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Sediment Organic Carbon and the PBT Contents of Lagos Lagoon, Nigeria

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Abstract

An important way of evaluating the trends in nonpolar organic compounds, such as Persistent, Bioaccumulative, and Toxic (PBT) organic micropollutants is the assessment of the effect of organic carbon on their concentrations. Being the only sorptive phase present in sediment, organic carbon is used in the traditional form of the Biota-Sediment Accumulation Factor (BSAF) model for chemical bioavailability study. In this study, total organic carbon contents, along with the PBT concentrations of the Lagos lagoon sediments, were spatially and temporally assessed. A steady increase in organic carbon content, with corresponding increase in sum PBTs, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and organochlorine pesticides (OCs), was observed in the lagoon sediments in Feb., 2004, Dec., 2006, and May, 2007. Very positive correlations (R^2=1) were obtained. The sum of the % organic carbon contents of the sediments in those three years were 61.81, 82.105, and 85.31%, and the sum of the mean PBTs were 316.34, 383.41, and 705.17ng/g respectively. High organic carbon content and PBT levels were obtained at locations close to urbanized areas, and vice versa. Low PBT levels were obtained from sandy sediments as their organic carbon contents were equally low. Organic carbon normalized concentrations revealed salient peaks of PAHs at the Mouth of Ogun River, a fluvial source; highest peaks of PCBs at Iddo, a location close to a disused power station; and highest peaks of OCs at Mouth of Ogun River, Iddo (a highly crowded area) and Okobaba (a slum settlement). The influence of organic carbon fraction on the partitioning capacity of the PBTs in the sediments of Lagos lagoon is presented.

Keywords: *Organic carbon, Organic micropollutants, Sediments, Lagos lagoon*

Background to the Study

Most of the wastes (say about 80%) generated in Lagos are mainly organic. These wastes are either dumped directly into the lagoon, or water channels, or openly incinerated at different locations without control. One of such locations is a sampling site (Okobaba) in this study, where there is an incessant burning of sawdust and other domestic wastes just at the lagoon shore.

Lagos lagoon is also a recipient of urban wastewater which contains large quantities of nutrients (phosphorous and nitrogen) and oxygen demanding substances, i.e. organic matter. In the water column most PBTs tend to absorb to particles and to be deposited to the underlying sediments. In addition to sorption to sediment, PBTs in aquatic environments bind to dissolved humic material. Sediments represent an association between mineral particles, organic matter, and resident organisms. It was reported by Gobas et al (2004) that a direct relationship exists between the hydrophobicity of PBTs and the affinity for binding to dissolved humic material.

Sediment organic carbon contents vary with variation in sediment type, and subsequently influence contaminants distribution pattern and bioavailability (Pazdro, 2002 & Leeuwen et al., 2007). The typical approach of adjusting for variations in organic carbon in sediment samples therefore is to normalize concentrations with organic carbon. Organic carbon partition coefficient K_P of organic chemicals is often proportional to the organic matter content of solid phase. For comparative reasons, the solids-water partition coefficient (K_P) is often adjusted with respect to organic carbon content (f_{OC} = %OC / 100) and an organic carbon partition coefficient is thus defined:

$$K_P = K_{OC} * f_{OC} = C_S / C_W \text{ (Leeuwen et al., 2007).}$$

Where K_{OC} is the OC-normalized K_P, and C_S and C_W are the chemical concentrations in sediment and water respectively. The standard value for f_{OC} in sediment is set at 0.05. For neutral organic chemicals K_{OC} is often estimated from K_{OW} using Log K_{OC} = Log K_{OW} -0.21 (Schorer, 1997). Typical values of Organic carbon content (OC) in sediment are in the range of 4 to 6%. (Schorer, 1997).

Total organic carbon was determined by Harwell et al (2003) in 21 surficial sediment samples from Lake Worth Sediment, Fort Worth, Texas and found to range from 0.91 to 2.85 percent by weight with a median of 2.38 percent. Two predominately sand samples had 0.91 and 1.09 percent total organic carbon while the remaining 19 samples were relatively homogeneous with respect to total organic carbon, ranging from 2.24 to 2.85 percent.

PBTs that are bound to sediment or particulate matter in the water column can exhibit slow desorption rates, rendering them essentially unavailable to aquatic biota. As noted by Thorsen, (2003), BSAF values in *E. complanata for petrogenic PAHs* were less than one for pyrogenic PAHs (PAHs of combustion origin). This signifies that the organism metabolized the PAHs and therefore they were not bioavailable. PCBs have a high affinity for suspended solids, especially those higher in organic carbon. This is supported by their low water solubility and high octanol / water partition coefficients (calculated Log Kow values range from 3.76 for biphenyl to 8.26 for decachlorobiphenyl) (CCME, 1992).

Lagos lagoon, the study area, is impacted by industrial, agricultural, municipal and oil related activities that keep increasing with the ever growing population of Lagos, the most highly populated city in the country, presently harboring not less than 15% of the total population (100 million) and about 80-85% of the industries in Nigeria. Sediments from the lagoon receive inputs of organic material from a wide variety of sources. Web (1958) observed that there is a high variation in sediment quality as a result of the variations in Lagos lagoon sediment sources, (Fig. 2). This study therefore seeks to assess as the spatial and temporal variability of PBT contents in relationship with the organic carbon contents of surficial sediment of the lagoon.

Fig. 1: Map of Lagos lagoon showing sample locations and a dumpsite

Fig. 2: Sediment variation at different locations of the Lagos lagoon (from top row left are sediment samples from locations A, A2, A3, B, B2 and B3; from bottom row left are C, C2, D, D2, E, and E2 samples)

Table 1: Sample locations on the Lagos lagoon

LOCATIONS	DESCRIPTION	COORDINATES
A	Iddo	N6°28" 2.4', E3° 23" 2.9'
A2	Five cowrie creek	N6°26" 2.7.7', E3° 24" 16.3'
A3	Lagos harbour at Marina	N6°26" 48.9', E3° 23" 26.6'
B	University of Lagos lagoon front	N6°31" 7.5', E3° 24" 11.9'
B2	Ibesse and Offin villages	N6°33" 5', E3° 28" 17.2'
B3	Okobaba	N6°28" 48', E3° 23" 31.3'
C	Ikoyi park view fore shore	N6°27" 30.2', E3° 27" 8.9'
C2	Ajah	N6°28" 24.3', E3° 33" 29.2'
D	Mouth of Ogun river near Ikorodu	N6°36" 13.9', E3° 28" 35.8'
D2	Ikoordu	N6°36" 21.3', E3° 28" 47.9'
E	Palava Island	N6°30" 47.4', E3° 33" 41.4'
E2	East of Palava Island	N6°31" 38.5', E3° 33" 41.9'

Experimental

Sampling and Sample Preparation

Sampling locations (Fig. 1 & table 1) were selected based on accessibility, and areas close to or far from high municipal, shipping, and industrial activities. Sampling was carried out on 12 selected locations between February 2004 and May 2007.

Sediment samples were collected using a Van Veen Grab sampler operated from a speedboat at the depths of 0.5 - 10m. The samples were air-dried in aluminium wrapped trays for about a week, sieved through a 2mm mesh screen, and packed in 100ml amber glass bottles with aluminium sealed caps prior to soxhlet extraction. Moisture and organic carbon contents of the sediments were determined according to Lazar et al (1992). Sediment extraction was by soxhlet method (EPA method 3540C), using Acetone / Hexane (1:1) (v / v) as extraction solvent. Samples mixed with clean anhydrous sodium sulphate were extracted for 24 hours and extracts concentrated by rotoevaporation and back extraction was carried out where necessary, before florisil clean up of extracts. Sulphur cleanup was then carried out using activated copper for sulphur removal before GC analysis.

Sample Analysis

Sample preparation and analysis were performed at the analytical laboratory of the Great Lakes Institute for Environmental Research (GLIER), University of Windsor, according to the Canadian Association for Environmental Analytical Laboratories (CAEAL) requirements. The reference material used for sediment was NIST SRM 1944, with certified values for some PAHs, PCBs, and OCs. Sample extracts obtained after florisil cleanup were combined and rotoevaporated to approximately 2ml (or as appropriate) and analyzed for Polycyclic Aromatic Hydrocarbons (PAHs), Polychlorinated Biphenyls (PCBs) and Organochlorine pesticides (OCs) by gas chromatography [Hewlett-Packard (Avondale, PA) Model 5890/5970 Gas Chromatograph with a mass selective detector (quadrupole mass analyzer, 70eV) equipped with a Hewlett-Packard 7673A autosampler and a 30m x 0.25mm. I.D. X 0.10 µm DB-5 film thickness column] 1µl sample was injected using a splitless injection mode at 250^{O}C injection temperature and GC-MSD interface temperature of 280^{O}C.

Results and Discussion

The Organic carbon contents of the Lagos lagoon ranged between 0.28 and 28.02 (Fig. 3). The values compare well with the carbon contents of the sediments (ranging from 0.15 to 21.23 %) of the Gulf of Gdansk of the Baltic Sea reported by Pazdro, (2002). In Fig. 3, organic carbon contents of the lagoon sediments were high at locations A, B2, B3, C, C2, & D2 and they increased over the years, possibly as a result of regular organic inputs at these locations.

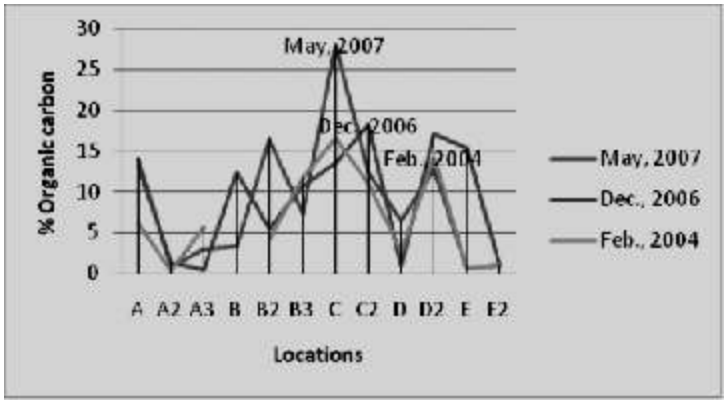

Fig. 3: Organic carbon content of Lagos lagoon between Feb., 2004 and May 2007

Low organic carbon contents were obtained at locations A2 (5 cowrie creek) and A3 (Lagos harbor) because of the nature of sediment (sandy) at those locations (see Fig. 2). Organic matter poor, sandy sediments are less contaminated than organic matter rich muddy sediments (Pazdro, 2002). The results obtained in the present work confirmed this statement, as the PBT levels were lowest at locations A2 (five cowrie creek) and A3 (Lagos harbor) even though these locations were within the areas of high anthropogenic activities, (Figs. 1, 2, 3 & table 2).

Table 2: Sum PBTs (ng/g) in Feb., 2004 to May, 2007sediments of Lagos lagoon

	Feb., 2004			Dec., 2006			May-07		
Locations	PAHs	PCBs	OCs	PAHs	PCBs	OCs	PAHs	PCBs	OCs
A	1093.06	1.96	10.41	647.84	214.05	8.13	1339.13	149.52	64.32
A2	149.99	0	0.26	46.23	4.32	0	85.95	0	0
A3	189.17	66.13	1.29	37.61	1.15	0	142.13	34.72	3.70
B				346.94	15.04	2.78	498.48	20.86	8.65
B2	118.26	1.43	7.61	287.22	27.76	12.72	113.97	0	0.83
B3	509.45	134.42	30.27	955.51	0.17	17.68	860.21	105.52	12.83
C	151.07	14.46	0	75.51	4.59	1.20	85.68	35.84	6.98
C2	70.24	4.21	0.37	104.79	2.09	23.72	170.10	6.71	3.71
D	670.13	0.13	0.66	286.03	3.73	22.05	4473.80	2.71	1.31
D2	198.41	41.25	5.33	352.35	2.61	15.03	207.46	17.01	0.49
E	3.46	0	1.27	28.65	0	4.14	2.20	0.04	0.45
E2	3.48	0.43	1.01	12.32	0.11	2.40	6.25	0	0.48

In Dec., 2006, the lowest total PAH concentrations, 12.32, 28.65, 37.61, and 46.26ng / g (Figs. 16 & 17, and table 2), were from East of Palava Island, Palava Island, (locations far from Urban activities), Lagos harbour (shipping and oil related activities), and 5 Cowrie creek (which are predominately sand) respectively. The organic carbon contents at these four locations in Dec., 2006 sediments were 0.96, 15.43, 0.42, 1.29%, respectively. PAHs and other nonpolar organic compounds are strongly associated with the organic fraction in sediments (Smith et al., 1998). Therefore, low total PAHs in high organic contents at locations far from urban activities agrees with the report by Van Metre et al., (2000), that the largest concentrations of PAHs generally are found in urbanized areas, where the potential sources include atmospheric deposition, surface runoff, municipal wastes, sewage effluents, industrial effluents, and spills and leakage of fossil fuels.

From Fig.4, the sum of the mean PBTs in Feb., 2004, Dec., 2006, and May 2007 reflected a steady increase (316.34, 383.41, and 705.17ng / g respectively).

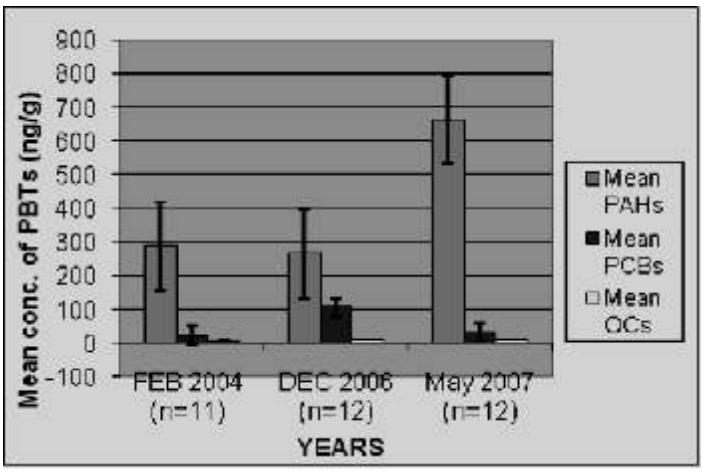

Fig. 4: Mean concentrations of PCBs in Feb., 2004, Dec., 2006, and May 2007 sediments

Comparing Fig. 4 (PBT levels) and Fig. 3 (organic carbon contents), same pattern of steady increase was observed in the sum of the % organic carbon contents of sediments in Feb., 2004, Dec., 2006, and May 2007 (61.81, 82.11, and 85.31%). This showed that the PBT levels increased with corresponding increase in organic carbon contents of the sediments within the study period. According to Drouillard et al (2006), organic carbon fraction also influences the partitioning capacity of the chemicals in the sediments. This was in agreement with the results obtained in Lagos lagoon (Figs. 3, 4, & 5).

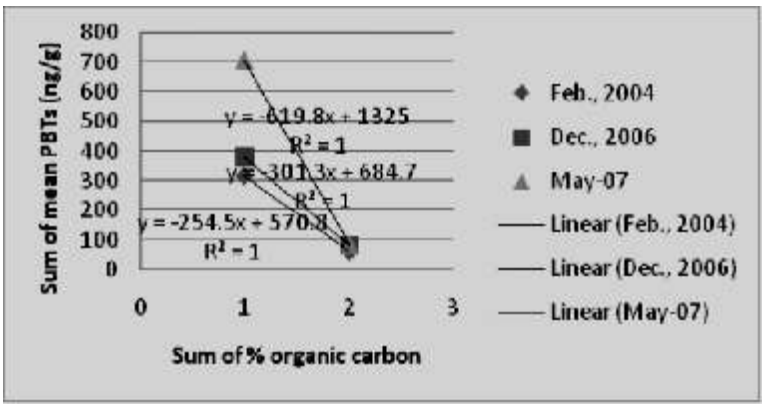

Fig 5: Correlation of organic carbon with PBTs in Lagos lagoon sediments

Very positive correlations (R^2=1) were observed between the total organic carbon contents and PBTs (PAH, PCB, OC) levels of the Lagos lagoon sediments, Fig. 5. This result compared well with the work of Pazdro, (2002), whose set of data from the study on Persistent Organic Pollutants in Sediments from the Gulf of Gdansk, yielded a positive correlation between total and individual PBTs levels and organic matter content (r>0.65). Sediment organic carbon content and grain-size distributions are main parameters influencing contaminants pattern and bioavailability (Pazdro, 2002). Evidence by Leeuwen et al (2007) suggests that the bioavailability of PBTs in sediments can be a function of different matrices (i.e., soil and organic carbon type) and time.

As shown in Fig. 2, variation in sediment type at different locations lead to a high variation in the organic carbon contents of the Lagos lagoon. To adjust for variations in organic carbon in sediment samples PBT concentrations were normalized with organic carbon. In Feb. 2004, carbon-normalized trends in total PAH indicated salient peaks at 5 Cowrie creek (A2), the mouth of Ogun River (D), and a little peak Okobaba (B3) (Fig. 6). In Dec., 2006, carbon-normalized trends in total PAH indicate salient peaks at the mouth of Ogun River (D), Lagos harbour near Marina (A3), and Okobaba (B3) (Fig. 7).

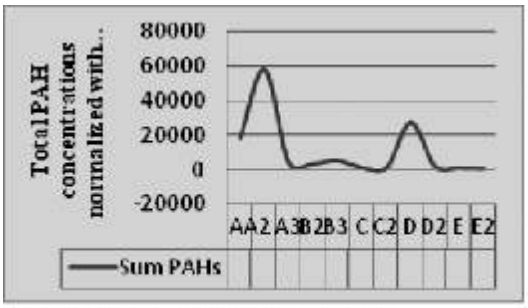

Fig. 6: Sum PAHs in Feb., 2004 sediment

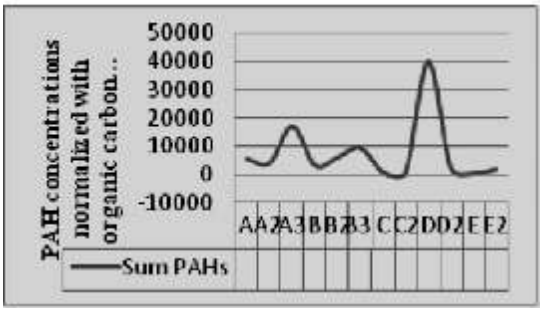

Fig. 7: Sum PAHs in Dec., 2006 sediments

In May 2007, carbon-normalized trends in total PAH indicated salient peak at the mouth of Ogun River (Fig. 8). A regular growth of total PAH input was noticed at the mouth of Ogun River from Feb., 2004, through Dec., 2006 to May 2007 (Figs. 6, 7 and 8). This reflected additional PAH inputs from intervening urban development.

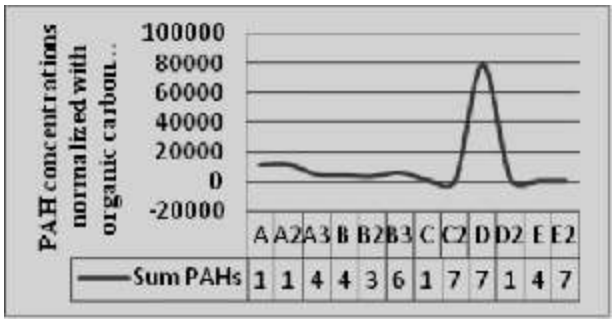

Fig. 8: Sum PAHs in May 2007 sediments

This was in agreement with the report by Kowalewska et al (1997) which showed that in coastal areas, direct deposition of atmospheric PAHs may be relatively minor compared to fluvial inputs, but in open ocean areas it can dominate.

For total PCBs, prominent peaks were obtained at Okobaba and Lagos harbour (Fig. 9) in Feb., 2004; at Iddo, Ibesse & Offin, Mouth of Ogun River, and Lagos harbour (Fig. 10) in Dec., 2006; and at Iddo, Lagos harbour, Okobaba, and Ikorodu (Fig. 11) in May 2007.

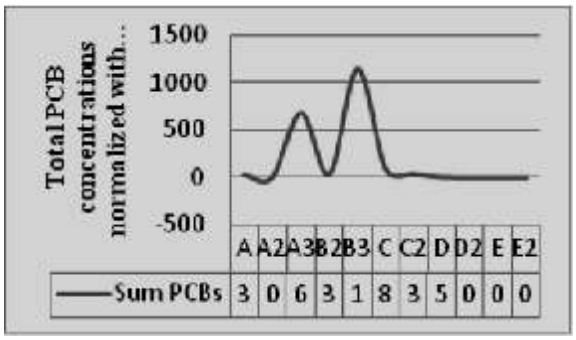

Fig. 9: Sum PCBs in Feb., 2004 sediments

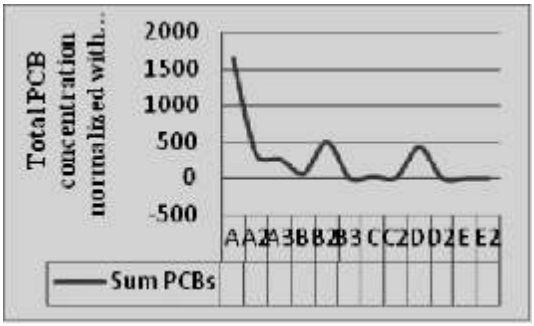

Fig. 10: Sum PCBs in Dec., 2006 sediments

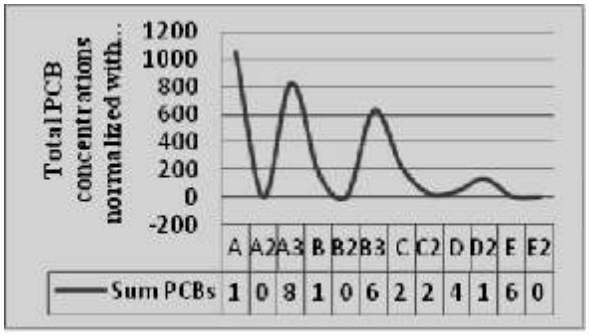

Fig. 11: Sum PCBs in May 2007 sediments

Total PCB was most pronounced at Iddo (Fig. 9, 10, & 11), and so Iddo contributed more PCBs than the other locations.

Ocs were found to spread and also increase in concentrations across the different locations on the lagoon from Feb., 2004 to Dec., 2006. A tremendous decrease was observed by May 2007, (Figs. 12, 13 & 14) though an increase was noticed at Iddo.

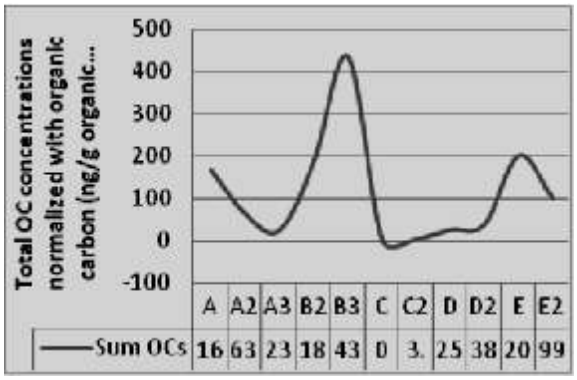

Fig. 12: Sum OCs in Feb., 2004 sediment samples

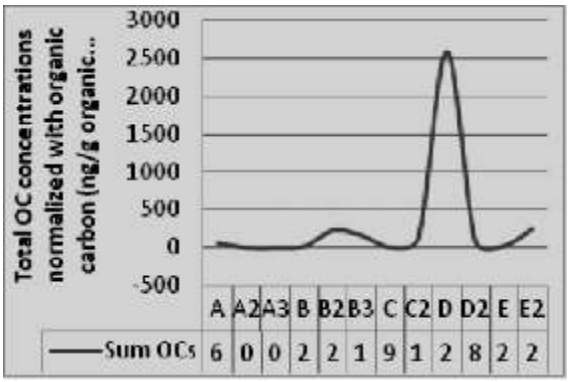

Fig. 13: Sum OCs in Dec., 2006 sediment samples

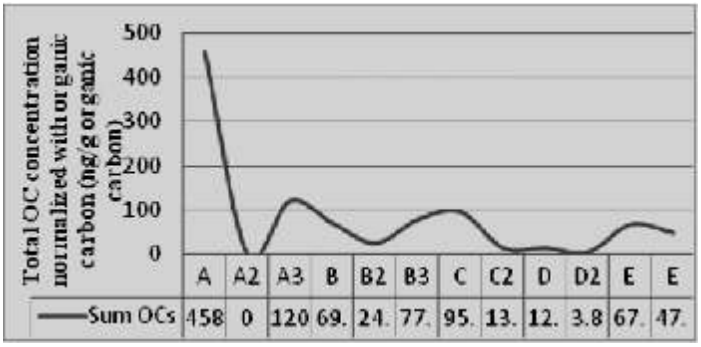

Fig. 14: Sum OCs in May 2007 sediments

Total OCs were found to be contributed from almost all the locations and their concentrations also increased over the time, due to the pattern of use. This agreed with Mackay et al (1997) which stated that one of the factors responsible for variation in the concentrations of OCs in the environment is the pattern of use. Different locations seemed to use OCs in varying concentrations in the different years. In Feb., 2004, two slum settlements, Ilaje community by Unilag lagoon front (B2) and Okobaba (B3) used more OCs. In Dec., 2006 Ikorodu community near location D (Mouth of Ogun River) used OCs most, but in May 2007, Iddo community used it most.

A direct relationship therefore was found to exist between the hydrophobicity of PBTs and the affinity for binding to dissolved humic material. So in agreement with Gobas et al (2004), the sediment partition coefficient (Kp) for PBTs was directly related to the organic carbon content of the sediment.

Conclusions

PBT levels increased with corresponding increase in organic carbon contents of the sediments within the study period. Very positive correlations (R^2=1) were observed between the total organic carbon contents and PBTs (PAH, PCB, OC) levels of the Lagos lagoon sediments. PBT and organic carbon contents were high at locations close to high human activities. Therefore it can be concluded that heavy loads of organic wastes, which result in high concentration of very toxic organic micro pollutants, are increasingly being generated and introduced over time into the Lagos lagoon, where the people of Lagos and its environs depend upon as their major source of sea foods.

Recommendations

The author's recommendations the Great Lakes Institute for Environmental Research (GLIER), University of Windsor, Ontario, Canada for provision of facilities and the University of Lagos, Nigeria for the study leave to Mrs. Rose Alani to visit Canada.

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