

# Phthalates and Other Plastic Additives in Surface Sediments of the Cross River System, S.E. Niger Delta, Nigeria: Environmental Implication

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## Abstract

Quantitative determination of phthalates and other plastic additives was carried out using GC-MS in order to understand the distribution and fate of these compounds in surface sediments of the Cross River System. Results show the concentration ranges (mean±standard deviation) of the three phthalates as: di(ethylhexyl)phthalate (DEHP; 1.97– 86.76 [24.06 ± 29.88 mg/kg dry weight dw]); di(n-butyl)phthalate (DnBP; 0.16 – 17.41 [3.25 ± 5.03 mg/kg dw]); di(isobutyl)phthalate (DiBP; 1.14 – 29.64 [9.82 ± 10.23 mg/kg dw]). However, examination of n-hexane procedural blank (used also in the study for clean-up protocol) GC trace revealed the presence of certain amounts of DEHP and tris-2,6-di(t-butyl)phenylphosphite (PhP) which interfere with the targeted analytes. Therefore, extract/blank (E/B) ratios were calculated and were in the range 1.05 – 12.54, indicating that the concentrations of DEHP and PhP previously assigned to the sediments were partly derived from laboratory artifacts. Differences in grain size distribution, partitioning behavior, volatility and solubility in the aqueous phase as well as localized influx may account for the observed spatial variation of phthalates and other plastic additives in the river system. The primary sources of these phthalates and tris-2,6-di(t-butyl)phenylphosphate (PhP') were considered to be the result of direct discharge of untreated effluent/solid waste and emission arising from burning of refuse containing plastic materials, respectively. The occurrence of certain anti-oxidant degradation products in sediments (not in the blank) such as 2,6-di(t-butyl)-4-hydroxybenzaldehyde (HBA) and 2,6-di(t-butyl)quinine (Qn) and PhP' (a compound proposed here as a possible marker for plastic combustion for the region/air basin), suggests that phthalates contamination had occurred before sample contact with laboratory artifacts.

**Keywords:** Phthalate, tris-2,6-di(t-butyl)phenylphosphate, source, distribution, environmental implication, cross river system

## 1. Introduction

Over the past few decades, phthalate compounds have become one of the most abundant pollutants in the environment from a variety of industrial discharges, particularly in tropical developing economies (such as Nigeria) with their attendant poor disposal systems. In 1999, the top U.S 100 companies reported total di(n-butyl)phthalate (DnBP) discharges of more than 300, 000 pounds. The same year, the top U.S 100 companies emitting DEHP reported nearly 1.2 million pound of discharges. These reports however, exclude phthalate discharges to the environment from the use or disposal of finished consumer products (Staples, Charle, Dennis, & Peterson., 1997). Similar estimate has not yet been documented for the sub-saharan tropical region of Africa. Therefore, the present study provides baseline data for future inventory estimate of phthalate load in sedimentary environment for the region.

Phthalates are used as plasticizers to soften plastics and as solvents in a wide range of products such as perfumes, nail polish, hair spray, detergent, toys and food packages. Most of the mid- to high-molecular weight phthalates are used in the manufacture of PVC while the low molecular weight counterparts such as DnBP are used in epoxy resin, cellulose ester bound plastics and specialized formulation. Thus for this reason, phthalates have been found in virtually in all compartments of the environment including fresh water, lake sediments, marine

environments, sewage treatment plants and sewage sludge (Aranda, O'Connor, & Ekeman, 1989) as well as in buried PVC in landfill leachates and in atmospheric aerosols (Simoneit, Standley, & Cox, 1988). Phthalates have also been detected in rain water of Los Angeles, USA with DEHP as the dominant homolog (Simoneit & Mazurek, 1989).

According to Simoneit et al. (2005), the major components of plastic extracts are n-alkanes, DEHP (plasticizer) and anti-oxidants (AO) as well as lubricant/anti-adhesive (IRGANOX 1075, IRGAFOX 168). We have also detected phthalates, non-specific n-alkanes (mainly of even carbon numbered predominance), 4-hydroxybenzoic acid and biphenyl as well as minor amounts of polycyclic aromatic hydrocarbons in organic solvents believed to have been kept in plastic containers prior to dispensing into bottles by commercial chemical vendors in Nigeria (Ekpo, Oyo-Ita, Oros, & Simoneit, 2011).

The general populace is exposed to phthalates through food, water, air and the use of phthalate-containing consumer products that may be eaten, inhaled or applied directly to the skin and absorbed. Phthalates and their by-products have been detected in urine and blood of individuals exposed to phthalates (National Institute of Public Health and Environmental Protection [NIPHEP], 1991; Meeker, Sheela, & Shama, 2009). DEHP is a compound of special concern among the plasticizers because it has been described as a probable human carcinogen by the United State Environmental Protection Agency (USEPA, 1992). Toxic and carcinogenic effects of phthalates are well established in experimental animals (Ashby, 1994; Jim-Carlisle, Henkel, Ling-Hongly, & Pagepainter, 2009), even though such ability to produce similar effects in human is yet to be documented. Evidence that humans are not at serious risk from exposure to phthalates has also been proven (NIPHEP, 1991; USEPA, 1992).

Phthalates may come in contact with sediments during sample collection, storage and analysis. One of the challenges in the present study was to establish whether the phthalates and other plastic additives found in sediment samples from the Cross River System were indigenous or that they were introduced into the samples during laboratory protocols. To achieve this, the composition and concentrations of phthalates and other plastic additives in the sediment samples were determined in relation to the laboratory blank (n-hexane). Since these compounds may be globally distributed (Simoneit, Medeiros, & Didyk, 2005), the additional thrust in the present study was to present data that could add to knowledge of the fate and factors that control the distribution of these compounds in the environment. To achieve this, we compared these compositions and concentrations in samples (which were obtained about 10 years ago) with those samples recently obtained from the same location for analysis of lipids.

Compounds such as tris-2,4-di(t-butyl)phenylphosphate and 1,3,5-triphenylbenzene have been identified as markers in smoke particles from burning of plastic materials in the USA air-basin (Simoneit et al., 2005). For purposes of improving emission inventories and air quality management for policy making strategy, this is the first elucidation and measurement of a compound (proposed here as a marker) in sediments of the Niger Delta river network. This proposed marker compound could be utilized as an assessment tool for the contribution of refuse combustion to Nigerian air-basin and other environments worldwide where plastics with similar chemical composition may be in use. The main objectives of the study therefore were to report on the levels, fate and distribution of phthalates and certain plastic additives in sediments of the Cross River System, as well as evaluate the environmental implication of their occurrence.

### *1.1 Study Area*

The study area (Figure 1) extends from Mbo River to 1 km beyond Itu bridge and included part of the upper Calabar River, a distance of approximately 195 km covering remote areas. The Cross River System is one of the river systems of the southeastern Niger Delta of Nigeria, which lies between longitudes 2°03'E and 10°00'E and latitudes 4°00'N and 8°00'N and covers an area of 54,000 km<sup>2</sup>, of which 14,000 km<sup>2</sup> lies in Cameroon and 39,000 km<sup>2</sup> is in Nigeria. The river is formed from numerous tributaries arising from the western slopes of the Cameroon mountains and flows south-westwards into the Atlantic Ocean with a discharge of between 879 and 2533 m<sup>3</sup>/sec (Asuquo, Ogri, & Bassey, 1999). The system is exposed to temporal flooding depending on the tides and season, and has large fluctuation in hydrographical conditions (Lwenberg & Knzel, 1992; Pisani., Oros, Oyo-Ita, Ekpo, Jaffe, & Simoneit, 2013). Calabar and Great Kwa Rivers are the major tributaries of the Cross River System.

### *1.2 Sample Collection, Preservation and Preparation*

Cross River System was divided into four zones, each depicting a peculiar type of regional impact: Zone I consists of samples collected from the estuary-near Oron beach. This is a highly populated area that receives a significant amount of untreated domestic sewage, agricultural run-off, garbage/refuse discharge, possible oil

spills from offshore operations and ship/boat traffic pollution. Zone II consists of samples obtained from area near Oku Iboku beach and thick mangrove swamp forest that receives effluents from a paper mill and garbage/refuse discharge; Zone III consists of samples collected from area near Itu beach that receives domestic sewage discharge, agricultural run-off as well as boat traffic pollution and garbage/refuse discharge; Zone IV consists of samples collected from the upper Calabar River that receives mainly untreated waste water/solid waste from a rubber processing/plastic industry as well as emission arising from burning of garbage/refuse containing plastic materials at a nearby waste dump.

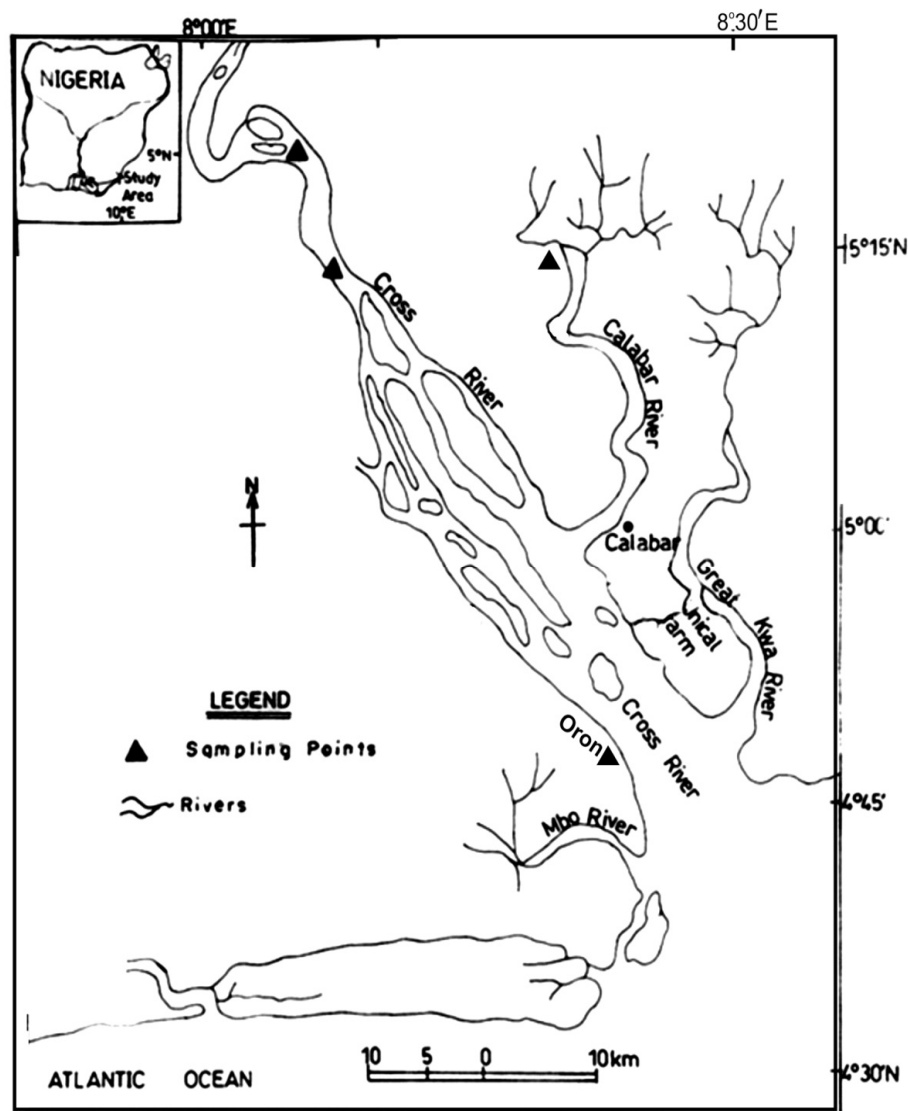


Figure 1. Map of the cross river system showing the sampling locations

Sediments were collected about 10 years ago (April, 2003) during raining season with a Van-Veen grab sampler ( $0.1 \text{ m}^2$ ), wrapped in aluminum foil and stored frozen at  $-4^\circ\text{C}$  until further analysis is carried out. Freeze-dried sediments were ground using a mortar/pestle and subsequently sieved through 230 mesh sieve to obtain  $< 63 \text{ m}$  fraction. Grain size analysis was performed on the sediment according to the method described by Folk (1974). Similar treatments were performed on sediments collected recently from the same locations which were being analyzed for lipids in another study.

## 2. Materials and Methods

### 2.1 TOC Determination, Extraction and Clean-up

The following solvents-dichloromethane (DCM), methanol (MeOH), hexane, ethyl acetate and acetone-were used for the analysis. The vessels used for analysis were pre-cleaned with ethyl acetate followed by acetone and heated overnight at 300 °C. Prior to the extraction protocol, freeze-dried sediment samples were decarbonated in 37% hydrochloric acid in several stages until bubbling stopped and rinsed in deionised water to neutral pH. The total organic carbon (TOC) content of the sediments was determined by flash combustion at 1024 °C, followed by thermal conductivity detection in triplicate in a CHNS Elemental Analyser, Carlo Erbar 1108.

Extraction of 2 g sediment sample in a test tube was performed sequentially by sonication with DCM/MeOH (2:1) and DCM in triplicate (Grimalt, Vam-Drogge, Ribes, Vilanova, Fernandez, & Appleby, 2004). Clean-up was performed by adsorption chromatography in an open glass column packed with 1 g anhydrous sodium sulfate (top), 2 g neutral alumina (middle; activated at 400 °C, 5% water deactivated) and glass wool (bottom). Elution with hexane yielded fractions enriched in aromatic compounds. The collected fractions were concentrated in a stream of N<sub>2</sub> gas to almost dryness.

### 2.2 Instrumental Analysis

Individual phthalates and associated plastic additives were identified and quantified using gas chromatography-FID and gas chromatography-mass spectrometer (GC-MS) on a Hewlett-Packard model 6890 GC coupled to a Hewlett-Packard model 5973 quadrupole MSD. Separation was achieved on a fused silica capillary column coated with DB5 (30 m x 0.25 mm i.d., 0.25 µm film thickness). The GC operating conditions were as follows: temperature hold at 65 °C for 2 min, increased from 65 to 300 °C at a rate of 6 °C min<sup>-1</sup>, with final isotherm hold at 300 °C for 20 min. Helium was used as carrier gas. The sample was injected in “splitless” mode with the injector temperature at 300 °C. The mass spectrometer was operated in the electron impact mode (EI) at 70 eV ionization energy and scanned from 50 to 650 dalton or using selected ion monitoring (SIM) mode. Data were acquired and processed with the Chemstation software. Individual compounds were identified by comparison of mass spectra resolution with authentic standards and interpretation of mass spectrometric fragmentation pattern, as well as comparison of their GC retention indices with those of reference standards.

One analytical blank (hexane) was run with every batch of 2 - 3 samples to check background contamination during the clean-up step. To remove background contamination, we corrected phthalates and plastic additives concentrations by subtracting mean concentration of the analytical blank from the concentrations of individual target compounds. A calibration curve (detector response versus amounts injected) was performed for each compound to be quantified. The linear range of the detector was estimated from the curve generated by plotting detector signal versus amount injected. All measurements were performed in the linear ranges for each target compound. In few cases, the samples were re-diluted and re-injected to fit within the linear range of the instrument. The limit of detection (LOD) in the SIM mode ranged from 0.02 to 0.10 ng/g dw. The lower limit of determination of these target compounds was estimated from the smallest peak (signal-to-noise ratio > 3:1 in the chromatograms) that could be integrated. The triplicate sample relative percent difference (i.e. relative standard deviation) for all the samples were less than 20% for all compounds. Validation of the accuracy of data arising from the quantitative measurements of these compounds was done by analyzing with the certified reference material “CRM-104” (Resource Technology Corporation, USA), obtaining accuracy from 79% to 109% compared with the certified values.

## 3. Results and Discussion

### 3.1 Sediment Bulk Geochemical Properties

The results of bulk geochemical parameters for the sediments including the characteristic features of the environment are presented in Table 1. The grain size distribution data revealed predominance of clay fraction at the upper Calabar River stations while the estuary stations were predominated by silt/sand fraction. The TOC contents for the sediments ranged between 1.27 and 4.56%, with a maximum value recorded at station CR4 and a minimum value recorded at station CR8, while soluble organic matter (SOM) varied between 1,140 and 4,140 mg/kg dw with maximum and minimum values found at stations CR6 and CR9, respectively. There was no significant relationship between grain size distribution (silt/clay fraction) and TOC contents of sediments (correlation coefficient  $r^2 = 0.2314$ ;  $p > 0.01$ ). This result is at variance with documented data of other sedimentary environments which (in most cases) show strong relationship between these two variables (indicating greater ability of fine-grained particles to adsorb organic matter than coarse-grained particles; Unlu & Alpar, 2006; Oyo-Ita & Oyo-Ita, 2013).

### 3.2 Composition and Concentrations of Phthalates and Other Plastic Additives in Sediments and Blank

Three phthalate compounds were detected in surface sediments of the Cross River System with DEHP exhibiting the highest abundance in almost all the sampling stations. The concentrations of DEHP were in the range 1.97–86.76 mg/kg dw with an average of  $24.06 \pm 29.88$ , while those for DnBP ranged from 0.16 to 17.41 mg/kg dw with an average of  $3.25 \pm 5.03$  and 1.14 – 29.64 mg/kg dw with an average of  $9.82 \pm 10.23$  were found for DiBP. Other associated plastic additives identified in sediments were 2,6-di(t-butyl)-4-hydroxybenzaldehyde (HBA), 2,6-di(t-butyl)quinine (Qn), tris-2,6-di(t-butyl)phenylphosphite (PhP) and tris-2,6-di(t-butyl)phenylphosphate (PhP'). On the other hand, variable levels of DEHP, di-octyladipate (DOA), PhP and trace amounts of n-alkanes and polycyclic aromatic hydrocarbons were found in the blank. The mass chromatogram for the phthalate compounds in sediments is shown in Figure 2a while the total ion current GC trace for n-hexane blank is presented in Figure 2b.

Blanks are required to determine the fraction of individual contaminants in sediment extracts that are derived from laboratory background. To determine whether the DEHP and PhP found in the sediments were indigenous or exclusively/partially introduced during laboratory protocol (clean-up stage), we computed extract/blank (E/B) ratios. E/B is the concentrations of individual target compounds in sediment extract relative to laboratory blank. E/B values < 20 were previously reported to be regarded conservatively as indicators for background contamination (Brocks, Buick, Logan, & Summons, 2003a; Brocks, Grosjean, Logan, & Graham, 2008). In our case study, we estimated E/B ratios for DEHP and PhP as these were the only target compounds detected in both the sediments and blank, and values < 20 were recorded (Table 1). The low  $E/B_{DEHP}$  and  $E/B_{PhP}$  values indicate that DEHP and PhP detected in the sediments were not exclusively derived from analytical procedure and that some levels of these compounds were indigenous. As DEHP is one of the most commonly used plasticizers, its relative abundances in the blank and sediments are expectedly high. Since DEHP and PhP in the blank may interfere with those in the sediments, we subtracted their concentrations in the sediments from those in the blank. The corrected DEHP and PhP concentrations in the sediments varied as presented above.

Comparing data, higher concentrations of DEHP were found in levels exceeding 90 mg/kg dw in sediments from lake Mead, a national park in US whereas lower levels of DEHP (25 mg/kg dw) were recorded in Ocean sediments at sewage outfall point, New Jersey, USA (Staples et al., 1997).

### 3.3 Identification and Sources of Phthalates and Other Plastic Additives

The three phthalate compounds were identified on the basis of their retention times window compared with authentic standards, monitored using key fragment ion m/z 149 (Figure 2a), while identification of the plastic additives was done by interpretation of mass spectra fragmentation patterns. A compound detected in some sediment samples (not in the blank) with molecular ion m/z 234 and a major fragment ion at m/z 219 was identified as 2,6-di(t-butyl)-4-hydroxybenzaldehyde (HBA). This compound appears as underivatized parent compound in the mass spectrum (Figure 3a) as silylation is inhibited by the steric hindrance of tert-butyl groups in the ortho positions to the aldehyde or hydroxyl group. The compound and its oxidized form (Figure 3b) having a molecular ion at m/z 220 and a major fragment ion at m/z 177, identified as 2,6-di(t-butyl)quinine are considered here as diagenetic products of butylatedhydroxylbenzene (BHB) based anti-oxidants used as additives in a wide range of products including petroleum based lubricants and plastics (Grosjean & Logan, 2007).

Table 1. Characteristic features of the environment, bulk geochemical parameters and extract/blank ratios of sediments from the Cross River System

ZONE	I				II			III			IV		
Sample code	CR1	CR2	CR3	CR4	CR5	CR6	CR7	CR8	C-9	CR10	CR11	CR12	CR13
Coordinate	N4°	N4°	N4°	N4°	N4°	N5°	N5°	N5°	N5°	N5°	N5°	N5°	N5°
	43.96'	46.53'	49.92'	52.67	56.87'	00.43'	04.31'	04.31'	12.72'	12.25'	18.05'	18.15'	18.22'
	E8°	E8°	E8°	E8°	E8°	E8°	E8°	E8°	E8°	E8°	E8°	E8°	E8°
	21.32'	18.90'	15.50'	12.74'	09.33'	07.06'	06.25'	06.25'	03.49'	00.22'	23.16'	23.18'	23.21'
Location name	Oron beach area				Oku Iboku beach area			Itu beach area			Upper Calabar/Great Kwa Rivers area		
Characteristic features of the environment.	Untreated sewage, agricultural waste, oil spills, ship/boat pollution, garbage/refuse discharge.				Paper mill untreated waste effluents and garbage/refuse discharge.			Boat traffic Pollution, domestic sewage, agricultural waste, garbage/refuse discharge			Rubber processing/plastic industry discharge and agricultural waste, garbage/refuse discharge.		
Sediment texture	Silty	silty	Sandy	Sandy	Sandy	Silty	Silty	Sandy	Sandy	Silty	Clayey	clayey	Clayey
TOC(%)	4.03	3.64	4.35	4.56	4.2	4.38	2.77	1.27	2.66	4.26	3.78	3.95	4.08
SOM (mg/kg dry wt.)	3,000	3,680	1,920	2,950	3,710	4,140	2,650	1,510	1,140	1,850	2,376	2,124	3,468
E/B <sub>(DEHP)</sub>	9.95	4.21	4.94	1.65	3.16	1.05	3.17	1.61	1.65	1.42	10.23	0.89	12.54
E/B(PhP)	5.76	3.23	4.98	2.86	3.98	1.82	2.95	1.56	2.05	2.74	5.23	1.21	1.75

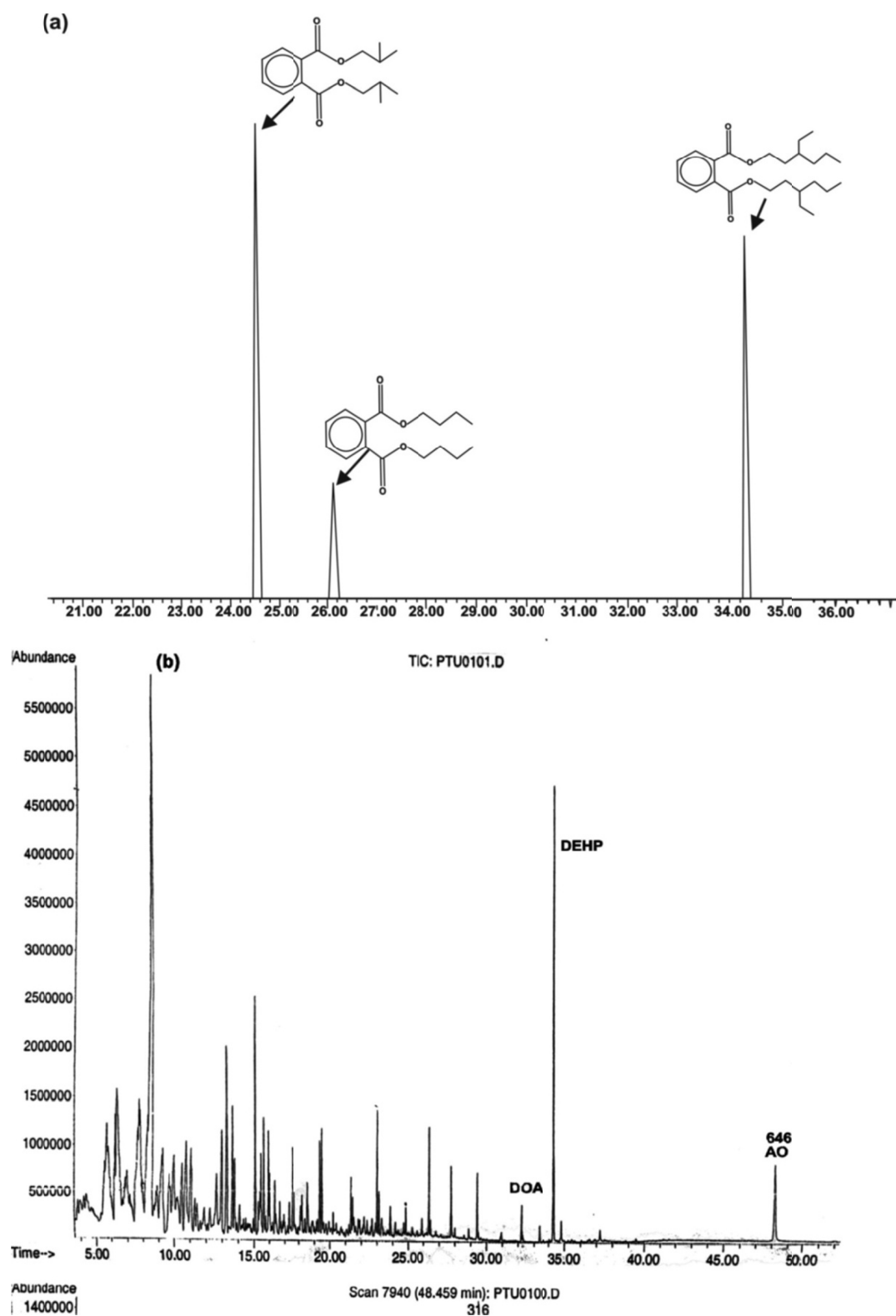


Figure 2. (a) Mass chromatogram of phthalate compounds monitored with  $m/z$  149 key fragment ion detected in sediments of the cross river system. and (b) total ion current GC trace for the hexane blank

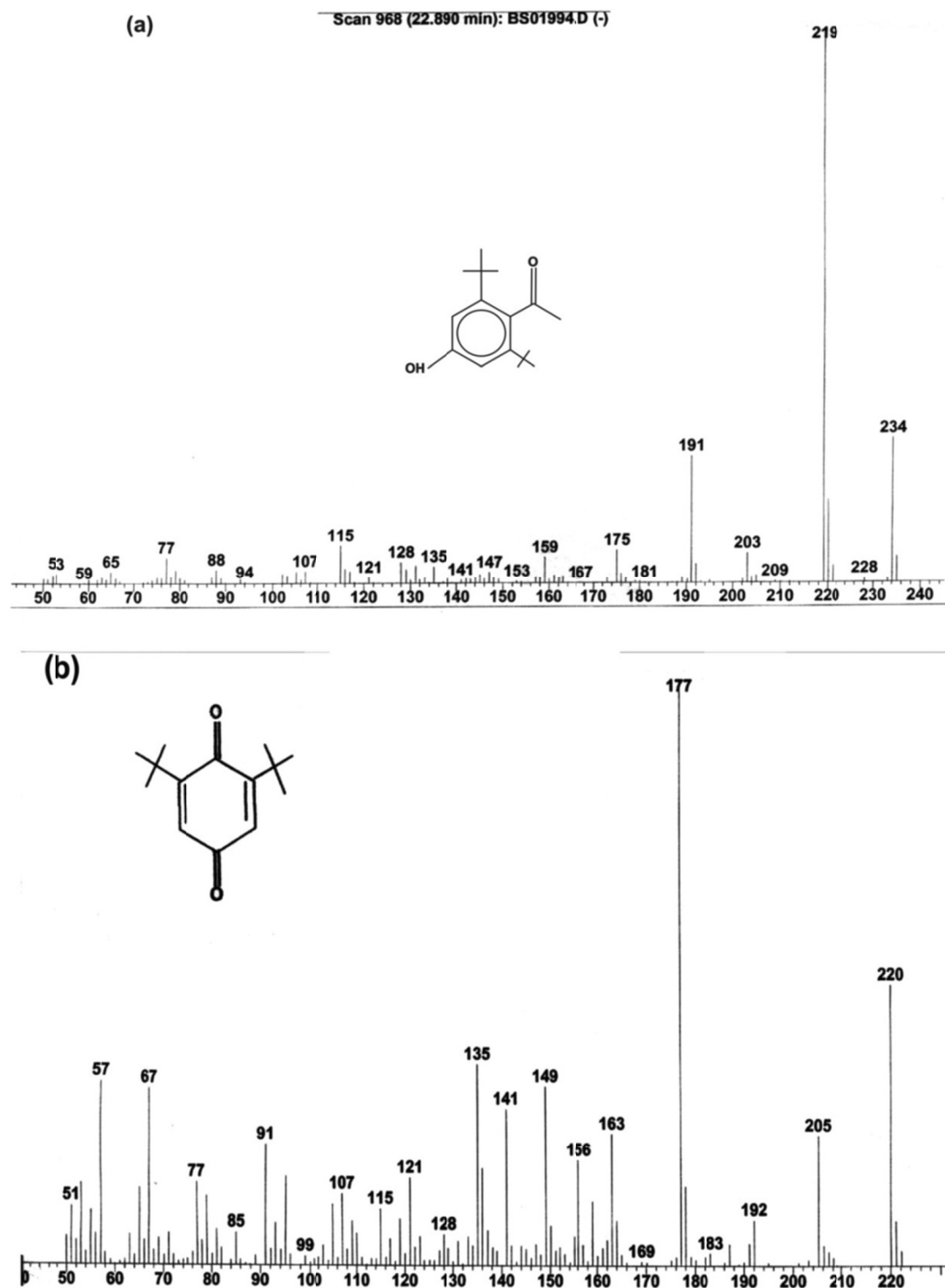


Figure 3. Mass spectra of (a) 2,6-di(t-butyl)-4-hydroxybenzaldehyde and (b) 2,6-di(t-butyl)quinone detected in sediments of the cross river system

An anti-oxidant compound (detected in both sediments and blank), with a weak molecular ion at  $m/z$  646, eliminates a di(t-butyl)phenoxy moiety on fragmentation in the ion chamber to give the base peak at  $m/z$  316 and minor fragment ions at  $m/z$ , 367, 291, 191, 147 and 57, was identified as tris-2,6-di(t-butyl)phenylphosphite (PhP; Figure 4a). A related compound with a base peak at  $m/z$  647, key fragment ion at  $m/z$  316 and a molecular ion at  $m/z$  662, identified as tris-2,6-di(t-butyl)phenylphosphate (PhP'; Figure 4b), is analogous to tris(2,4-di-butyl)phenylphosphate (a compound previously identified in plastic combustion products (Simoneit et



al., 2005). In this study, PhP' is proposed as a marker for plastic combustion for the region/air basin. Therefore, future measurement of the proposed plastic combustion marker in the Nigerian air-basin should be a good assessment tool for the contribution of refuse combustion to air-borne contamination and should provide further information to improve emission inventories and air quality management.

The detection of PhP in the blank suggests contact of the blank with plastic material probably during clean-up procedure while its presence in sediments at higher levels most likely indicates additional input arising from leeching of plastic materials to the sedimentary environment. However, the detection of PhP' in the sediments (not in the blank) implies input from atmospheric deposition during or after burning of refuse containing plastic materials. It appears that during this process, the volatilized PhP became oxidized in the atmosphere at high temperature to PhP'. Once in the sediments, the marker compound underwent degradation and may be responsible for the occurrence of HBA and Qn in some sediment samples of the study area. This scenario indicates that sediments of the Cross River System were influenced by phthalates and plastic additives contamination before sample collection, storage and contact with laboratory artifacts.

Primarily, phthalate compounds in the river system was considered to originate from direct discharge of untreated effluent/solid waste produced by the plastic and rubber processing industry located about 5 km north-east of the study area. This deduction is based on the detection of higher phthalate levels in sediments from the Upper Calabar River (zone IV).

### 3.4 Spatial Distributions of Phthalates and PhP' in Sediments

The low molecular weight phthalate components (DnBP and DiBP) occurring at relatively reduced levels in all the sampling stations (except CR6) may be linked to their relatively high volatility, and being more soluble, might have been retained in the aqueous phase more than being adsorbed in the solid matrix (Figure 5). Experimental data on physicochemical properties of phthalates such as partitioning behavior and vapor pressure show an eight order of magnitude in octanol-water partition coefficient, and a four order of magnitude in vapor pressure decreases as alkyl chain length increases from 1 to 13 (Staples et al., 1997). These data support the observed low levels of low molecular weight phthalates in the sediments. The implication here is that the low molecular weight phthalates (DnBP and DiBP) might not have been strongly partitioned on the solid matrices compared to the high molecular weight homolog (DEHP), and could become easily solubilized and volatilized.

In addition, the spatial variation in the concentrations of these phthalate compounds may be partly a reflection of the differences in sediment grain size distribution (Table 1; Figure 5), proximity of samples to contamination source and the effect of sediment re-suspension at the river mouth arising from turbulent mixing. This scenario suggests that long range regional eolian or river current transport may not be an important factor that determines the distribution of these compounds in the system and that localized contamination was more significant.

Additives are released to the environment from plastics by leaching, contact interference and direct volatilization into smoke during burning of refuse containing of plastic materials (Braun, 2004). The variation in spatial distribution of the marker compound (PhP') in the study area is shown in Figure.5. Among the sampling stations, those of Zone IV show much higher levels of PhP', supporting the fact that long range eolian transport or river water current trajectory was not important in the distribution of the marker compound. Besides the strong affinity of PhP' towards sedimentary organic carbon predominated by clay textural fraction, wet precipitation of air contaminant load following plastic combustion emission as well as differences in refuse disposal pattern among inhabitants of the catchments might have played a significant role.

### 3.5 Environmental Implication

Although phthalates are lipophilic and of low volatility, experimental evidence shows that these compounds are not persistent and are rapidly photo-chemically and biologically degraded in the environment (Shanker, Ramakrishna, & Seith, 1985; Schnitzer, Scheunert, & Korte, 1988; Barron, Albro, & Hayton, 1995; Adeniyi, Dayomi, & Okedeyi, 2008). The sediment samples in the present report were collected about 10 years ago, and it is worthy of note that analysis of lipids in recently obtained sediment samples from the same sampling area (reported elsewhere) shows absence or trace levels of phthalates. This observation may be linked to the rapid photochemical and biological degradation of phthalates in the sediments. In addition, the non-operation of the existing plastic industry in the vicinity of the upper Calabar River for the past five years might have also accounted for this absence.

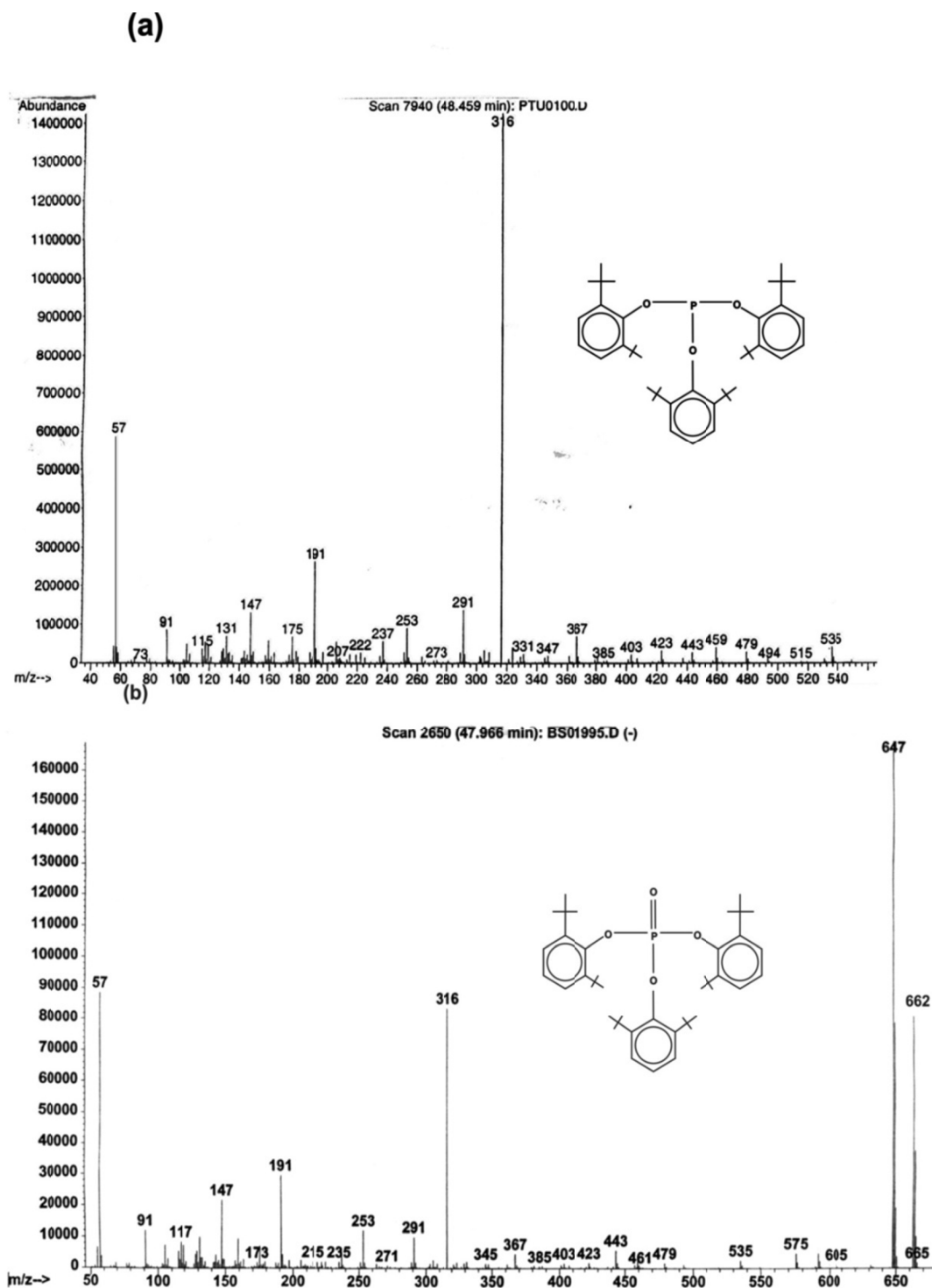


Figure 4. Mass spectra of (a) tris(2,6-di(t-butyl)phenyl)phosphite detected in sediments and blank and (b) tris(2,6-di(t-butyl)phenyl)phosphate detected in sediments of the cross river system

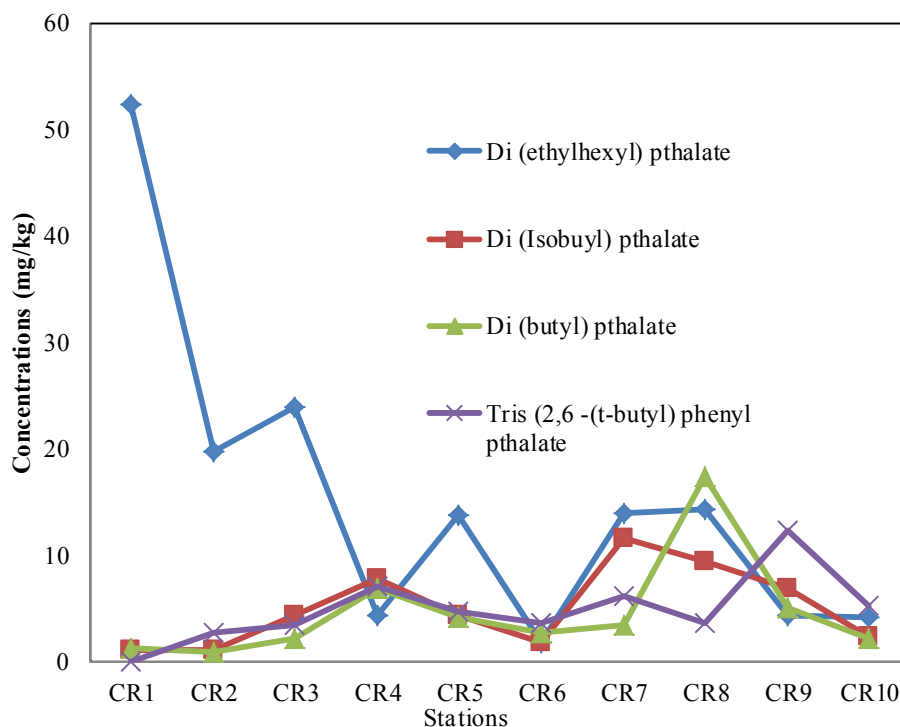


Figure 5. Spatial variation in the concentrations of Phthalate and other plastic additives amongst sampling stations of the cross river system

Staples et al. (1997) show that under aerobic and anaerobic conditions, phthalates in sewage sludge undergo > 50% ultimate biodegradation within 28 days. According to these authors, these phthalates may be used by aerobic and anaerobic microbes as a source of carbon and energy. Numerous experimental data have shown that the bioaccumulation of phthalates in the aquatic and terrestrial food chains is limited by their biotransformation which increases with the increasing trophic level (Staples et al., 1997). Therefore, the relatively high levels of phthalates found in sediments of the Cross River System might not have posed any serious health threat to both resident organisms and humans. The compounds might have been rapidly degraded in the sediments and metabolized by aquatic organisms to less harmful compounds.

#### 4. Conclusions

The present study has demonstrated the efficacy of extract/blank (E/B) ratio as indicator of background contamination in environmental samples and indicates that DEHP and PhP found in sediments of the Cross River System were not exclusively derived from laboratory artifacts, and that some levels of these compounds in the sediments were indigenous. The detection of certain anti-oxidant degradation products indicates that the sediments were influenced by phthalates contamination before sample collection, storage and contact with laboratory artifacts.

The occurrence of phthalates and PhP' in the sediments are considered to originate primarily from direct discharge of untreated effluent/solid waste by the rubber processing/plastic industry and emissions arising from burning of refuse containing plastic materials, respectively. Long range eolian transport or river water current trajectory did not play a significant role in the distribution of these compounds in the sediments, rather wet precipitation and localized influx were more important. Therefore, future measurement of the proposed plastic combustion marker in the Nigerian air-basin should be a good assessment tool for the contribution of refuse combustion to air-borne contamination and should provide further information to improve emission inventories and air quality management for policy making strategy.

The levels of phthalates contamination found in sediments of the river system, though relatively high, might not have posed serious health threat to resident organisms and subsequently humans via food chain as these compounds are readily degraded in the sediment and metabolized in aquatic organisms to less harmful products.

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