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# Assessment of the levels of polychlorinated biphenyls in sediments of new Calabar River, Niger Delta Region, Nigeria

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**Abstract**. The concentrations of polychlorinated biphenyls (PCBs) in sediment samples from the New Calabar River in the Niger Delta Region of Nigeria were determined. Grab sediment samples were collected from five stations in the river and analyzed for individual PCB congeners using gas chromatography – mass spectrometer. The $\sum_8$PCB (sum of eight congeners) identified in the samples ranged from 0.21 to 2.16 mg/kg. Congener 105 and 194 were the most and least abundant with 34.65 % and 2.46 % respectively. The lower chlorinated congeners (below PCB 101) were prominent with 54.68 % of the total PCBs concentration in the sediments. The results of this study should make PCBs contaminants of grave concern in the Niger Delta Region.

*Keywords*: sediments, New Calabar River, Niger Delta, polychlorinated biphenyls, congener.

## 1. Introduction

Polychlorinated biphenyls (PCBs) are persistent organic pollutants with significant bioaccumulation potentials in environmental systems. They are a worrisome group of persistent organic pollutants (POPs) due to their specific characteristics such as low degradation rates in the environment, potential toxicity to organisms and the capacity for bioaccumulation. Some of the most known POPs are the PCBs, which are a class of 209 congeners, each of which consists of two benzene rings and one to ten chlorine atoms [1]. They are synthetic compounds, used as coolants and insulating fluids in the production of transformers and capacitors. They are also used as hydraulic fluids, plasticizers, additives in paints, adhesives, lubricants, plastics, and pesticides [2-4].

Exposure to PCBs has been linked to cancer, cardiovascular disease and neuropsychological malfunction in children, reproductive impairments and endocrine disruption [5-8]. The level of toxicity exhibited by each PCB congener is a function of the pattern of chlorine substitution [9]. Environmental occurrence of persistent organic pollutants is a global problem. They are produced and temporarily washed down the aquatic environment over time where they subsequently end up in ports, estuarine and coastal sediments including in regions where they have never been used or produced [10, 11]. Although the production, usage and disposal of PCBs have been regulated or prohibited in most developed countries, PCBs are still used in many developing countries. Sources into the marine environment include destruction and disposal of industrial plants and equipment or from emissions and leakages from construction materials and old electrical equipment [12, 13].

The New Calabar River is among the important water resources in the Niger Delta region of Nigeria. It is a significant water source for agricultural, recreational and domestic purposes. The river is also subjected to municipal runoffs and effluent discharges from industries including from oil and gas related activities in the region; yet only a few environmental studies have been conducted on PCBs in the Niger Delta due to much focus on petroleum hydrocarbons [14-16]. This is not surprising as the region suffers from perennial environmental negligence resulting from drilling, production and refining of crude oil as well as industrial use of petroleum products [17-20]. Hence, the aim of this study is to determine the levels of concentration of PCBs in sediment samples from New Calabar River in the Niger Delta region of Nigeria.

## 2. Experimental

### *2.1. Study area*

The entire New Calabar river course is situated between longitude 7°60'E and latitude 5°45'N in the coastal area of the Niger Delta and empties into the Atlantic Ocean. The river is subjected to municipal runoffs and effluent discharges from industries including discharges from crude oil exploration. There are markets, slaughter houses, municipal waste

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disposal and incineration points along the banks of the river. Dredging, fishing and recreational activities also occur in the river. The river once served as a ship construction yard and is presently littered with abandoned ships and boats.

***2.2. Sample collection***

Sediment samples were collected from five different stations using a Van-Veen grab sampler. At each station, samples were collected from three points across the river and then thoroughly mixed to form a composite sample. The samples were packed in ice boxes and stored at 4 °C until analysis. Samples were air-dried at ambient temperature, ground with porcelain mortar and pestle and passed through 0.5 mm sieve.

***2.3. Extraction***

Sediment samples (2 g) were separately weighed into glass bottles and 20 ml hexane was added to each glass bottle for extraction. Glass bottles with contents were placed in an ultrasonic shaker for 1 hour. The process was repeated twice; after which the extracts were pooled and concentrated to 2 ml using a rotary evaporator. Clean up of extracts was done using column chromatography. Packing of the column was done using the slurry method and silica gel (130-270 mesh) as stationary phase.

Table 1. GPS coordinates of the sampling stations.

| Samples | Coordinates |
|---|---|
| Sample A | Latitude: 4.8872<br>Longitude: 6.8924 |
| Sample B | Latitude: 4.8921<br>Longitude: 6.8988 |
| Sample C | Latitude: 4.8842<br>Longitude: 6.8936 |
| Sample D | Latitude: 4.8892<br>Longitude: 6.8985 |
| Sample E | Latitude: 4.8979<br>Longitude: 6.8999 |

The concentrated extract was introduced into an already packed 15 cm × 1 cm glass column and eluted with 30 ml dichloromethane (DCM) to obtain the fraction containing the PCBs. The fractions were concentrated to 2 ml using a rotary evaporator and then analyzed using gas chromatography – mass spectrometer (GC-MS). Concentrations of PCBs in the fractions were monitored with Agilent 7820A gas chromatograph equipped with Agilent 5975 series mass spectrometer detector (MSD). A fused - silica capillary column (30 m × 0.25 mm × 0.25 μm) was used for the quantification. The oven temperature was programmed from an initial temperature of 50 °C (1 min) to 290 °C at the rate of 10 °C min$^{-1}$ and was maintained at 290 °C for 20 min. Helium was used as the carrier gas. PCBs concentrations were determined through comparison of the retention times of the chromatographic peaks of the samples to the external standard solution. Compound identification was confirmed with the MSD in SIM mode (scan range 40 – 350 amu). Concentrations of individually resolved peaks were summed to obtain the total PCBs concentration in each sampling station.

***2.4. Quality Control***

The quality control procedures included the analysis of the reference materials and procedural blanks. The results of the reference materials were within the certified range for the representative PCBs.

## 3. Results and discussion

The analyzed sediment samples from the New Calabar River showed the presence of eight PCB congeners: 2-chlorobiphenyl (PCB 1), 2,3-dichlorobiphenyl (PCB 5), 2,2',5 - trichlorobiphenyl (PCB 18), 3,3',4,4' - tetrachlorobiphenyl (PCB 77), 2,3,3',4,4' - pentachlorobiphenyl (PCB 105), 2,3,3',4,4',5 - hexachlorobiphenyl (PCB 156), 2,3,3'4,4'5,5' - heptachlorobiphenyl (PCB 189) and 2,2',3,3',4,4',5,5' - octachlorobiphenyl (PCB 194) (Table 2) [21]. The total PCBs obtained from all sampling stations were higher than the recommended sediment quality guidelines for the protection of aquatic life [22]. They were also higher than results obtained from similar studies of different locations in the Niger Delta Region [14-16]. The $\sum_8$PCB concentration ranged from 0.21 to 2.16 mg/kg. Congener 105 and 194 were the most and least abundant with 34.65 % and 2.46 % respectively (Figure 1).

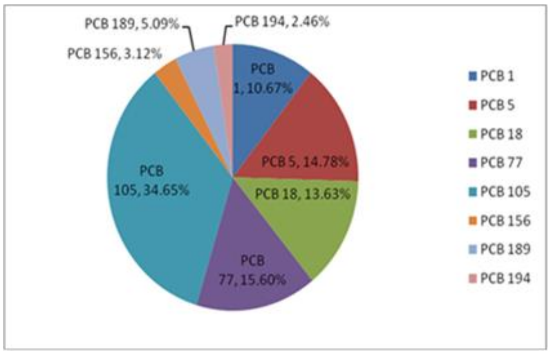


Figure 1. Percentage contribution of each congener to the total PCBs in the sediments.

The lower chlorinated congeners (below PCB 101) represented 54.68 % of the total PCBs concentration in the sediments. The dominance of lower chlorinated congeners suggests that there are no significant local sources of the PCBs. This may be because lower chlorinated PCBs are usually transported to a further distance from the source than the highly chlorinated PCBs [23]. It may also be as a result of depletion of the higher chlorinated congeners [11, 24]. It is important to note that congeners 105, 156, and 189 identified in these samples are among the most toxic PCB congeners known as the dioxin-like PCBs (DL-PCBs) [25]. The presence of PCBs in the sediments of the New Calabar River may be due to wastes dump as well as the industrial and shipping activities within the vicinities of the river. PCB 105, which is the most prominent PCB congener in this study has been implicated as a derivative of paint additives [26]. Other PCB sources include incinerators, indiscriminate disposal of solid and liquid waste, industrial discharge, human faeces and runoffs from market [9, 13].

Table 2. PCB concentration in the sediments of New Calabar River.

| PCBs | Mass to charge ratio | PCBs concentration (mg/kg) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Sampling sites | | | | | ∑PCBs |
| | | A | B | C | D | E | |
| PCB 1 | 188 | 0.01 | 0.11 | 0.21 | 0.21 | 0.11 | 0.65 |
| PCB 5 | 222 | 0.08 | 0.12 | 0.20 | 0.28 | 0.22 | 0.90 |
| PCB 18 | 256 | 0.05 | 0.05 | 0.23 | 0.25 | 0.25 | 0.83 |
| PCB 77 | 292 | 0.07 | 0.07 | 0.27 | 0.27 | 0.27 | 0.95 |
| PCB 105 | 326 | ND | 0.01 | 1.00 | 0.10 | 1.00 | 2.11 |
| PCB 156 | 360 | ND | 0.01 | ND | 0.10 | 0.08 | 0.19 |
| PCB 189 | 394 | ND | 0.02 | 0.01 | 0.09 | 0.19 | 0.31 |
| PCB 194 | 428 | ND | 0.01 | 0.09 | 0.01 | 0.04 | 0.15 |
| **$\sum_8$PCB** | | **0.21** | **0.40** | **2.01** | **1.31** | **2.16** | **6.09** |

ND: Not detected

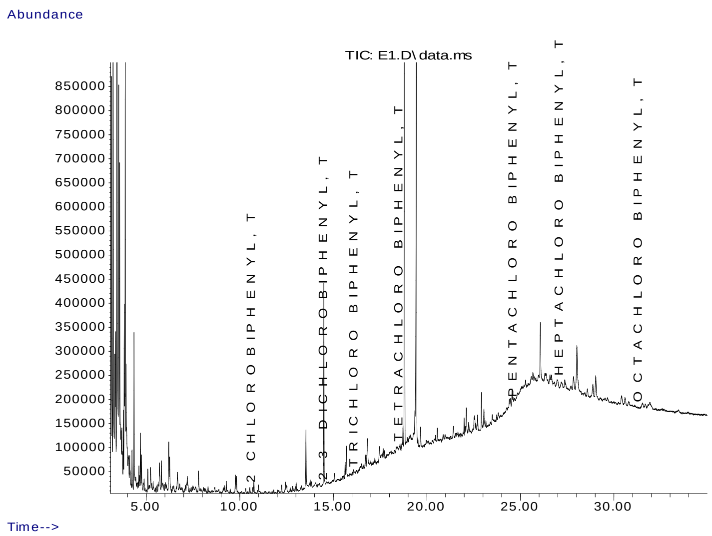


Figure 2. Chromatogram of sample E.

## 4. Conclusion

The sediments of New Calabar River in the Niger Delta Region of Nigeria were contaminated by polychlorinated biphenyls (PCBs). While PCB 105 was the most prominent congener, the lower chlorinated congeners (below PCB 101) represented 54.68% of the total PCB concentration in the sediment. This study provides results that can be used as a reference regarding PCBs levels in New Calabar River and by extension, the Niger Delta region. It underscores the significance of increasing anthropogenic activities in the region besides oil and gas as well as the need to extend environmental monitoring to pollutants other than petroleum hydrocarbons.

## Conflict of interest

The authors declare that there is no conflict of interest regarding this research article.

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