

LEVELS OF POLYCHLORINATED BIPHENYLS RESIDUES IN WARRI RIVER NIGERIA

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ABSTRACT

Sum of individual PCBs congeners in surface water and sediment samples from Warri River system, a coastal river of Niger Delta, Nigeria were measured between March and June 2003. Specific individual PCBs analysis was by HPGC series 6890. Mean concentrations of Σ PCBs in surface water samples ranged from $0.35\mu\text{g l}^{-1}$ (Tori Creek) to $1.30\mu\text{g l}^{-1}$ (Crawford Creek). Sediment samples had higher levels ranging from 2.00ng g^{-1} (Tori Creek) to 7.00ng g^{-1} (Crawford Creek). Null hypothesis of normality was rejected at $p>0.05$ indicating significant difference between the matrices. Concentrations of PCB were compared with ecotoxicological benchmarks and regulatory guidelines to determine potential concern for effects on aquatic life and human health. Measured mean concentrations in surface water and sediments samples from Crawford creek station indicated concern for environmental and public health because of their exceedence of the US EPA PCB limit for drinking water ($0.0005\mu\text{g l}^{-1}$) and water quality criteria for chronic exposure (79pg l^{-1}) through drinking water and fish ingestion.

KEYWORDS: PCBs, Water, Sediment, Hazard, and Warri River.

INTRODUCTION

Polychlorinated biphenyls, a well - known environmental contaminant present in matrices such as air, water and soil, (Fisher et al 2003). Was first manufactured in the 1950s for use in electrical insulators, politicizes and carbonless copy paper (Mayes et al 1998). Although the production was banned in the United States in the 1970s, they are resistant to natural degradation process and so persist in the environment. About 209 individual congeners exist each distinct in its configuration of chlorine molecules attached to the biphenyls rings (Safe, 1994; Connell et al 1996). Polychlorinated biphenyls cause a variety of adverse health effects to humans and wildlife. Accidental exposure or consumption of PCB's contaminated fish have been reported to alter endocrine immune and nervous system particularly in developing children (Sher et al, 1998; Patandin et al 1998; Faroon et al, 2001 and Gore, 2001) In wildlife including amphibians, fish and birds PCBs reduce several and alter reproductive system function (Bowerman, 2000; Femi et al 2001; Fisher et al 2003)

Environmental baseline studies of Warri River, its creeks and selected ponds of Warri catchments started in 1981, and so predate most baseline and impact assessment investigation of the multiple oil companies operating in the western Niger Delta (Egborge 2001). These studies concerned aspects of the physico - chemical, (Atuma and Egborge, 1986; Egborge 1991), phytoplankton (Opute, 1990, 1991), zooplankton (Chigu, 1987; Egborge and Tawari, 1987; Gabriel 1986), benthos (Olumukoro, 1996) fishes (Tetsola, 1988; Tetsola and Egborge 1991; Ezemonye, 1992; Agada, 1994). Studies on waters sediments and fish of the main channel and creeks of Warri River in latter years (1992 - 2000) confirmed the creeks as breeding nursery and feeding grounds of many Warri River species.

Studies on status of organic contaminants in the aquatic environment are virtually non - existence in Nigerian Niger Delta ecological region. The absence of data on the levels of PCBs in the water, sediment and biota of Niger Delta water bodies is therefore critical, considering the fact that PCBs are persistent and bioaccumulative in fatty tissues of organisms causing adverse effects. This gap in information has affected the formulation of benchmark levels (acceptable limit) of organic contaminants in the waters, sediment and

biota in Nigeria Rivers. Site specific hazard evaluation requires knowledge of the pollutants concentrations, potential to spread and its distribution in surface water and sediment of Warri River and its tributaries. This is with a view to assessing potential ecological and human hazard using known ecotoxicological benchmarks.

DESCRIPTION OF STUDY AREA

Warri River

The study area is Warri River of western Niger Delta ecozone, which is made up of fresh, brackish, and marine environment. The sampling stations were chosen to reflect the upstream and downstream status of the rivers; it was also selected along the areas of possible sources of pollution. The need to incorporate oil/gas based and non - oil/gas activities and possible control sites guided the rationale for the selection of the River stations. Three sampling stations were chosen based on the result of the heavy metal pollution given by Atuma & Egborge (1986), Ezemonye, (1992) and pollution studies on Western Niger Delta (NDES 1998). The stations were chosen along the main river course upstream at Agbarho including two major downstream creeks that are interconnected with the river (Tori and Crawford).

Agbarho is the upstream station, which acts as the control station for the Warri River Stations. The water in the area is relatively undisturbed, as industrial and transportation activities are almost non existent in the area.

Tori creek located between latitude $5^{\circ}30'$ 20N and longitude $5^{\circ}43'$ E is one of the principal creeks of Warri River. The creek drains Nigeria National Petroleum Corporation (NNPC) housing estates, Refinery and Petrochemical complexes.

Other establishments and activities in this catchments area are, Saipen and Snaprogetti housing estates, movement of large vessels such as ships, speedboats and barges often docking adjacent to the chevron oil company (Gulf oil company). Wastewaters containing film of petrol and oil were common contaminants observed in this area.

Crawford Creek

The best known and utilized of the creek is Crawford creek whose confluence with Warri River lies between the NNPC jetty and NPA port. This creek drains much of the

downstream swamps carrying effluents from Ifie, Ubeji, Tori, and Ekurede – Urhobo creeks within the Warri metropolis. Notable companies around this station are SPDC industrial

and residential areas, which discharged effluents into the creeks. Visible commercial and recreational transportation activities occurred here.

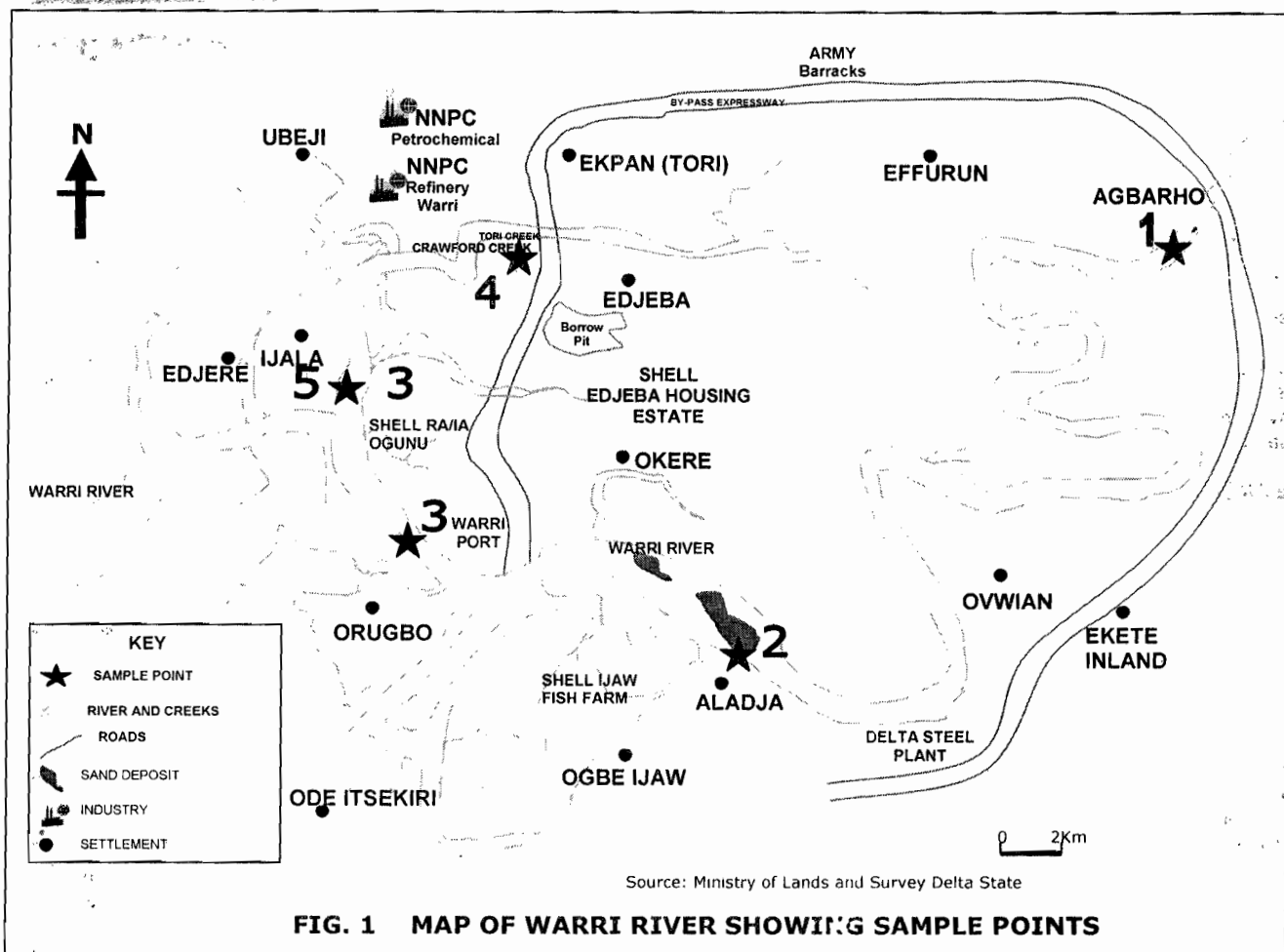


FIG. 1 MAP OF WARRI RIVER SHOWING SAMPLE POINTS

MATERIALS AND METHODS

All samples were collected in pre – cleaned glass bottles between March – June, 2003 from all the designated stations. They were analyzed at Global Environmental Laboratory, Facodes, Nigeria (Certified by Directorate of Petroleum Resource (DPR), Federal Ministry of Environment, Shell Thornton, and ISO 9001 complaint).

Water samples were collected from less than 1 meter below the water surface using hydrobios water sampler while the were collected with van – veen grab. All samples analyses were performed using a high performance (temperature – programmed) gas chromatograph (HPGC, Hewlett – Packard, 6890 series serves with auto sampler). Following liquid: liquid extraction into acetone (for aqueous samples) and liquid: solid extraction into mixture of pentane and acetone (for solid samples). Further details of the method of extraction, clean up, concentration, fractional separation and GC analysis are described elsewhere (Duinker and Hillerbrand 1978; Boonet al 1985; Labunska et al 2000 and Blais et al 2003). As part of the QA/QC protocol, duplicate samples were collected and analyzed. Chemical blanks were run in parallel with all

samples and recovery test were perform using distilled water. Also during sampling, the samples and bottles were closed to outside contamination. Extreme precaution was taken to minimize, if not eliminate the introduction of contaminants.

ΣPCBs (Sum polychlorinated biphenyls) were calculated from the sum of 8 individual congeners. These congeners were selected on the basis of their predominance in commercial PCBs mixtures and both biotic and abiotic matrices. Amongst other considerations, congener specific data are essential ecotoxicological tool for PCBs evaluations in the aquatic environment (Harrad et al, 1994).

Statistical Analysis

Null hypothesis of homogeneity was tested using SPSS (Excel) Statistical package. Assessment of potential Ecological and Human Health hazard was done by comparing measured values with pre – determined regulatory ecotoxicological benchmark (Moraes et al, 2003).

RESULT

Mean concentrations of ΣPCBs from surface water and sediment samples from three stations (river channel and creek) were analyzed. The results are presented in Table 1 with further illustrations in fig 2 – 9.

Table 1: Concentrations of ΣPCBs (8 Congeners in Water (µg l⁻¹) and Sediments (ng g⁻¹) of Warri Rivers.

Stations	Water	Sediment			SE	Range	source	
		Mean± SD	SE	Range				
Warri River	Agbarho	0.43±0.43	0.2175	ND-1.00	2.13± 1.05	0.5258	0.80 – 3.30	“
	Tori Ck.	0.35± 0.13	0.0645	0.20 –1.40	2.00 ± 1.66	0.9563	0.40 – 3.70	“
	Crawford Ck	1.30± 1.76	0.8822	0.20 –3.90	7.00±5.45	2.724	0.70 – 13.30	“

PCBs in Surface Water

Concentration of ΣPCBs in surface water varied in time and space as shown in fig 2. The values varied from ND µg l⁻¹ - 1 µg l⁻¹ (Agbarho), 0.2 – 0.50 µg l⁻¹ (Tori creek) to 0.2- 3.90 µg l⁻¹ (Crawford creek).

The highest levels were observed in the month of May, 3.9 µg l⁻¹ (Crawford creek) while the lowest was reported in June ND (Agbarho). The mean levels showed order of concentration in decreasing order as follows: **Crawford creek (1.30) > Agbarho (0.43) > Tori creek (0.354)**. The months of May had high PCBs concentrations in most stations compared to other months (fig3).

The pattern of PCBs congeners in surface water from Warri River System shown in fig 3 – 5 was dominated by PCB 98, PCB 171 and PCB 5 (penta, hepta and di-

chlorobiphenyls). Similar observations have been reported for Ethiopie and Benin Rivers of western Niger Delta (Ezemonye, 2004). Figure 4 showed that in Agbarho, PCB 171 (hepta chlorobiphenyls) dominated accounting for 58.82%, closely followed by PCBs 5 (di chlorobiphenyls) and PCB 98 (penta – chlorobiophenyls) both accounting for 35.29%. In Tori creek PCB 5 was the predominant PCB congener accounting for 54.14% and 35.71% for PCB 171. While PCB 98 accounted for 90.30% in Crawford creek. (Figs 5 and 6).

Of the eight congeners analyzed PCB 1 (chlorobiphenyls), PCB 29 (trichlorobiphenyls), PCB 47 (tetra chlorobiphenyls) and PCB 201 (octochlorobiphenyls) were not reported in the surface water samples. Crawford creek contributed for 32.62% of the ΣPCB congener concentrations in the entire Warri River system.

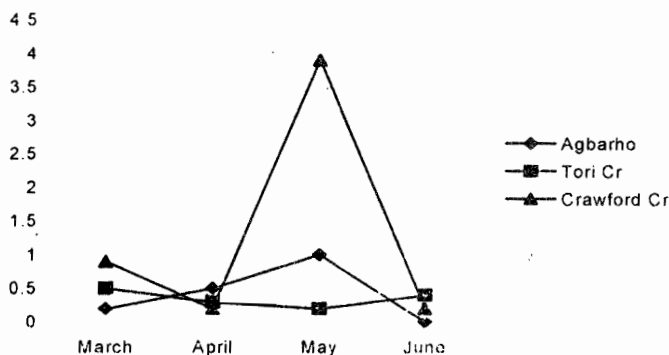


Fig. 2: Monthly and Spatial Variations in Surface Water PCBs Concentration in Warri River

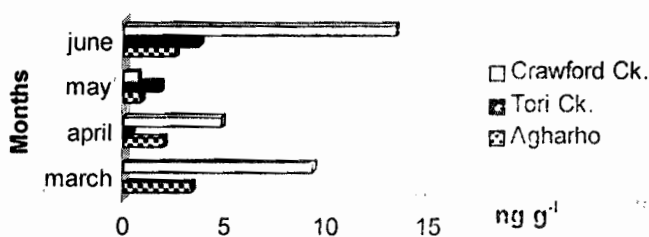


Fig. 3: Monthly and Spatial Variations in Sediment PCBs Concentration in Warri River

WARRI RIVER STATIONS (SURFACE WATER SAMPLES)

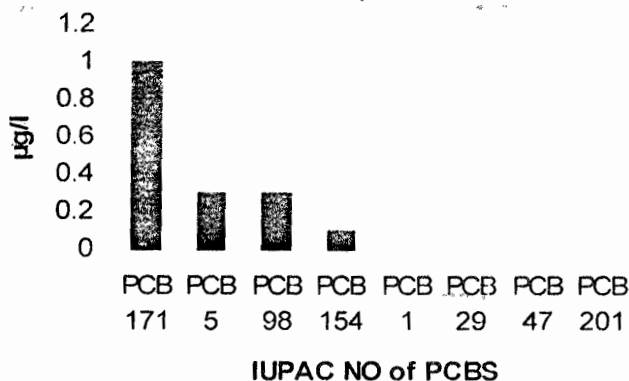


Fig. 4: Distribution of 8 individual Congeners in Surface Water from Warri River at Agbarho station

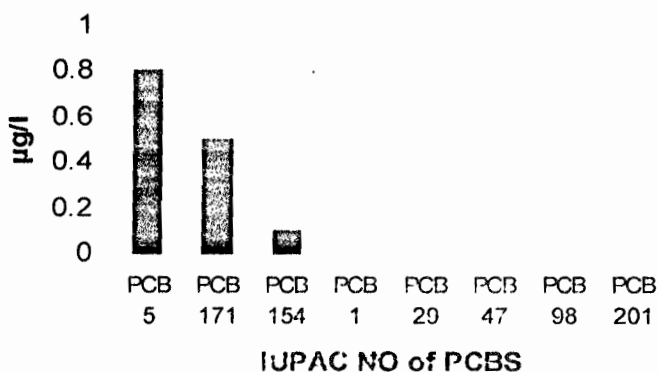


Fig. 5: Distribution of 8 individual Congeners in Surface Water from Warri River at Tori Creek Station

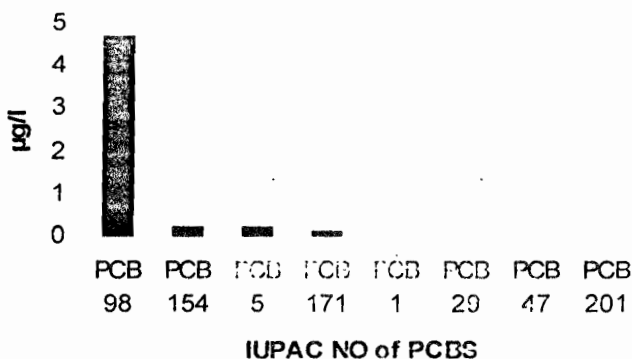


Fig. 6: Distribution of 8 individual Congeners in Surface Water from Warri River AT Crawford Creek Station

PCBS in Sediment

Contaminant levels in sediment usually give a true reflection of status of contamination, because they are known to act as sink to pollutants. Mean values reported for sediment samples were higher than surface water levels and ranged from 2.0ng g⁻¹ (Tori creek),

2.13ng g⁻¹ (Agbarho) to 7.00ng g⁻¹ (Crawford creek). The highest levels were observed at Crawford creek (13.3ng g⁻¹) in June while the lowest was at Tori creek (0.4ng g⁻¹) in April. Hypothesis of normality was rejected for ΣPCBs level in water and sediment suggestive of significant difference between the matrices at p>0.05.

Varying congener configurations were reported in figs 7- 9. In the entire Warri river system (channels and Creeks combined) PCD 98 dominated, accounting for 73.82%. At Agbarho, it account for 61.18%, 44.06% in Tori and 83.92% in Crawford creeks. Again as earlier observed in surface water PCB 1 and

PCB 29 was not reported in all stations. PCB 5 accounted for about 15.33%, while other congeners accounted for the remaining 10.84%. Crawford creek contributed 66.03% of total PCBs congener's concentrations in the Warri River system.

WARRI RIVER STATIONS (SEDIMENT SAMPLES)

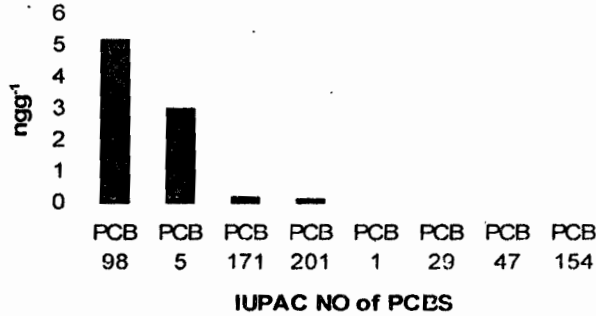


Fig. 7: Distribution of 8 individual congeners in Sediment form Warri River at Agbarho Station

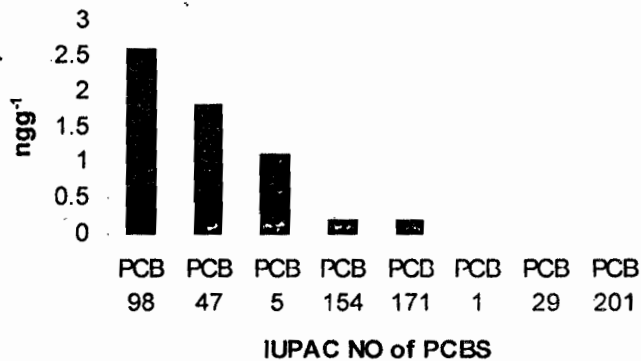


Fig. 8: Distribution of 8 individual congeners in Sediment form Warri River at Tori Creek Station

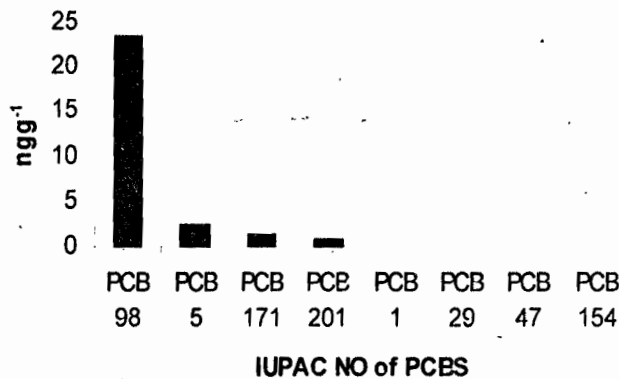


Fig. 9: Distribution of 8 individual Congeners in Sediment form Warri River at Crawford Creek Station

DISCUSSION

PCBs residues were detected in surface water at all studied sites in the western Niger Delta, Nigeria, which further

supports the ubiquitous and cosmopolitan nature of PCBs (Harrad et al, 1994, IEM, 1995; Bavel, 1996). The study did not reveal marked differences in concentrations between upstream and downstream stations, which were characterized by

industrial activities on the banks of the rivers. PCBs have been known to occur in remote areas devoid of industrial activities (IEM, 1995, UNEP, 1999). Similar observation was reported in this study. Relatively high mean concentrations of PCBs were found in Agbarho station a town with no major industrial activities or human settlements are present, indicating that sources of contamination is not restricted to point source discharges only.

Possible sources of contamination are through aerial transport from coastal industrial regions where industrial activities are intense as shown in Tori and Crawford Creek catchments. Other sources include storm runoff from streets, parking lots, automobile stations and farmlands (Ezemonye, 2003, 2004). Large amount of PCBs are released into the environment through improper disposal practices of municipal and industrial wastes, accident, from industrial facilities and leaching from contaminated landfills, these often end up in rivers (Fielder, 1997, Moraes *et al*, 2003).

A lower level of PCBs observed in surface water compared to the sediment samples concentrations is expected. PCBs have very low solubility in water, (Hutzinger *et al* 1974). They usually get bound to suspended particles in water and settle to the bottom, therefore accentuating the sediment concentrations. In aquatic environment, the high lipophilicity of PCBs causes their compounds to partition out of water and become preferentially absorbed to sediment (ATSDR, 2000). Consequently sediment concentrations are much higher than the overlying waters.

Higher levels of PCBs were observed in surface water and sediment samples from the coastal station at Crawford creek. Crawford creek drains much of the down stream swamps carrying effluents from industrial and residential areas which explain the reason for the higher PCBs levels in the samples from the station. This observation is supported by the study of Philips 1995, which reported that levels of PCBs decreased with distance from the sea. The present study indicated that coastal water stations had high PCBs levels probably because of the magnitude of industrial activities taking place in the region. Generally, the stations studied seem to show possible active loading of PCBs from atmospheric precipitation, poorly maintained toxic dumpsites, municipal landfills, and runoffs from industrial areas and agricultural farmlands. Sediment contamination arising from previous oil spillage in the study catchments has been reported (Egborge, 2002; Ezemonye, 2004).

High wet season values observed could be presumably due to increased resuspension, erosion and transport of PCBs associated with municipal runoff. Prevalence of pesticides, aerosols and agricultural additives are applied seasonally. These sources are not themselves generators of PCBs; rather they are merely conduits of PCBs that have been inadvertently, or deliberately introduced into the environment. Significantly more PCBs (up to 60 times) enter the rivers during wet season than during dry season. The study region, which is known for oil exploration and exploitation activities, has often experience frequent oil spills, blows – outs and discharge of untreated oil effluents into water bodies, some of which serves as the only source of drinking water (Ezemonye, 1992, Egborge, 2001, 2002; Onu 2003).

The presence of the di – through to octa – chlorinated benzenes suggest the possibility of varied sources of contaminations. Di-through to penta - chlorinated benzenes have been manufactured as chemical intermediates for the preparation of other chlorinated chemicals, and in some cases as pesticides and deodorizing chemicals (Labunska *et al*, 2000). The presence of the di-through to penta-chlorinated biphenyls in the water and sediment however is not suggestive of a particular industrial source. The dominance of PCBs 98 (Penta-chlorinated biphenyls) in sediment samples is remarkable and probably not unconnected with the fact that it is commonly used as solvents in PCB formulations (Labunska *et al*, 2000). Because of its dominance, PGB 98 is recommended for use as marker of exposure for other PCBs in the river studied.

A comparison of the concentrations of PCBs in this study with those of other Nigerian inland and coastal waters (Table 2) leads to the conclusion that the coastal Warri River in western Niger Delta is more contaminated with PCBs than the water bodies in other regions to the magnitude of five to ten times. This may be attributed to the high – level industrialization and commercial activities taking place in the region. Natural and anthropogenic changes are taking place in the western Niger Delta ecozone resulting from coastal zone modification, upstream dam construction, urban growth, deforestation, agriculture, fishing, industrial development and the exploitation of natural resources, principally oil and gas operations both onshore and offshore, as well as population pressure (Egborge, 1991; Onu 2003).

Table 2: Comparison of PCBs Levels in Nigerian Inland and Coastal Waters (Water $\mu\text{g l}^{-1}$ and Sediment ng g^{-1})

Location /Water type	Water	Sediment	References
River Ogun	0.087 (ND-0.241)	Not Determined	Agunloye 1984,
River Imo	0.121 (ND-0.241)	-	"
Cross River	0.120(ND-0.470)	-	"
Ikwa Ibom	0.330 (ND-1.000)	-	"
River Ogunkpa	Not Determined	ND	Sunday 1990
River Ona	-	ND	"
River Onifere	-	0.004(ND-0.014)	"
Warri River	1.00(ND-3.90)	4.28(0.40-13.70)	This Study

Regulatory values used in evaluating the potential concern of the effects of PCBs on aquatic life and human health are a combination of multiple endpoints. They are intended to protect aquatic species and human health within acceptable confidence limits (Europeans community 1992, Erickson 1997,

Ministerio da Sau'de 2000, Moraes et al 2003). All stations had HMEC, which exceeded USEPA recommended limit of 0.0005ppm, and the Water Quality Criterion for PCBs chronic exposure through drinking water and fish consumption (table 3).

Table 3: Comparison of highest measured environmental concentrations (HMEC) of PCBs in surface water sediment with Guidelines for preservation of Aquatic Life (GPAL), Drinking Water Quality standards (DWQS), Recreational Water Quality Standard (RWQS) and Irrigational Water Quality Standard (IWQS) All concentrations in $\mu\text{g l}^{-1}$ $\mu\text{g g}^{-1}$

PCBs Congeners	HMEC in River Stations		GPAL Crawford Cr.	DWQS (Suter, 1996; TSDR, 2003 and Moraes, et al. 2003)	RWQS	IWQS
	Agbarho	Tori Cr.				
Sum of PCBs Congeners in surface water samples	1.0	1.4	3.9	0.1	0.5	0.5
Sum of PCBs Congeners in Sediment samples	3.3	3.7	13.3	0.02		

CONCLUSION

This study presents the first site – specific data on PCBs contamination in Warri River of Niger Delta, Nigeria. The observation in this study indicates that current industrial activities, poorly managed municipal solid wastes and absence of any regulatory restriction on PCBs levels in the environment may have a profound effect on aquatic life and human health. This is because the levels of highest measured environmental concentration of PCBs in surface water and highest measured environmental concentration of PCBs in surface water and sediment samples exceeded USEPA regulatory concentrations for drinking water demonstrating a problem for human health. The observation in this study also suggests that aquatic organism in the studied stations may be exposed of PCBs contamination in water or bound suspended particles or sediments.

The highest measured concentrations, which exceeded **US EPA, GPAL, RWQS and IWQS** (Suter, 1996; ATSDR, 2003 and Moraes. *et al* 2003) indicate concern for the preservation of aquatic life.

Ecological risk levels may increase since these organisms may be exposed to toxicological synergetic and additive interactions of PCBs and other related contaminants such as PAH and Heavy metals stemming from increased industrial activities (oil and gas exploration and exploitation) (Edema, 1994; Egborge, 1991, 2002 ; Moraes *et al* 2003; Onu 2003). Finally, logistics difficulties have limited the number of samples available in this study and further sites – specific studies in the region including time series and effect of PCBs at different level of biological organization are recommended in order to develop regulatory values indigenous to African region.

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