Occurrence of Biphenyl and Alkylbiphenyls in Source Rocks from Tertiary Niger Delta Basin, Nigeria.

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ABSTRACT

*S*ource rocks from the offshore Niger Delta basin, Nigeria have been analyzed by gas chromatography-mass spectrometry (GC-MS) in terms of their thermal maturity, based on the distribution of biphenyl and its derivatives. The source rocks were characterized by the dominance of C_2-biphenyl over other alkylated homologues. 3-methylbiphenyl predominated over other methylbiphenyl isomers in rock samples. 3,3'-dimethylbiphenyl occurred as the most abundant compound among the C_2-biphenyl compounds in the rock samples while 3,5,4-trimethylbiphenyl dominated over other C_3-biphenyl compounds in the source rocks. The distributions and abundance of the biphenyl and alkylbiphenyls were found not to be influenced by source facies and thermal maturity. The maturity dependent parameter computed from alkylbiphenyl distributions (MBpR, DMBpR-x and DMBpR-y ratios) indicated that the source rocks have wide variations in maturity status and that the rock samples are within immature to oil window maturity status and this is further supported by other maturity parameters computed from the saturate and aromatic biomarkers. This study showed that the abundance and distribution of biphenyl and its derivatives can be used for thermal maturity of source rocks in the Niger Delta Basin.

Keywords: Biphenyls, alkylbiphenyls, source rocks, Niger Delta, maturity

INTRODUCTION

Biphenyl and Alkylbiphenyls are important constituents of petroleum and petroleum source rocks, but have also been found in coal extracts (Alexander *et al*., 1986). Their biological origin is uncertain. The compounds are present in organic matter originating from different geological ages and different source types. Their occurrence can be dated back to the Middle Cambrian, a period that predates the evolution of higher plants (Cumbers *et al*., 1987). Biphenyl and alkylbiphenyls are combustion products of benzene and alkylbenzenes (Takatsu and Yamamoto, 1993). Kruge *et al*. (1994) found high proportions of biphenyl in samples that showed high concentrations of semifusinite and pyrofusinite. Semifusinite and pyrofusinite result from the partial combustion of organic matter. Alexander *et al*. (1994) showed that the relative abundances of alkylcyclobenzenes and alkylbiphenyls in crude oils are of the same magnitude. The authors therefore suggest, that these compounds are formed via deposition of oxygen-rich source materials in oxic depositional environments. Alkylcyclohexyl-benzenes and alkylbiphenyls may be products of the oxidative coupling of phenols (Alexander *et al*., 1994). Besides the little knowledge on direct biological precursors of alkylbiphenyls their potential as maturity indicators is also sparse.

It has been reported that many of the aliphatic biomarker maturity parameters do reach equilibrium before the main stage of the oil window and in some cases show inversion at high maturity levels and as such are not effective maturity indicators (Farrimond *et al.,* 1998). Aromatics hydrocarbon maturity parameters have been reported to be more sensitive to maturity differences in the mid to late parts of the oil generation window (Radke, 1988). Biphenyl compounds have also been demonstrated to be very important in evaluating the maturity of crude oil and source rock (Alexander *et al*., 1986; Cumbers *et al*., 1987; George and Ahmed, 2002;). However, biphenyl and alkylbiphenyls have not been studied or reported in the Niger Delta source rocks. This work is aimed at investigating the occurrence and distributions of biphenyl and alkylbiphenyls in the Niger Delta source rocks in relation to their origin and thermal maturity level.

MATERIALS AND METHODS

Reagents : n-hexane, methanol, dichloromethane, silica gel and alumina (purity = 98%; Laboratory of Dr. Ehrenstorfer, Augsburg, Germany).

Sampling

Twenty one rock samples from three wells located at three different fields in the offshore Niger Delta Basin were selected and analyzed.

Extraction and Analysis
Rock samples were crushed into powder < 100 mesh and extracted in batches using Soxhlet apparatus with 400mL dichloromethane : methanol (93:7, v:v) for 72 h. The rock extracts were separated into saturated and aromatic hydrocarbon fractions using silica gel/alumina chromatography columns eluted with n-hexane and dichloromethane : n-hexane (2:1, v:v), respectively.

The GC-MS analyses of the saturate and aromatic fractions were performed on an agilent 5975i gas chromatography (GC) equipped with an HP-5MS (5% phenylmethylpolysiloxane) fused silica capillary column (60m x 0.25mm i.d., x 0.25μm film thickness) coupled to an agilent 5975i mass spectrometry (MS). The GC operating conditions were as follows: the oven temperature was held isothermally at 80°C for 1 min, ramped to 310°C at 3°C/min and held for 16 min (Li et al., 2013c). Helium was used as the carrier gas with constant flow rate of 1.2 mL/min. The MS was operated in the electron impact (EI) mode at 70eV, an ion source temperature of 250 °C and injector temperature of 285°C. The identification and elution order of biphenyl and its derivatives were determined by comparison of their mass spectra and relative retention times in the corresponding mass chromatograms with those reported in literature (Alexander et al., 1986; Cumbers et al., 1987; George and Ahmed, 2002; Li et al., 2013a, 2013b; Li and Ellis, 2015). The relative abundance was calculated from integrated peak areas in the relevant ion chromatograms.

RESULTS AND DISCUSSION
Occurrence of Biphenyl and its Derivatives in Source Rock Extracts from Niger Delta Basin.
The m/z 154+168+182+196 mass chromatograms showing the distributions of biphenyl and its derivatives in the rock samples are shown in Figures 1. The rock samples are characterized by the predominance of C_2- biphenyl over other alkylated homologues (Figures 1, Table 1). The dominance of C_2-byphenyl over other alkylated homologues of biphenyl have been reported in rock samples from the cratonic region of the Tarim Basin NW China (Li et al., 2013b), Proterozoic source rocks from middle Velkerri Formation, McArthur Basin, Australia (George and Ahmed, 2002), petroleum and ancient sediments from Australia (Alexander et al., 1986; Cumbers et al., 1987) and crude oils and sediments from Potwar basin, Pakistan (Asif et al., 2010). Among the methylbiphenyl isomers in the source rocks , 3-methylbiphenyl is the dominant compound while 2-methylbiphenyl occur as the least or below detection limit in some source rocks (Figures 1). The predominance of 3-methylbiphenyl over other

isomers of methylbiphenyl have been previously reported in sediments from Tarim Basin NW China (Li et al., 2013b; Li and Ellis, 2015), crude oils and sediment extracts from Potwar basin Pakistan (Asif., 2010). 3,3'-dimethybiphenyl (3,3'-DMBP) is the most abundant compound among the C_2-biphenyl isomers while 2,3'-dimethylbiphenyl (2,3'-DMBP) occur as least in the source rocks (Figures. 1). This pattern of distributions whereby 3,3'-DMBP is the most abundant among the C_2-biphenyl isomers have been previously reported in petroleum and source rocks (Alexander et al., 1986; Cumbers et al., 1987; George and Ahmed, 2002; Asif, 2010). Also, there is predominance of 3,5,4-trimethylbiphenyl (3,5,4-TMBP) over other C_3-biphenyl isomers in the rock samples (Figures 1). This observation is consistent with the results that have been previously published in the literature (Li et al., 2013b; Luo et al., 2016).

Source facies, depositional environment and thermal maturity of organic matter are important factors controlling the distributions and concentrations of most molecular markers in source rocks and crude oils. In this study, the effect of source, depositional environment and maturity on the distributions of biphenyls in the source rocks were investigated by plotting the abundance of C_0-C_3 biphenyl against well-established source and maturity parameters obtained from the saturate and aromatic distributions in the oils (Figure 2). Figures 2a shows the cross plots of the abundance of biphenyl (C_0-C_3) against pristane/phytane (Pr/Ph) values in the source rocks. The plots clearly showed no correlation with the source and depositional parameters (Pr/Ph), indicating that source facies has no influence on the distributions and abundance of the biphenyl compounds in the rock samples. Similarly, the abundance of C_0-C_3 biphenyl in the source rocks are plotted against saturate (20S/(20S + 20R) C_{29} steranes) and aromatic (MPI-1) maturity parameters in Figures 2b, and 2c respectively. The plots also lack any correlation with the maturity parameters showing that thermal maturity has no effect on the distributions and abundance of the biphenyl and alkylbiphenyls in the source rocks.

Thermal Maturity Status of Niger Delta Source Rocks based on the Presence of Biphenyl and Alkylbiphenyls.
Alexander et al., (1986) proposed MBpR (3-/2-methylbiphenyl ratio) as a thermal maturity parameter while Cumbers et al., (1987) proposed DMBpR-x (3,5-/2,5-dimethylbiphyl ratio –x) and DMBpR-y (3,3'-/2,3'-dimethylbiphenyl ratio-y) maturity indicators in crude oils and ancient sediments from Australia. George and Ahmed (2002) applied these parameters to maturity study in Mesoproterozoic sediments of the McArthur Basin, Australia and observed that the alkylbiphenyl ratios were sensitive to maturity variations in the peak to late part of the oil window

but show little change at lower maturities. Alkylbiphenyl ratios (MBpR, DMBpR-x and DMBpR-y) have also been successfully applied to assess the thermal maturity level of the sediments from Mesoproterozoic Hongshuizhuang Formation, Northern China (Luo et al., 2016).

The 2-methylbiphenyl is very low or below detection limits in most of the rock samples in this study, therefore, MBpR could not be used to for the thermal maturity assessment of the source rocks. The DMBpR-x and DMBpR-y values in the rock samples range from 4.63 to 19.42 and 9.49 to 32.53 (Table 1), suggesting immature to early mature source rocks (Luo et al., 2016). The 20S/(20S + 20R) C_{29} sterane (0.13 to 0.52, Table 1) and MPI-1 (methylphenanthrene index-1) (0.12 to 0.62, Table 1) maturity values support immature to early maturity status for the rock samples (Peters et al., 2005). However, the cross plots of DMBpR-x and DMBpR-y against burial depths lack any particular trend with increasing burial depths (Figs. 3a and 3b). Also, in order to facilitate comparism, DMBpR-x and DMBpR-y are plotted against well-established saturate (20S/(20S + 20R) C_{29} steranes) and aromatic (MPI-1) maturity paramers (Figs. 4a and 4b). The plots clearly showed that there is no relationship between the maturity parameters.

CONCLUSION
The occurrence and distributions of biphenyl and its derivatives in the Niger Delta source rocks have been investigated by gas chromatography-mass spectrometry (GC-MS). Geochemical characterization of the source rocks based on biphenyl and its derivatives showed that the rock samples were within immature to oil window maturity status. The source rocks were characterized by the dominance of C_2-biphenyl over other alkylated homologues. 3-methylbiphenyl predominated over other methylbiphenyl isomers in the rock samples. 3,3'-dimethylbiphenyl occurred as the most abundant among the C_2-biphenyl compounds in the rock samples while 3,5,4-trimethylbiphenyl dominated over other C_3-biphenyl compounds in the source rocks. The distributions and abundance of the biphenyl and alkylbiphenyls were found not to be influenced by source facies and thermal maturity. The maturity dependent parameter computed from alkylbiphenyl distributions (MBpR, DMBpR-x and DMBpR-y ratios) indicated that the oils and source rocks have wide variations in maturity status and that the rock samples are within immature to oil window maturity status. This was further supported by other maturity parameters computed from the saturate and aromatic biomarkers.

This study showed that the abundance of biphenyl and its derivatives can be used for assessment of thermal maturity of source rocks in the Niger Delta Basin.

ACKNOWLEDGEMENTS

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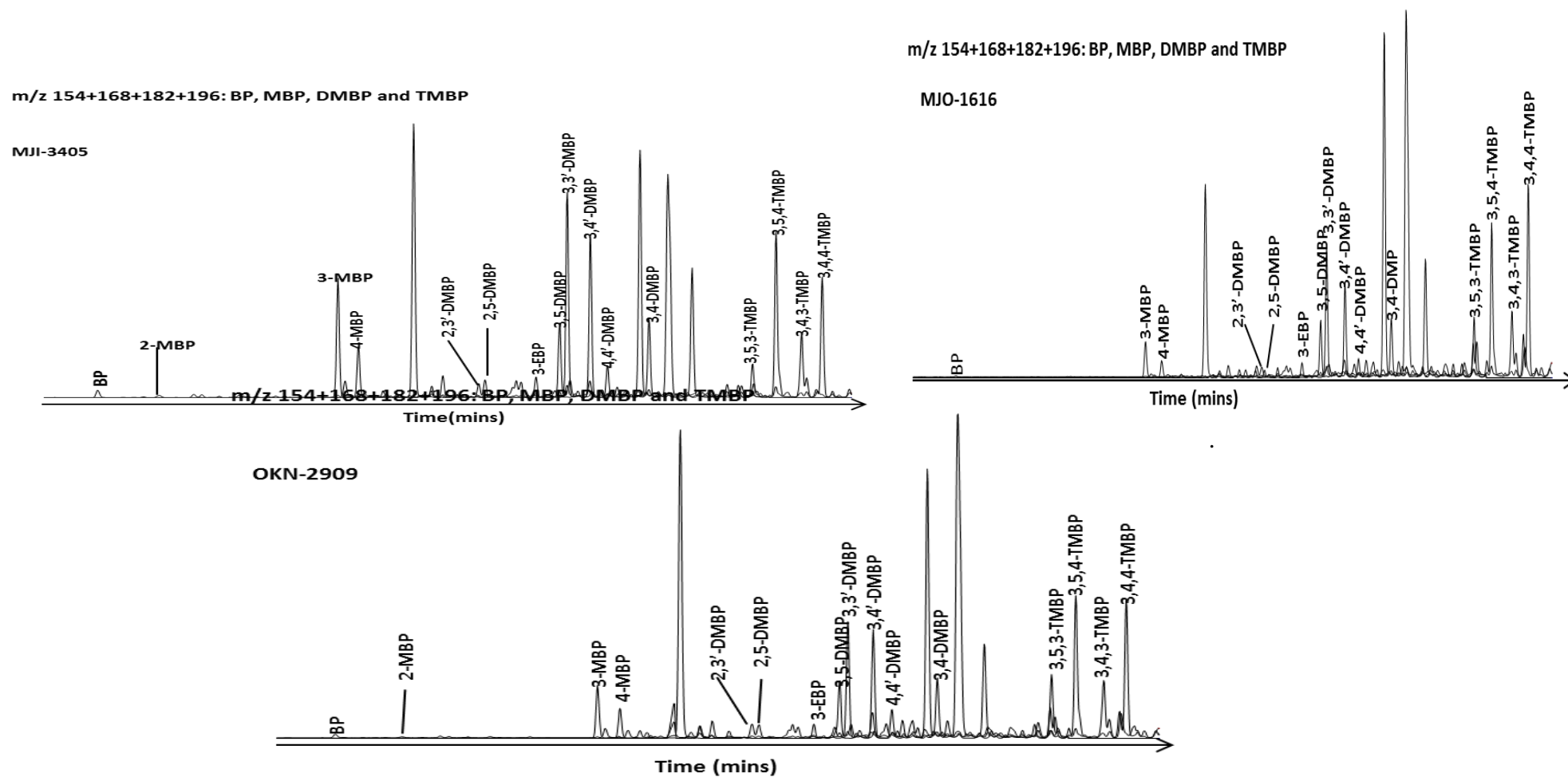
Fig. 1: m/z 154+168+182+196 Mass chromatograms showing the distributions of biphenyl and alkylbiphenyls in the Niger Delta rock samples.

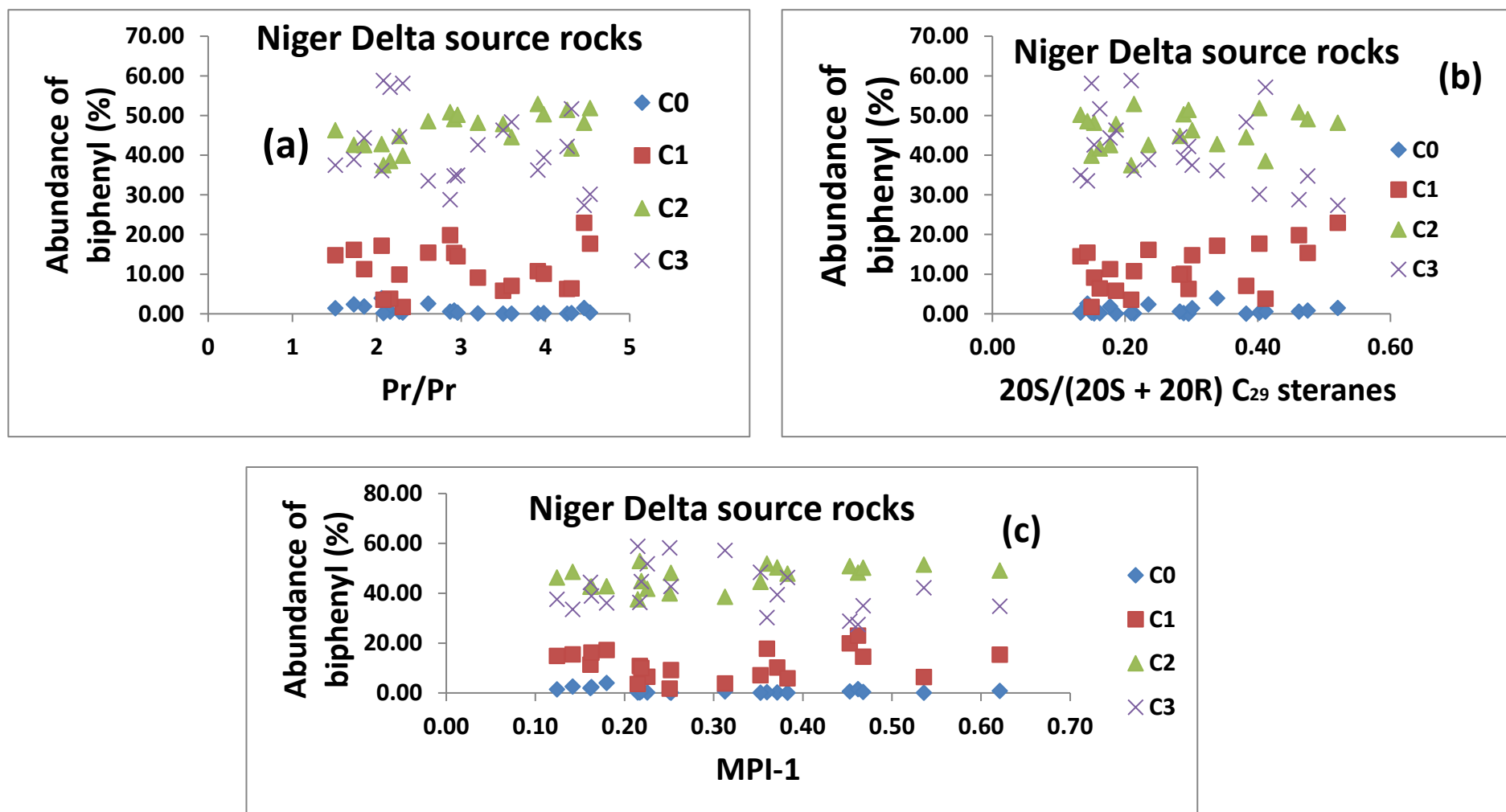**Fig. 2:** Cross plots of C_0-C_3 biphenyls versus (a) Pr/Ph, (b) 20S/(20S + 20R) C_{29} steranes and (c) MPI-1 for Niger Delta source rocks.
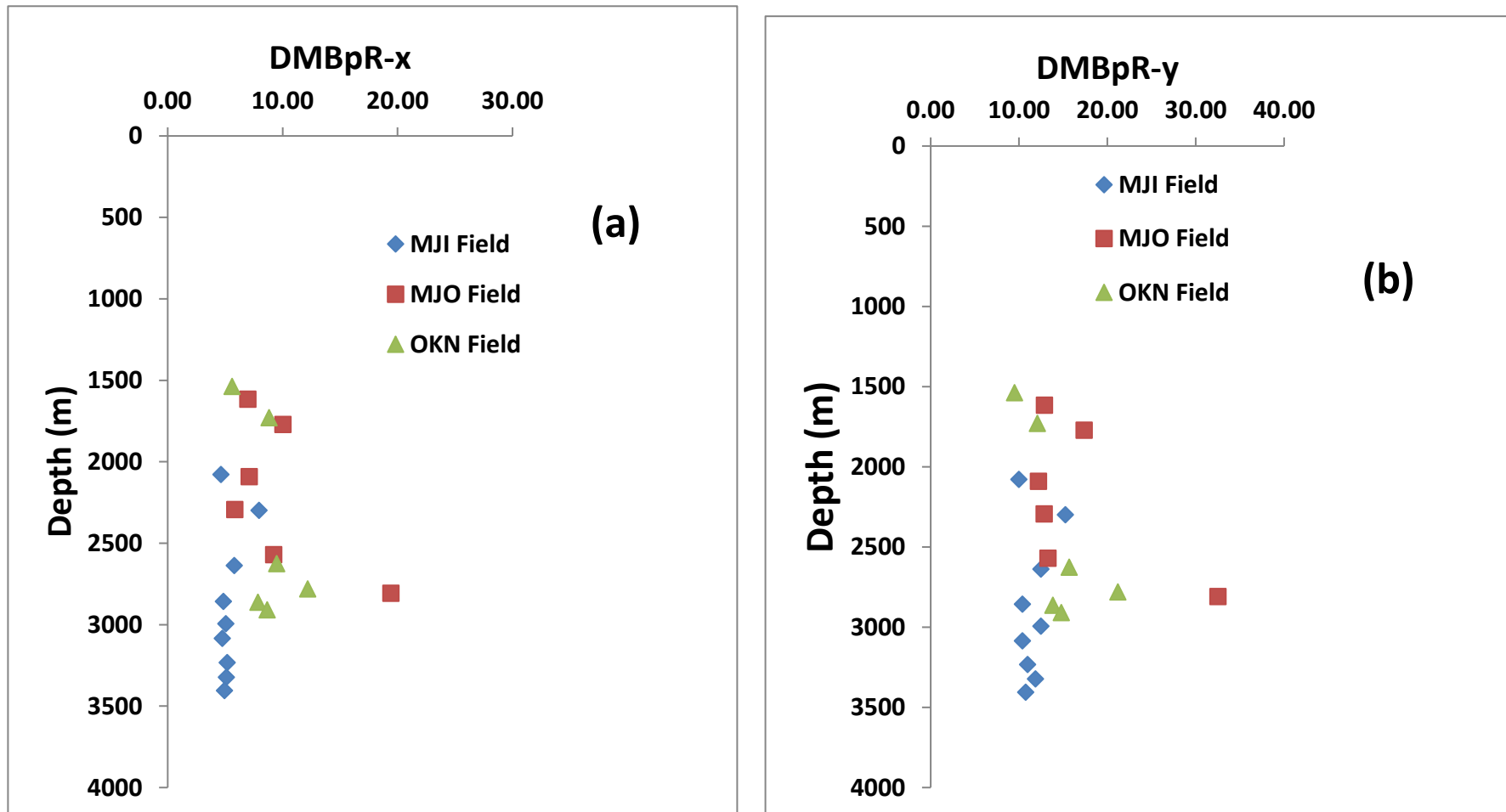
Fig. 3: Cross plots of burial depths versus (a) DMBpR-x and (b) DMBpR-y for Niger Delta source rocks.
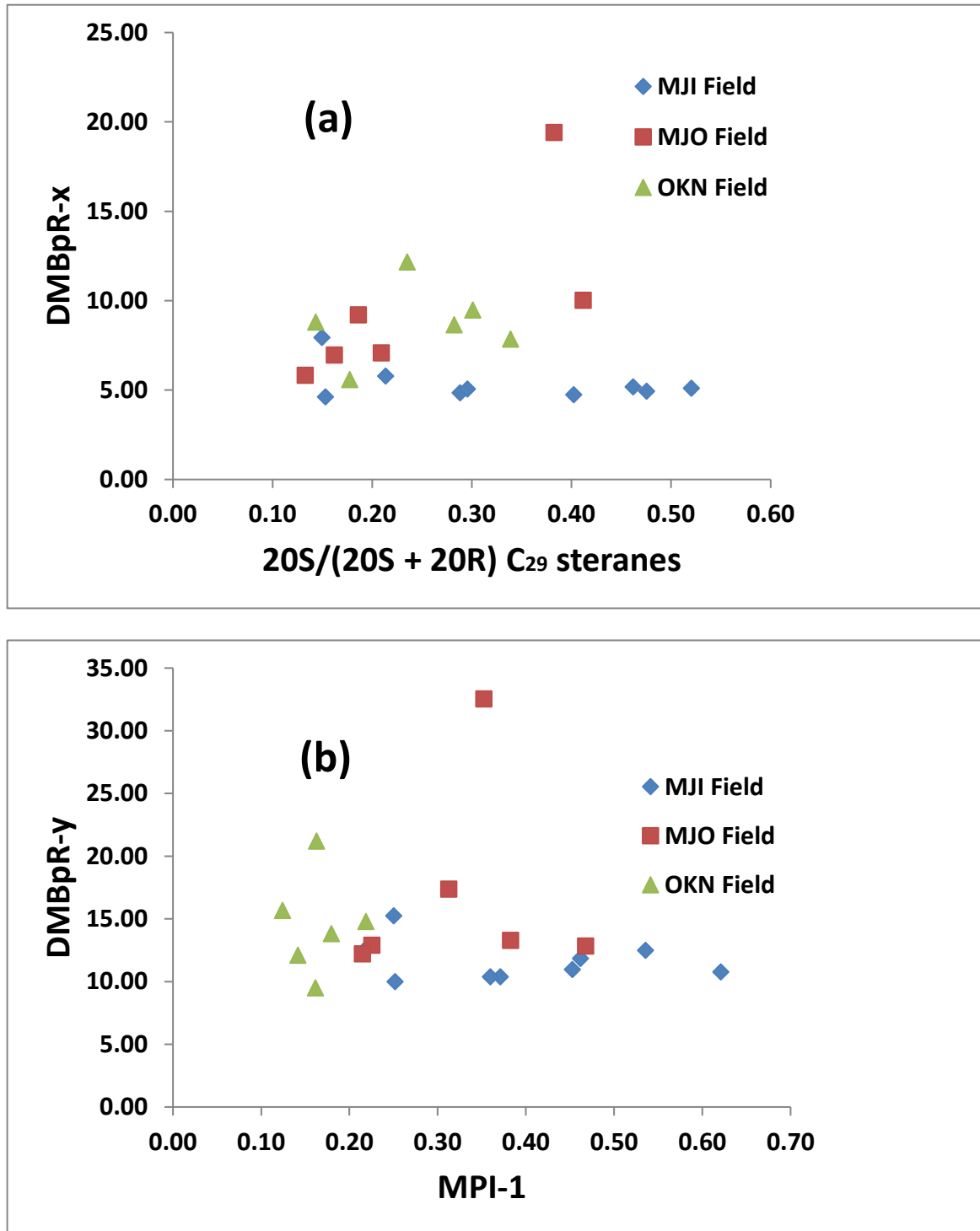
Fig. 4: Cross plots of (a) DMBpR-x versus 20S/(20S + 20R) C_{29} steranes, (b) DMBpR-y versus MPI-1 for Niger Delta source rocks.

Table 1: **Geochemical parameters computed from biphenyl compounds and related parameters in Niger Delta source rocks.**

| Field | Depth(m) | Biphenyl (%) | | | | DMBpR-x | DMBpR-y | Pr/Ph | 20S/20S+20R | MPI-1 |
		C_0	C_1	C_2	C_3				C_{29}	
MJI	2079-2098	0.09	9.12	48.15	42.63	4.63	9.99	3.2	0.15	0.25
MJI	2299-2308	0.31	1.70	39.89	58.09	7.95	15.24	2.31	0.15	0.25
MJI	2637-2655	0.12	10.75	52.89	36.23	5.79	12.48	3.91	0.21	0.22
MJI	2857-2875	0.16	10.12	50.32	39.41	4.85	10.39	3.98	0.29	0.37
MJI	2994-3012	0.06	6.29	51.46	42.18	5.07	12.48	4.26	0.30	0.54
MJI	3085-3104	0.30	17.67	51.89	30.14	4.74	10.39	4.53	0.40	0.36
MJI	3232-3250	0.54	19.85	50.85	28.76	5.19	10.96	2.87	0.46	0.45
MJI	3323-3332	1.50	22.92	48.21	27.38	5.11	11.85	4.46	0.52	0.46
MJI	3405-3424	0.80	15.36	49.09	34.75	4.94	10.76	2.92	0.48	0.62
MJO	1616-1707	0.19	6.40	41.69	51.72	6.97	12.90	4.31	0.16	0.23
MJO	1771-1872	0.55	3.80	38.51	57.13	10.03	17.36	2.16	0.41	0.31
MJO	2091-2101	0.19	3.54	37.47	58.80	7.09	12.21	2.08	0.21	0.21
MJO	2293-2366	0.31	14.53	50.20	34.96	5.84	12.84	2.96	0.13	0.47
MJO	2570-2588	0.04	5.83	47.86	46.27	9.22	13.29	3.5	0.19	0.38
MJO	2808-2817	0.06	7.02	44.53	48.39	19.42	32.53	3.6	0.38	0.35
OKN	1537-1555	1.86	11.29	42.52	44.33	5.60	9.49	1.85	0.18	0.16
OKN	1729-1747	2.55	15.40	48.54	33.51	8.82	12.09	2.61	0.14	0.14
OKN	2625-2643	1.43	14.77	46.32	37.48	9.48	15.68	1.51	0.30	0.12
OKN	2780-2799	2.35	16.14	42.62	38.89	12.17	21.21	1.73	0.24	0.16
OKN	2863-2881	3.95	17.14	42.81	36.10	7.86	13.82	2.06	0.34	0.18
OKN	2909-2927	0.57	9.94	44.85	44.64	8.66	14.79	2.27	0.28	0.22

An Estimation of Daily Intake of Potentially Toxic Elements from Urban Dust of Abakaliki, Nigeria

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ABSTRACT
This study examined the total concentration of eight potentially toxic elements (PTEs) in urban dust of Abakaliki and also calculated the daily intake (DI) of these PTEs. Fifteen samples were investigated and the result revealed that the range of mean total PTE concentrations was found in this order: 3.59 – 15.3 mg/kg (As); 66.8 -172 mg/kg (Cd); 0.288 – 1.36 mg/kg (Cr); 25.4 – 86.6 mg/kg (Cu); 55.5 – 1815 mg/kg (Pb); 397 – 1389 mg/kg (Mn); 22.3 – 52.7 mg/kg (Ni) and 73.3 – 434 mg/kg (Zn). For each element the highest concentration (representing the worst-case scenario was used to calculate the daily intake and it was observed that only Pb with a DI of 4.88 µg kg_{bw}^{-1} day^{-1} exceeded Pb recommended tolerable daily intake (TDI) of 3.6 µg kg_{bw}^{-1} day^{-1}. Based on a soil and dust ingestion rate of 50 mg /day for children between the age of 1 and <6 year, the amount of dust that a child would ingest in order to exceed the recommended tolerable daily intake TDI was also calculated.

Keywords: urban dust, potentially toxic elements (PTEs), oral ingestion, Abakaliki, tolerable daily intake (TDI)

INTRODUCTION

Dust is an environmental component that has been found to house contaminants particularly urban dust. Dust is derived from soil, and represents the small particles that have settled onto humans, outdoor objects and surfaces due to either wet or dry deposition. It consists basically of natural and anthropogenic components (Amato *et al*., 2009). The natural components include plant residue, fragmented rock and volcanic release while the anthropogenic constituents include vehicular exhausts particles, lubricating oil residues, tyre wears, engine coating wears, brake lining wear particles, heating systems, municipal waste incineration, constructions, renovations, mining and extraction processes, smelting, corrosion of galvanised metal components and building deterioration (Zhao *et al*., 2006). Dust particles released from contaminated sites travel long distances and could be in constant contact with humans due to outdoor activities. This is because these dust particles have light weight. They are known to be fine solid particles and settle out under their own weight but could also remain suspended for some time in the atmosphere depending on its particle size (Hojai *et al*., 2012). Thus, urban dust is a repository of environmental contaminants and need to be investigated regularly for total elemental concentrations.

Oral ingestion of dust occurs deliberately or involuntarily. It is common among all the exposed population. Due to the pervasive nature of dust, it is constantly in contact with the skin, clothes and any other objects not specially protected. It has been noted (Abrahams *et al*., 2002) that every exposed population particularly in the urban environment would possibly ingest a small quantity of dust. This easily happens because dust adhering to our body, especially the fingers, may be unintentionally ingested due to hand-to-mouth activity. Moreover, fruits and vegetables could easily come in contact with dust and if not properly washed could lead to unintentional soil ingestion. Moreover, eating of dropped foods could also lead to soil ingestion (Elom *et al,* 2013). Exposure via the pathways (oral, dermal and inhalation) to these PTEs could cause potentially adverse effects, carcinogenesis and development of numerous health effects including: Skin and internal cancer, DNA damage, neurological effects and alterations to endocrine system (Guito *et al,* 2011). However, the effects depend on the dose and exposure duration. Interaction of dust particles with the eyes and the ears are known to cause irritation (Biasiol *et al* 2007).

MATERIALS AND METHODS
Sample collection and preparation

Abakaliki is the capital of Ebonyi State. Dust samples were collected within the capital territory. All sampled sites were selected randomly but with due regard to high volume of traffic,