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Distribution of Organochlorine Pesticides in Water, Sediments and Fish in the Niger Delta Environment

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Several hundred pesticides of different chemical nature are currently used for agricultural purposes all over the world. Because of their widespread use, they are detected in various environmental matrices, such as water, soil, sediments, water and air. Pesticides are divided into many classes of which the most important is organochlorine compounds. Organochlorine pesticides are known to resist biodegradation and therefore they can be recycled through food chains and producea significant magnification of the original concentration at the end of the chain. Dichlorodiphenyltrichloroethane (DDT) and other chlorinated pesticides: aldrin, dieldrin, endrin and isodrin remain stable in the environment for many years (up to 40 years) after use. The long residence time of these substances in the environment has generated sustained interest in examining the pollution they cause. Although their use has been prohibited worldwide, the chemicals still find their way into local markets in developing countries where they are still used in diverse pest-control activities. Pesticide residues reach aquatic environment through direct run-off, leaching, indiscriminate disposal of empty containers, equipment washing, etc. To study the fate and transport of pesticides in aquatic environment requires efficient sample preparation and high performance analytical instruments to allow for the attainment of very low detection limits.

The distribution of organochlorine pesticides, OCPs, in different environmental matrices, water, sediment and fish samples from Ethiope River (at Sapele and Abraka), Warri River (at Enerhen) and Nun River (at Kaiama) Niger Delta is described in this report. The objective was to provide a summary of the concentration and distribution patterns of the OCPs in the matrices, conduct inter-matrix and spatial correlations of the OCPs flux and deduce any environmental significance of the levels of OCPs in the Niger Delta Environment.

Water, sediment and fish ***(Tilapiazilli)*** samples were collected at the designated locations (georeferenced) during the rainy and dry periods of 2012. Grab sampling technique was used to collect sub-surface (1metre below water surface) water samples in 1-L glass containers. The vials were carefully filled just to overflowing, without passing air bubblers through sample or trapping air bubbles in sealed bottles. Preparation of the vials included washing with detergent, rinsing with tap water, followed by ultrapore water (Millipor: Milli-205 plus and Milli Q plus 185), acetone (Analor grade) and drying at 150℃ for 2h. Samples were acidified to pH 2.5 with HCl to inhibit biological activity, filtered through fiber glass filter to remove any sand, grit or debris, and stored between 2 and 4℃ prior to extraction. Solid-phase extraction (SPE) disks followed by gas chromatographic techniques were used for the detection of the OCPs (APHA 1992, Barcelo, 1991, Edjere, 2015, Miliadis 1993). Sediment samples were collected at least 3m from the bank of the river from the same site as water samples,

wrapped with aluminum foil and taken to the laboratory in ice-cold container. The details of the procedures for the extraction, clean-up and chromatographic analysis of the OCPs are given elsewhere (Edjere 2015). Fish samples (***T.zilli***) six from each sampling location, wrapped in aluminum foil and taken to the laboratory in ice-cold container. The detail description of sample preparation, lipid removals clean-up and GC analysis of the OCPs are given elsewhere (Edjere 2015).

Table 1: Total average of organochlorine pesticides in the environmental matrices at each of the sampling locations ($\mu g.kg^{-1}$)

Sampling location	Rainy Season			Dry Season			
	Water	Sediment	Fish	Water	Sediment	Fish	Total
River Ethiope at:							
Abraka	1.402±0.120	52.00±0.01	128.0±3.0	1.152± 0.270	73.0±3.0	128.0±3.0	383.55±
Sapele	2.292±0.050	69.00±0.02	166.00±3.0	1.269±0.240	76.0±3.0	184.0±6.0	498.56±
Warri River at:							
Enerhen	0.976±0.05	107.00±0.06	134.0±2.0	0.855±0.186	114.0±4.0	183.0±6.0	539.83±
River Nun at:							
Kaiama	0.882±0.400	48.00±0.01	125.0±2.00	0.481±0.160	26.0±1.0	76.0±2.0	276.36±

Table 2: Average values of organochlorine pesticides in water, sediment and fish samples in Niger Delta environment.

Sampling locations ($\mu g.kg^{-1}$)	Water sample ($\mu g.kg^{-1}$)	sediment ($\mu g.kg^{-1}$)	Fish
River Ethiope at:			
Abraka	1.477±0.195	62.50±1.50	127.00±3.00
Sapele	1.781±0.145	72.50±1.51	175.00±3.00
Warri River at:			
Enerhen	0.911±0.118	110.50±2.03	158.50±3.00
River Nun at:			
Kaiama	0.681±0.280	37.00±0.50	105.50±2.00

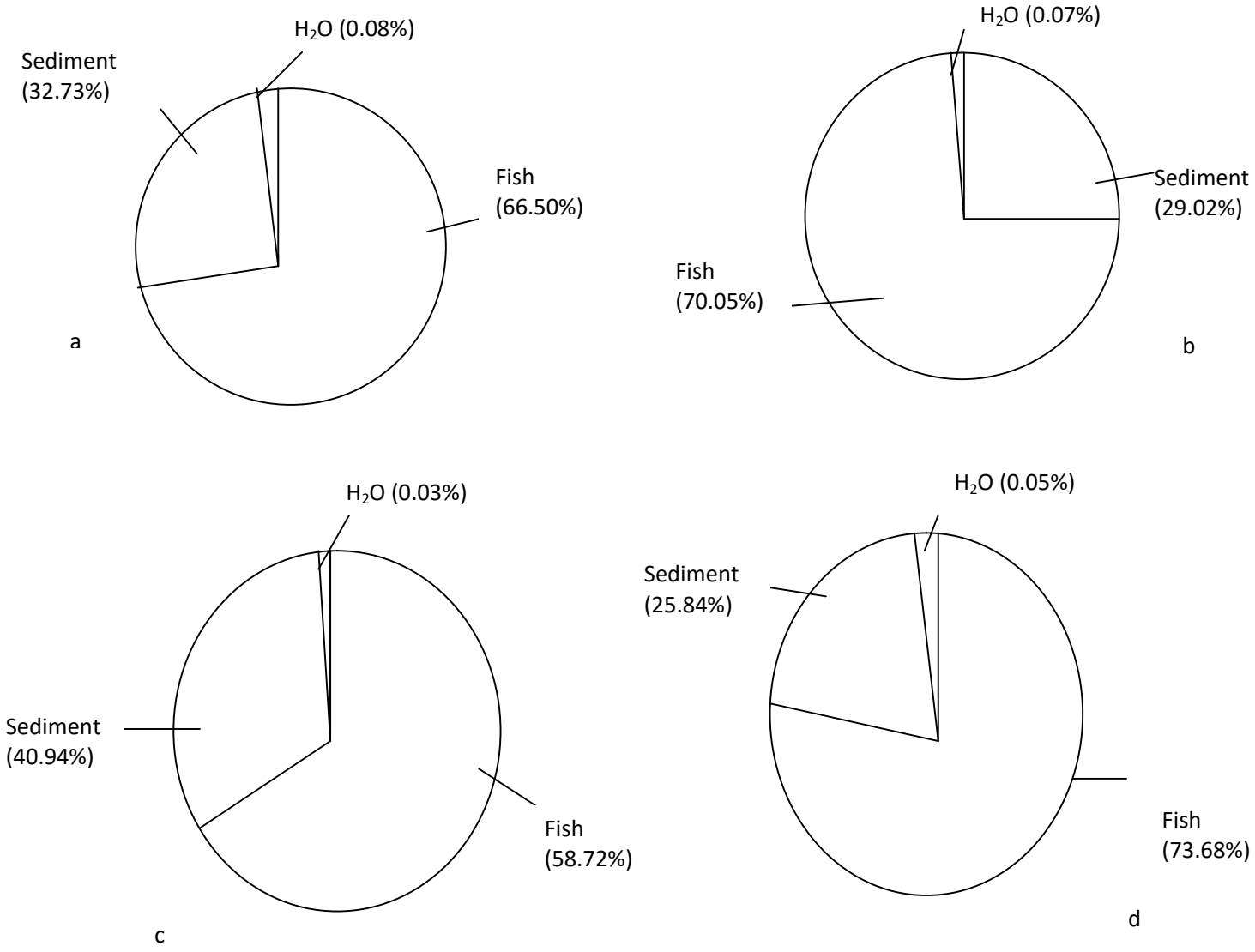

Fig 1: Distribution of OCPs in water, sediment and fish in (a) Ethiope River at Abraka, (b)Ethiope River at Sapele, (c) Warri River at Enerhen and d) Nun River at Kaiama.

The rainy and dry periods respectively; while the sediments of Nun River gave the lowest OCPs levels; 48.0 $\pm$ 0.01 μg.kg^{-1} and 26.0$\pm$ 1.0μg.kg^{-1} during the rainy and dry periods. The levels of OCPs in the fish samples were relatively high, generally higher than 100μg.kg^{-1}OCPs in both the rainy and dry periods. The average values of OCPs in water, sediment and fish samples in Niger Delta environment are given in Table 2 and shown in Fig.1. The fish samples clearly show disproportionally higher OCPS levels than the other two environmental matrices. Statistical analysis (2- way ANOVA) revealed significant difference ($P< 0.05$) in the OPCs levels in the environment matrices. The distribution of OCPs in the Niger Delta environment varied in the order Warri (539.83 $\pm$ 10.30 μ.kg^{-1})> Ethiope River Sapele (498.56 $\pm$14.29 μg.kg^{-1}) > Ethiope River Abraka (383.55 $\pm$ 10.39 μg.kg^{-1}> Nun River, Kaiama (273.36 $\pm$

36.56 μg.kg$^{-1)}$. There is however no significant statistical difference in the spatial variation of OCPs in the Niger Delta environment. The results in Table 2 allowed the indices of environmental and public health concern: partition coefficient, bioaccumulation index and hazard quotient, of the prevalence of OCPs in the Niger Delta environment (Table 3) to be determined. Partition coefficient is a measure of the level of OCPs in the sediment to the level in water. OCPs, being largely hydrophobic, will be expected to be associated with the sediment and occur (i). bound to the organic matter, in which case it will be relatively unavailable and of limited environmental concern; (ii) associated with the carbonate and exchangeable fractions of the sediment; and (iii) in the pore water of the sediment. The latter represent forms in which OCPs will be labile and present environmental consequences. The high values of partition coefficient determined at the sampling locations

Table 3: Partition coefficient, bioaccumulation index and hazard quotient of OCPs in the Niger Delta environment

Sampling Locations	Partition coefficient	Bioaccumulation index	Hazard quotient Sapele
River Ethiopeat:			
Abraka	40.72	98.29	1750
Sapele	48.94	100.23	1280
Warri Riverat:			
Enerhen	120.76	173.22	1585
RiverNunat:			
Kaiama	54.29	147.47	1005

have environmental consequences for bottom dwelling (benthic) organisms and for biomagnification along the food chain. Bioaccumulation index is a measure of the level of OCPs in the fish sample to the level in the water sample (***Tilipaizilli***) being largely a top-feeding fish species. These results show that the fish samples in the Niger Delta environment have bioaccumulated OCPs at least 100-fold above the levels in the water samples. Hazard quotient expresses the possibility of a contaminant being an ecological riskor acontaminant of potential ecological concern and it is determined as ratio of the OCPs in the test organism to toxicity reference values (regulatory limit of the contaminant). The results in Table 3 show that the levels of OCPs in the Niger Delta environment (at least 1000-fold higher than the regulatory limit) are of ecological concern. Recent survey of various aspects of the Nigerian environment for OCPs includes the report of Uyimadu (2002) and Adeyemi ***et al***., (2008) on OCPs residues in fish samples from Lagos Lagoon; Ize-Iyamu ***et al***., (2007) on OCPs in water and fish from various rivers in Edo State; and Okoya ***et al***., (2013) on OCPs in sediments and water from cocoa producing areas of Ondo State. The results from this study are consistent with those of these studies in concluding that the environmental matrices are contaminated by OCPs.

This study revealed the presence of 22 out of the 26 OCPs analyzed for in quantifiable amounts in three matrices: water, sediment and fish; and in four locations; Abraka (Ethiope River), Sapele (Ethiope River), Enerhen (Warri River) and Kaiama (Nun River). The levels of OCPs were lowest in the water samples and highest in the fish sample. The indices of environmental and public health concern

indicate that the studied environment of the Niger Delta is severely contaminated with OCPs. A more comprehensive study is recommended to include more intensive sampling protocol in the Niger Delta.

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