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THE LEVELS OF TRACE METALS IN PELAGIC TARS FROM IBENO/OKPOSO BEACH, NIGERIA.

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ABSTRACT

Tar ball samples collected from Ibeno/Okposo beach were analysed to assess the degree of metal enrichment of the tar. The metal concentrations found were: Pb (0.63-1.70ppm), Ni (0.15-0.66ppm), V (0.28-69.44ppm), Fe (0.30-1.99ppm), Mn (0.06-0.20ppm) and Cu (0.13-0.39ppm), with distribution patterns following the sequence: V>Fe>Pb> Ni>Cu>Mn. In all cases, V was the most abundant and Mn the least abundant metal. Very low enrichment was observed for all the metals. High correlations existed only for the relationships Pb: Mn(r = +0.70) and V: Mn (r = + 0.82), while the other metals exhibited moderate and low correlations. The absence of strong correlation between the metals and the low levels of metal concentrations predicts low anthropogenic influence and indicates that the tar balls are mixed origin.

KEY WORDS: Trace metals, tar balls, Ibeno/Okposo beach, Nigeria.

Pelagic tars (tars balls) are ubiquitous in the Nigerian marine environment (Asuquo, 1994). They can remain undegraded for several months if submerged in sandy beaches. Inherently, tars contain the same metals as their parent oils but the concentration may be high or low depending on whether subsequent enrichment or loss occurred during the pollutant journey to the shore.

Trace metals in the aquatic environment have been studied in sediment (Everaarts and Swenner, 1987; Ntekim et al., 1993) in water (Bruland, 1980; Zubillaga, 1986) and organisms (Denton and Burdon-Jones, 1993; Etim et al., 1991). The use of tar balls to monitor trace metal levels in the marine environment have been implied by few authors (Wong et al, 1976; Shekel and Ravid, 1977; Albaiges et al., 1979;

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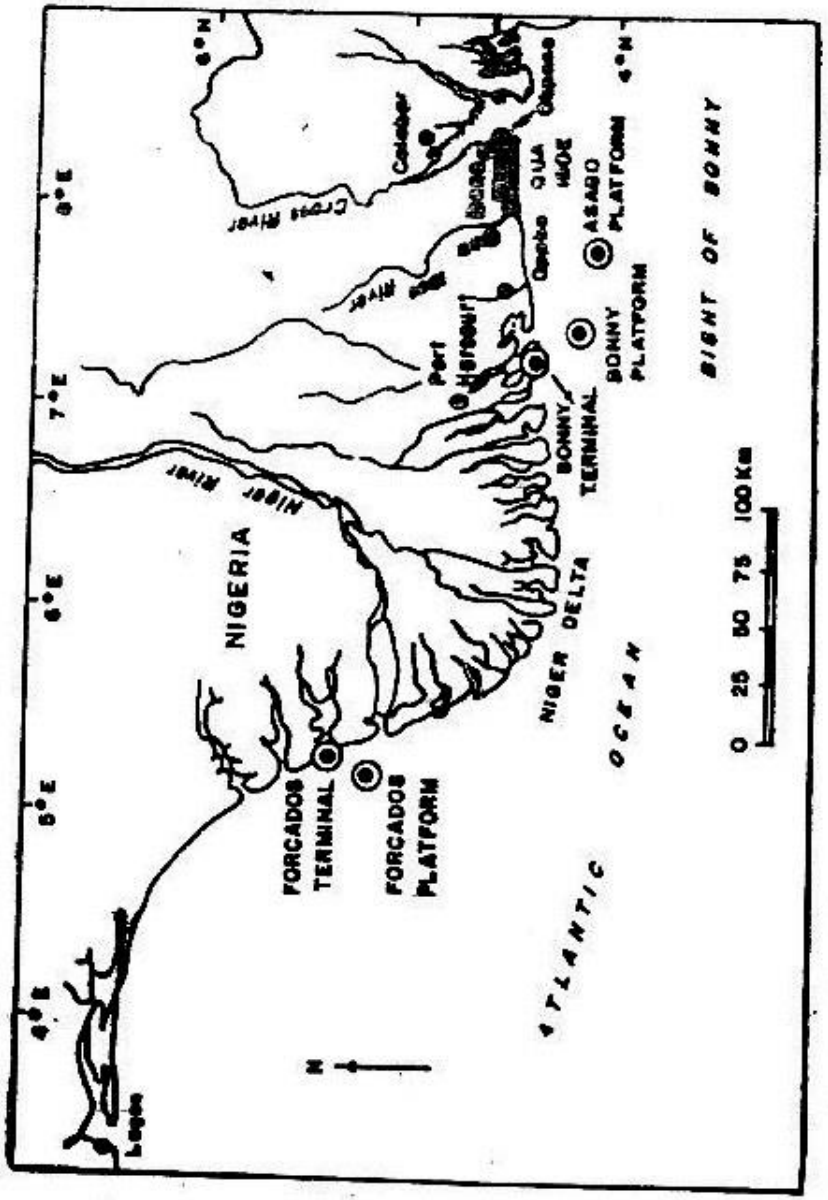

Fig. 1: The Ibeno-Okposo Beach and major oil terminals along the Nigerian coastline

Albaiges, 1980). Such studies were carried out to determine the degree of enrichment of tar by metals (Wong et al., 1976), to compare metal levels in pelagic and benthic tars(Alcazar et al, 1989) and to trace the source of pelagic tars (Shekel and Ravid, 1977, Albaiges et al., 1979, 1979; Alcazar et al., 1989).

In the present study, the tar samples were analysed to provide baseline data on metal levels in the tar and to identify the interrelationships between the samples to aid in the determination of the degree of enrichment and the probable source of the stranded pelagic tars.

METHODOLOGY

The study area and major oil terminals on the Nigerian coastline are shown in Fig. 1.

Trace metals were determined as reported previously (Asuquo et al., 1995). The method consists of dissolving 1.0 to 2 gm of tar sample in 10 ml redistilled tetrahydrofuran/water mixture (9:1) before diluting to 50ml using the same miture. Standard solutions for calibration were made with the same mixture using salts of the metals being investigated (Pb, V, Ni, Fe, Mn and Cu).

Two replicates of each tar sample were run using Perkin Elmer Model 2380 Computerised Atomic Absorption Spectrophotometer (AAS). The highest metal concentration obtained was 80 ppm and the detection limit used was 0.01ppm. The precision of the method as percent coefficient of variation was 6.3, 8.0, 5.6, 4.2, and 5.0 for Pb, V, Ni, Fe, Mn and Cu respectively.

RESULTS

The concentration for all detectable metals analysed are given in Table 1 and are compared with data obtained from other areas of the world (Table 2). Generally, analyses for more than 2

Table I: Summary of metal contents in tar balls collected from Ibeno Okposo beach. (1989-1990)

Metal	Concentration range (PPM)	Mean	Number of samples
Pb	0.63 - 1.70	1.26 ± 0.40	10
Ni	0.15 - 0.66	0.26 ± 0.16	10
V	0.28 - 69.44	18.69 ± 23.14	10
Fe	0.30 - 1.99	0.86 ± 0.62	10
Mn	0.06 - 0.20	0.12 ± 0.05	10
Cu	0.13 - 0.39	0.29 ± 0.05	10

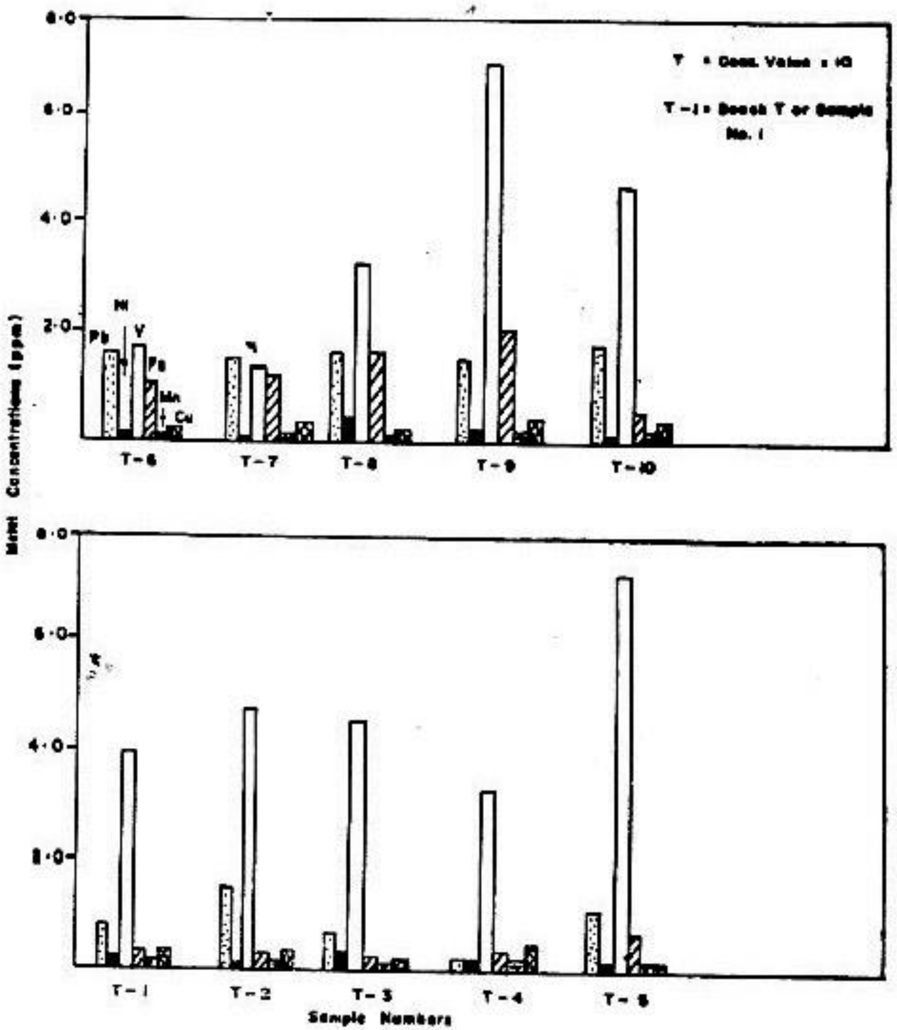

Fig. 2 Distribution of Pb. Ni. V. Fe. Mn and Cu in Nigeria Beach Tars.

metals in tar residues are few and may be due to the persistently low levels of these metals in parent crude oils. Table 3. shows the inter-relationship between the trace metals in the tar balls analysed and Fig. 2 illustrates the distribution of the metals in the tarry residues.

DISCUSSION

Pb: Lead concentrations ranged from 0.63-1.70ppm with more than 70% having concentrations above 1.0ppm. The results show that lead conentrations ranked the third most abundant metal in the tars analysed. Pb correlated with V (r = 0.50), Fe (r = 0.62), Mn (r = 0.50) but show very poor correlation with Ni (r = 0.08).

Ni: Nickel concentrations were vey low in the tar samples analysed (0.15-0.66ppm) considering the fact that it is the second most abundant metal in petroleum (Bar-wise, 1990). The relatively lower value of Ni than Fe and Pb is associated with its replacement by other metals in the source rock, especially V since Vanadium complexes are more stable than Ni. Biochemical alteration processes such as sulphate reduction in petroleum source have been reported to favour V incorporation than Ni (Barwise, 1990). Once the ratio is fixed in the source rock it becomes a characteristic ratio of the oils and weathered residues. Ni gave low metal-metal ratios for the tar balls analysed

Table 3: Tar-tar correlation matrix of trace metals in tar balls samples from Ibeno Okposo beach

	Pb	Ni	V	Fe	Mn	Cu
Pb	1.00	0.08	0.50	0.62	(0.70)	0.50
Ni		1.00	0.42	0.51	0.03	0.05
V			1.00	0.66	(0.82)	0.40
Fe				1.00	0.68	0.22
Mn					1.00	0.51
Cu						1.00

(Highly correlated variable are in parentheses).

Table 2: Some chemical characteristics of pelagic tars worldwide.

Variable Location	Pr/Ph	nC_{17}/Ph	Fe ppm	Ni ppm	V ppm	V/V+Ni	Reference
Gulf of Mexico	0.9	0.6	-	3.9-58.3	20.4-270	0.79-0.93	Van Vleet and Pauley 1969, Alcazar et al 1989.
Pacific Tars	-	-	10,000	170	-	-	Wong et al 1976.
South Atlantic tars (Nigeria)	0.1-1.51*	0.34-1.87*	0.3-1.99	0.15-0.66	0.28-69.44	0.94-1.0	This study.

(* Data from Asuquo 1994).

(Asuquo et al., 1995). It showed little or no correlation with other metals except Fe (r = 0.51).

V: The concentrations of vanadium found in the tar balls were the highest for all the metals analysed (0.28 - 69.44ppm). Few tars (40%) had concentrations between 32-69ppm. Apart from vanadium incorporation into kerogen matrix in the source rock, slight enrichment have occurred considering the enhanced levels compared to other metals analysed. V showed good correlation with all metals except Ni (r =0.42) Cu (R=0.40). It thus appears that some of the tar balls originated from high sulphur oils. High V oils have been shown to correlate with high sulphur oils. Nigerian oils have low sulphur (<2.0pm) and low metal (> 1.30ppm) contents, and high correlation exists between component metals (Asuquo, 1994).

Fe: The iron concentrations were generally low (0.30 - 99ppm). Higher values of iron were reported for Pacific tars (Tables 2). The enrichment of iron in the tar is generally attributed to anthropogenic sources arising from rust particles picked up from the tanks of tankers during tank-washing operations (Wong et al., 1976). Therefore the low concentration of iron metal observed in this study shows that enhanced iron enrichment by scavenging of metal from sea water or anthropogenic inputs has not occurred. Fe correlated well with all metals except Cu (r = 0.22).

Mn: The concentration of manganese varied considerably ranging from 0.06-0.20ppm. Although the values were generally low depicting little or absence of enrichment, it gave good correlations with all metals except Ni (= 0.03).

Cu: The concentration of copper showed little consistency for most of the tar balls analysed (0.13-0.39ppm). Cu levels were higher than the levels of Mn in the samples and depicts no contribution from external source (Fig.2). Copper gave marginal correlation with Pb and Mn (r = 0.50 and r = 0.51) but very low, correlation with Ni, V and Fe (r = 0.05, 0.40 and 0.022) respectively.

V/V+Ni ratio: The concentration of V/V+Ni ratios (0.94 - 1.0) obtained during this study is high and is different from similar ratios reported for Gulf of Mexico tars (0.79-0.93, Table 2), and Nigeria oils (0.61-0.83, Asuquo, 1994). This values and a pristane/Phytane ratio >2.0 is in direct contrast to offshore oils produced in Nigeria coastal environment, suggesting different sources for the beach tars.

The distribution of metals in the beach tars followed the order: V> Fe> Pb> Ni> Cu> Mn. The results show that the vanadium is the most important metal in all the samples analysed. Comparatively higher values of Fe and Pb in the tar samples, T-6, T-7, T-8 and T-9 in Fig. 2, than metals such as Cu and Mn indicate that the tars are of mixed origin. On the whole, metal levels in more than 90% of the tar analysed were higher than that found in Nigerian crude oils (> 1.30ppm, Asuquo 1994).

Table 3 shows that the metals exhibited generally moderate(r=0.50 to 0.68) and low correlation (r = 0.03 to 0.42). High correlations are evident only for the relationships Pb: Mn (r = 0.70) and V: Mn (r = 0.82). The absence of strong relationship between the variables suggest different geographical sources for the tar balls since metals from oils emanating from the same source rock always exhibit strong correlation.

CONCLUSION

High metal contents in tar occur mainly through anthropogenic additions from tank washing of oil tankers and scavenging for metals from water during the journey to the shore (Wong et al., 1976). In the present report, metal contents of the tar balls were genetally low except V. These suggest that the tars originate from high sulphur oils whereas Nigerian oils have low sulphur contents (Asuquo,1994).

The isoprenoid ratio, Pr/Ph and metal ratio V/V + Ni are known to be strong depositional environment parameters and are characteristic for a given geographical area (Van Vleet and Pauley, 1989). But the ratios obtained during this study are quite different from those of Nigerian oils. This information together with the absence of strong correlation between the metal predict that the tar balls originate from an environment different from Nigerian crude oils.

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