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Trace metals in crude oils and beach tars from Nigerian coastline

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Concentrations of six metals (Pb, V, Ni, Fe, Mn and Cu) in Nigerian crude oils and beach tars (tar balls) were studied. The metal concentrations were generally higher in tar balls than in the crude oils. Vanadium was most abundant metal in both, whereas manganese and lead were the least abundant metals in the tar and oils respectively. Application of metal ratios especially V/Ni and V/Ni + V ratios, for tentative source identification indicates that the beach tar originates from a reducing environment (high V/Ni) and less mature (high V/Ni + V) than the reference oil samples.

Petroleum is biogenic in origin and consists primarily of hydrocarbons and non-hydrocarbon compounds in addition to trace but quantifiable level of many metals[1,2].

Although the magnitudes of metal concentrations may differ remarkably due to metal adsorption or loss during tar (tar ball) formation and transportation, their respective concentration ratios are utilised for the maturity assessment of crude oils and asphaltenes[3,4]. Information is available on the trace metal contents of oils, asphaltenes and solid bitumens from other parts of the world[5,6], but information on metal contents of Nigerian oils, asphaltenes and shales[7,8] is limited. This paper reports concentration of heavy metals in Nigerian crude oils and beach tars and also attempts to establish the source of the tars.

Materials and Methods

Ten crude oil samples, supplied by Nigerian National Petroleum Corporation (NNPC), Lagos were collected from Qua Iboe offshore oil wells (Fig. 1) in glass bottles. The sampling technique, quantification and preliminary treatment of tar balls is carried out as described previously[10].

Standard solutions for calibration curves were made with THF/H_2O mixture using appropriate salts of the metals (Pb, V, Ni, Fe, Mn and Cu). Metal concentrations were thereafter measured with atomic absorption spectrophotometer (Perkin Elmer Model 2380). The AAS measurements were performed in duplicate on each sample. The coefficients of variation (CV) for the AAS technique was 6.3, 8.0, 5.6, 4.2, 3.2 and 5.0% for Pb, V, Ni, Fe, Mn and Cu respectively and the detection limit was 0.01 ppm.

Results and Discussion

Metal contents in the crude oils and tar balls analysed is given in Tables 1 and 2. The concentration of metals ranged from 0.01-69.44 ppm and 0.02-1.30 ppm for the tar balls and oils respectively. The metal concentrations obtained for the samples varied greatly. V and Ni were most dominant in the oils whereas V and Fe were dominant in the tar balls. The metals distribution pattern followed the sequence:

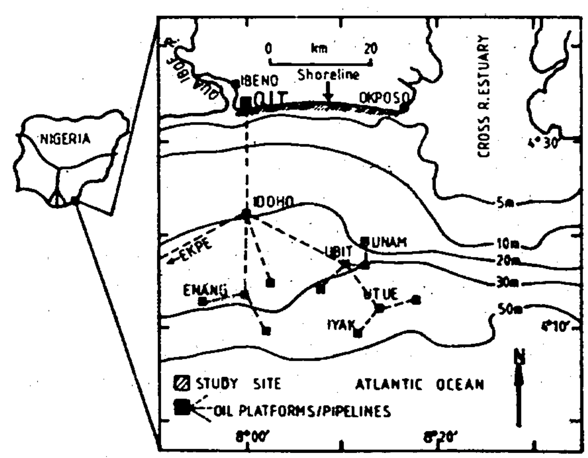

Fig. 1—The location map of Qua Iboe oil platforms where oil samples were collected (QIT: Qua Iboe Terminal)

Table 1—Metal contents in each crude oil and tar ball

Oil well	Qua Iboe crudes			Tar balls			
	Conc. range (ppm)	Most abundant metal	Least abundant metal	Tar sample	Conc. range (ppm)	Most abundant metal	Least abundant metal
Untue	0.02-0.78	V	Pb, Mn	TB. 11	0.06-4.0	V	Mn
Ubit	0.03-1.0	V	Pb	TB. 21	0.08-4.68	V	Mn
Enang	0.06-1.10	V	Mn, Cu, Pb	TB. 33	0.03-4.57	V	Mn
Iyak 5A	0.03-0.75	V	Cu	TB. 42	0.02-3.38	V	Mn
Iyak 6A	0.03-0.65	V	Mn, Cu, Pb	TB, 56	0.11-7.18	V	Mn
Unam	0.02-1.0	V	Pb	TB. 68	0.08-1.68	V	Mn
Iyak 9A	0.05-1.2	V	Mn	TB. 74	0.01-13.18	V	Ni
Idoho 2A	0.05-1.2	V	Cu, Pb	TB. 81	0.07-32.79	V	Mn
Idoho 6A	0.07-1.3	V	Pb	TB. 90	0.04-69.44	V	Mn
Ekpe	0.03-1.06	V	Pb	TB. 111	0.02-46.0	V	Ni

tar balls: V > Fe > Pb > Ni > Cu > Mn
crude oils: V > Ni > Fe > Mn > Cu > Pb

Metal contents of the oils were generally low. This observation is similar to the report made from the study of several crudes from Kuwait, Suez, North Sea, China, Indonesia and Gippsland Basin where V and Ni were the most abundant metals[6]. In crude oils, Ni and V are thought to exist predominantly as porphyrin complexes which in turn are mainly derived from chlorophyll precursors[1].

The metal levels in the tar balls indicate that an enhanced concentration of V occurs both in absolute quantities and relative to the amount of other metals in the tar samples (Table 2). Vanadium concentration varied greatly. The wide scattering of the data is attributed to sorption processes of the metal from seawater during mixing and to anthropogenic additions probably from different oil tanker ballast waters at high sea[6]. These processes also contribute to the slightly elevated concentrations of Fe and Pb than Ni. Seawater have been reported to contain higher concentration of Fe and Pb than Ni[11].

In maturity assessment of petroleum and petroleum products, metal ratios rather than absolute concentrations of specific metals are used[4]. It has been shown that Ni/C ratios appear to vary directly with aromatisation and inversely with H/C ratios in solid bitumen, either due to rank level or solid induced factors[3]. In this report, V/Ni and V/Ni + V concentration ratios are used as maturity-dependent parameters in assessing the Nigerian crude oils and defining the source of the tar balls (Table 3). The data show that a remarkable difference exists in V/Ni ratios of the oils and those of tars. While the ratios for the oils were persistently low, V/Ni ratios for the tar balls were comparatively high (range: 1.59-4.61 and 20-3000 respectively). The high V/Ni ratios for the tar

Table 2—Specific metal contents in Qua crude oils and tar balls

Metal	*Qua Iboe crudes* conc. range (ppm)	*Tar balls* conc. range (ppm)
Pb	0.02-0.07	0.63-1.70
Ni	0.20-0.82	0.15-0.66
V	0.65-1.30	1.69-69.44
Fe	0.20-0.42	0.30-1.99
Mn	0.02-0.10	0.06-0.28
Cu	0.05-0.08	0.13-0.39

balls is indicative of a reducing environment as the possible source of the tars. Similar observation was made for beach tars collected along the coast of Texas[11].

Distribution of V/Ni + V ratios in the tars gave a unique pattern and the values observed were always higher than the corresponding ratios for the crude oils. Relatively very high values for V compared to Ni are reflected in the V/Ni + V ratios becoming unity, indicating that some of the tar balls had pronounced enrichment from the above mentioned processes or related processes. This is similar to the observation made for pelagic tars from the Gulf of Mexico[13] where V/Ni + V concentration ratio was 0.79-0.93 (present study 0.95-1.0). The noticeable variation in the corresponding ratios for the crude oils is an indication of the different families to which the oils belong. The Nigerian oils studied were all medium-gravity oils (°API gravity: 23-39.6°) based on the recent classification of crude oils[14]. The V/Ni + V ratios decreased with increasing API gravity of the oils indicating that the slightly heavier oils contain a higher percentage of V than the higher oils. This difference in sequence is expected since API gravity can be altered during biodegradation process depending on the reservoir temperature[15,16].

Other metal ratios such as Fe/Ni, V/Cu, V/Pb and

Table 3—Ratio of some metals in oils and tar balls

Oil wells	V/Ni		Fe/Ni		V/Cu		Ni/Cu		V/Pb		Fe/Cu		Fe/Mn		V/(Ni+V)		Tar sample nos.	API* gravity
	CO	TB	CO	TB	CO	TB	CO	TB	CO	TB	CO	TB	CO	TB	CO	TB		
Utue	5.8	3060.87	1.8	37.87	33.3	121.99	6.67	0.84	58.8	27.18	6.67	1.47	5.0	2.74	0.83	1.00	TB.11	—
Ubit	4.55	496.82	0.95	23.98	20.0	108.22	4.4	0.22	33.33	21.17	4.2	5.22	7.8	11.81	0.82	1.00	TB.21	23.0
Enang	3.67	42.95	1.20	3.48	18.33	13.10	5.0	0.30	18.33	3.22	6.0	1.05	6.0	4.95	0.79	0.98	TB.33	30.6
Iyak 5A	3.75	152.4	1.1	6.03	25.0	34.38	6.67	0.23	18.75	7.22	7.33	1.36	5.5	2.87	0.79	0.99	TB.42	—
Iyak 6A	2.95	169.15	0.91	19.05	21.67	13.53	7.53	0.08	21.67	4.21	6.67	1.52	6.7	4.18	0.75	0.99	TB.56	—
Uname	5.52	1780.5	0.97	51.08	26.8	198.4	10.33	0.13	39.0	47.50	10.0	5.69	15.0	9.76	0.72	1.00	TB.68	37.7
Iyak 9A	2,35	68.33	0.71	7.26	20.0	55.62	8.5	0.81	20.0	6.53	6.0	5.91	7.2	6.0	0.70	0.99	TB.74	—
Idoho 2A	2.8	20.59	0.50	14.17	24.0	6.35	1.2	0.31	24.0	1.06	6.0	4.37	3.75	9.68	0.67	0.95	TB.81	(34.7)**
Idoho 6A	1.59	1318.0	0.51	128.3	16.25	39.23	10.25	0.03	18.57	8.55	5.25	3.82	4.2	7.42	0.61	1.00	TB.98	38.8
Ekpe	4.61	72.69	0.87	5.45	26.5	10.20	5.75	0.14	35.33	4.98	5.0	0.77	2.5	3.25	(0.82)	0.99	TB.111	39.6

CO Crude oil; TB Tar balls; *API Gravity-values supplied by Mobil Producing Nigeria Company PLC
** Values in parentheses are abnormal

Fe/Mn were computed to establish the relationship or similarity if any between the crude oils and tar balls analysed. The observed values showed no indications of similarity as the concentration ratios were distinctly different from each other (Table 3). The metal ratios for the tar balls were almost always higher than those for the oil samples.

Metals in environmental hydrocarbon samples are useful tools in source-correlation studies or source identification of the pollutants (tar balls). The difference observed between the metal concentrations of the oils and tar balls suggest different sources for the two samples. The enrichment of metals in tar (V, Fe and Pb), though minimal indicates addition from external source. The magnitudes of V/Ni and V/Ni + V ratios depict that both samples have dissimilar chemical composition. A lower V/Ni ratio for the oils is indicative of an oxidising depositional environment, with a comparatively higher maturity than the tar balls. Molecular characterisation of the samples show that the tar balls have lower methyl phenanthrene index (MPI) ratio (0.73-0.78, less mature) than the crude oils[16] (1-1.1). This supports the earlier observation from the V/Ni ratio for the tars (Table 3). This finding, in combination with the sampling history for the tar balls suggest that the beach tars had travelled long distances (foreign origin) and must have been transported to the shore by the interplay of oceanographic factors.

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References

1 Posthuma J, in *Proc Inter Workshop on petroleum hydrocarbons in the marine environment*, Aberdeen Publ No. 474, 1975.
2 Lijmbach G N M, Special paper 1, *9th World Petroleum Congress*, Tokyo, 1975.
3 Curiable J, *Org Geochem*, 10 (1986) 559.
4 Thompson K F M, Kennicutt M C & Brooks J M, *Amer Assoc Petrol Geol Bull*, 74 (1990) 187.
5 Barwise A J G, *Energy & Fuels*, 4 (1990) 151.
6 Wong C S, Green D R & Cretney W J, *Mar Poll Bull*, 7 (1976) 102.
7 Ndiokwere C L, *Radiochem Radioanal Letters*, 59 (1983) 201.
8 Odigi M I J, *Petrol Geol*, 10 (1987) 101.
9 Antia E E, *J Coastal Res*, 9 (1993) 1065.
10 Asuquo F E, *Mar Poll Bull*, 22 (1991) 151.
11 Duinker J C, Nolting R F & Michel D, *Thalassia Jugosl*, 18 (1982) 191.
12 May L A & Presley B L, *J Radioanal Chem*, 27 (1975) 439.
13 Alcazar F, Kennicutt M C & Brooks J M, *Org Geochem*, 14 (1989) 433.
14 Clayton J, *U S Geol Survey Bull*, No 1870 (1988) 54.
15 Seifert W K, Moldowan J M & Demaison G J, *Org Geochem*, 6 (1984) 633.
16 Asuquo F E, *Possible sources of tar balls collected from the Bight of Bonny, Nigeria*, Ph. D. thesis, University of Calabar, Nigeria, 1994.