Due to degradation, the n-alkane distribution of some of the tars was difficult to interpret. Generally, the beach tars were characterized by enhanced long chain n-alkanes above  $nC_{21}$ .

These observations seem to suggest that the beach tars did not emanate from the nearby offshore wells but elsewhere.

Shekel and Ravid (1977) had related the age of tar balls originating from crude oil/tanker sludge to the appearance of the first n-paraffin peak in the gas chromatogram. Two-week old tar balls showed the first peak in the  $C_{12}$  to  $C_{14}$  range, as against an age of two months for the first peak in the  $C_{15}$  to  $C_{17}$  range. In this study the first n-alkane peak of the beach tars appeared at  $nC_{14}$  to  $C_{16}$ , indicating an age of about 2 months. This suggests that the tar balls had a prolonged stay in the marine environment before being stranded on the beach.

The concentration ratios of  $nC_{17}/\text{Pr}$  and  $nC_{18}/\text{Ph}$  (Fig. 3) have been used as indicators of biodegradation of beach tar samples (Ehrhardt and Blumer 1972). Their mean values  $0.82 \pm 0.26$  for  $nC_{17}/\text{Pr}$  and  $1.05 \pm 0.3$  for  $nC_{18}/\text{Ph}$ , in the beach tars were very low. This indicates that degradation had occurred as is evident particularly with the highly degraded tars (Fig. 2). A similar observation was made for pelagic tars collected from the Gulf of Mexico by Van Vleet et al., (1983).

The magnitude of the isoprenoid ( $\text{Pr}/\text{Ph}$ ) ratio was observed to be much higher in the crude oil samples than the beach tars (Table 1, Fig. 3). This ratio in the tar samples was less than 1.5 compared to more than 2.4 for the crude oils from different geographical areas and is little affected by environmental factors (Ehrhardt and Derenbach 1971). The low  $\text{Pr}/\text{Ph}$  ratio of the tar samples suggest that the tars



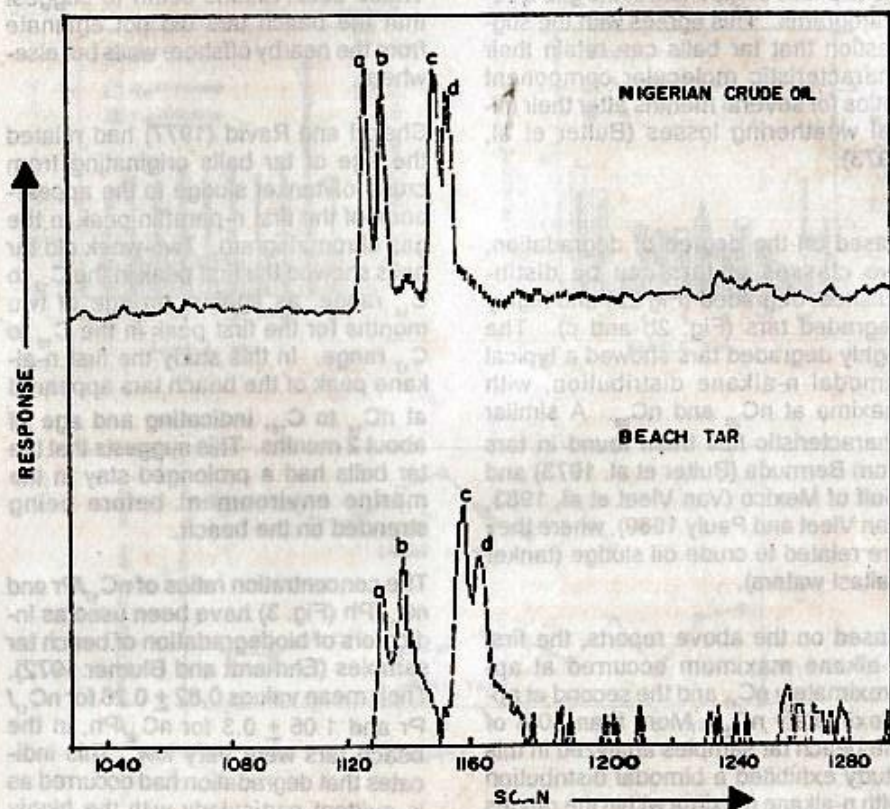


Fig. 4. Reconstructed mass chromatogram of methyl-phenanthrenes ( $m/z$  192): a, 3-methylphenanthrene; b, 2-methylphenanthrene; c, 9-methylphenanthrene and d, 1-methylphenanthrene in a Nigerian crude oil and the beach tar sample.

originate from a reducing environment (Haven et al. 1987). Pr/Ph ratios equal to or less than one have been reported from the Gulf of Mexico (Alcazar et al. 1989), which is similar to the present observations.

In source correlation studies of crude oils, metal ratios rather than the absolute concentrations of specific metals are used to assess rank levels (Lewan 1984). This is particularly true of Ni

and V. Although their absolute concentrations increase in weathered residues, the V/Ni ratio has been shown to be relatively constant, even after severe degradation and dissolution (Kennicutt 1988).

The relative stability of V/Ni ratios has been utilized in this study as a maturity-related parameter to identify the source of the beach tars. While the V/Ni ratios of the oils were persistently

low (1.6 to 5.0), those of beach tars were much higher (15 to 3000). High V/Ni ratios are due primarily to the reducing nature of the environment, thus suggesting that beach tars have a source different from the Nigerian crude oils studied.

Several biomarkers have also been utilized in characterizing hydrocarbons and to indicate their origin or sources (Seifert and Moldovan 1979), Kennicutt and Brooks 1983, Philp et al. 1989). The commonly used biomarkers, which also show the greatest potential as fingerprints, are the steranes ( $m/z$  217), pentacyclic triterpanes ( $m/z$  191), hopanes and the oleananes, and the oleananes are dominant in Nigerian crude oils (Ekweozor et al., 1979). The relative stability of the oleananes to environmental effects and biodegradation, just like the hopanoid triterpanes, enhances their utility for source identification purposes (Pym et al. 1975). Surprisingly, the beach tars analyzed did not show any trace of oleanane. This indicates that tar particulates originating from the Nigerian crude oil field were not present at the time of sampling and/or the tars came from elsewhere where the crude oils lack the oleanane component. However, the indications of extensive degradation of the beach tars tend to support the latter assertion.

The presence of methyl-phenanthrenes ( $m/z$  192) in the samples analyzed was also used as a signature of the beach tars (Fig. 4). In order to characterize the degree of maturation of the samples, the methyl-phenanthrene index (MPI) was calculated from the magnitudes of 3-methyl-, 2-methyl-, 9-methyl and 1-methyl phenanthrenes.

The use of MPI ratio as a maturation parameter has been reported by Radke et al. (1984) and Albaiges et al. (1986). Results from this study show that the MPI ratio of the beach tars ( $0.75 \pm 0.02$ ) is lower than that of the Nigerian crude oils ( $1.06 \pm 0.1$ ), thus indicating that the oils are more mature than the beach tars. This observation corroborates the results of Pr/Ph and V/Ni ratios that the beach tars are less mature and originated from other sources.

## CONCLUSION

This study shows that while the Nigerian crude oils are predominantly aliphatic, the beach tars showed two stages of degradation (degraded and highly degraded), characterized by the removal of lower aliphatics up to n-C<sub>14</sub>. Most of their n-alkane distribution patterns were bimodal, which is typical of oil tanker sludges. The relationship between the molecular constituents of the tars suggests an origin different from the local crude oils studied. The values of Pr/Ph, V/Ni and MPI ratios suggest that the beach tars are less mature than the Nigerian reference oil. These characteristic compositional differences thus indicate that the beach tars could not have originated from the production wells in the neighbourhood of the study area. The tar particulates found on the beaches most probably owe their origin to tanker ballast waters.

## ACKNOWLEDGEMENTS

The authors express their gratitude to Dr. E. E. Antia, Institute of Oceanography, University of Calabar, Nigeria for critically reviewing the manuscript.



One of us (FEA) gratefully acknowledges GKSS Centre, Germany for the support at the University of Kiel, Germany, where all the analyses were conducted.

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