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Organochlorine Pesticides in Soils of Municipal Solid Waste Dumpsites in Delta State: Spatial and Seasonal Variations, Potential Risks and Sources

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ABSTRACT: This study assessed the spatial and seasonal variations, potential risks and sources of organochlorine pesticides in municipal solid waste dumpsites (MSWDs) in Delta State. Soil samples were obtained from twenty-seven MSWDs in Delta State. Soil samples were extracted with hexane/dichloromethane and cleaned up in a column of silica gel and florisil. The OCPs in the extracts were quantified with a gas chromatograph-mass spectrometry (GC-MS). The ∑20 OCPs levels in the soils varied between 0.74 and 7.29 ng g^{-1} for the dry season and from 0.09 to 9.47 ng g^{-1} for the wet season. The result showed significant spatial and seasonal variation in the concentrations of OCPs in the soils. The distribution pattern of OCPs homologues in the soils of the MSWD was in the order of ∑Chlordanes > ∑BHCs > ∑Drins > ∑DDTs > ∑Endosulfans for the dry season and ∑Chlordanes > ∑BHCs > ∑Drins > ∑Endosulfans > ∑DDTs for the wet season. The computed soil quality guideline quotients (SQGQs) indicated that there is no adverse ecological risk of OCPs in the MSWD soils. The hazard index and total cancer risk values indicated that non-carcinogenic and carcinogenic risks were not associated with the OCPs exposure in these soils. The isomeric ratios indicated that the sources of OCPs in the MSWD soils include recent and historical pesticide usage.

Keywords: Soil, OCPs, MSWDs, SQGQs, Source identification, Risks

Introduction

The management of municipal solid wastes is one of the problems facing developing countries like Nigeria today. The population of Nigeria has increased tremendously in recent times and consequently led to an increase in solid waste generation (Tesi *et al*., 2020a). Municipal solid waste dumpsites (MSWDs) are repositories for management of wastes and have been sources of different pollutants in the ecosystem (Abdus-Salam *et al*., 2011). Due to increase in industrialization, urbanization and commercialization, MSWDs receive different kinds of waste from diverse resources (Sultan *et al*., 2019). In Nigeria, where separation of wastes is not a typical practice, the majority of MSWDs contain all types of wastes (Onojake *et al*., 2023). Since soils are the primary location of MSWDs, there has been extensive contamination of MSWD soils due to the historical dumping of wastes containing organic pollutants such as organochlorine pesticides (OCPs) and leachates from these MSWDs may contaminate the surrounding and neighbouring environmental matrices (Sultan *et al*., 2019; Lateef *et al*., 2015). Organochlorine pesticides are widely used to control and manage pests as well as increase yield by farmers. The use of OCPs was prohibited in 2008 by NAFDAC in Nigeria. Notwithstanding their prohibition, OCPs are among the most common environmental contaminants, and can be found in a variety of abiotic and biotic media. According to Minh *et al*. (2006), the primary sources of pesticides found in MSWDs are packing materials, household, garden, and agricultural wastes contaminated with pesticides during pests control activities, as well as the use of pesticides for hygiene and health-related reasons at disposal sites. In Nigeria, MSWDs are situated within the neighborhood of living communities, they are not lined and do not have basement for selective absorption of toxic substances. Hence, leachate from these MSWDs can pollute the surrounding soils, ground and surface water with organic pollutants such as OCPs (Onojake *et al.*, 2023). Consequently, there is need to investigate the occurrence of OCPs in soils of MSWDs. Studies on the occurrence and health risk assessment of OCPs in MSWD soils have been reported in several countries of the world including Vietnam, India and Cambodia (Minh *et al*., 2006), Ethiopia (Nigatu and Hussen, 2022), Pakistan (Sultan *et al*., 2019), Jordan (Jiries *et al*., 2022), Greece (Chrysikou *et al*., 2008) and Slovak republic (Veningerová *et al*., 1997). However, in Nigeria, investigating and estimating the occurrence and levels of OCPs in MSWD soils have not been an object of extensive research. Most studies on contaminants in MSWDs focused on heavy metals (e.g. Tesi *et al*., 2020a; Tesi *et al*., 2020b; Amos-Tautua *et al*., 2013; Ogbeibu *et al*., 2013), PAHs (e.g. Aralu *et al*., 2023; Okechukwu *et al*., 2021; Olayinka *et al*., 2015) and PCBs (e.g. Onojake *et al*., 2023; Ayoola *et al*., 2023; Edjere *et al*., 2019). There is no information on the occurrence of OCPs in MSWD soils in Nigeria in general and Delta State in particular to the best of our knowledge. Thus, the objectives of this study are to determine the spatial and seasonal variations, potential risks and sources of OCPs in MSWDs in Delta State, Nigeria with a view to providing information which will be useful for pollution history, local environmental quality, risk management and establishment of pollution control measures.

Materials and methods

Study area description: The study areas are selected municipal solid waste dumpsites (MSWD) located in Ughelli, Warri, Sapele, Ozoro, Oleh, Patani, Agbor, Kwale and Asaba. The area is located in the oil-rich Niger Delta region situated in the Gulf of Guinea between longitude 3°– 6°N and latitude 5° – 8°E (Figure 1). The area lies within the subequatorial climate underlain by the Oligocene – Pliestocene of the Benin Formation containing gravels, sands, clay and good aquifers (Emoyan *et al*. 2021). The weather and climatic conditions of this area are of the Niger Delta region, i.e. high temperature, rain forest zone and high humidity. The northeast trade wind and the southwest monsoon wind from October – March, and April – September respectively are the two prevailing air masses of the area.
Sample collection: Twenty-seven (27) soil samples were collected from MSWD from nine locations in Delta State. Within each location, three MSWD were sampled. The MSWD were selected from Sapele (SAP 1-3), Warri (WAR 1-3), Ughelli (UGH 1-3), Oleh (OLEH 1-3), Ozoro (OZO 1-3), Patani (PTN 1-3), Asaba (ASB 1-3), Kwale (KWL 1-3) and Agbor (AGB 1-3). The geographical coordinates of the sampled MSWD are SAP1 (5°52′20″ N 5°42′32″ E), SAP3 (5°52′22″ N 5°42′22″ E), UGH1 (5°28′43″ N 6°1′21″ E), UGH2 (5°28′47″ N 6°1′11″ E), UGH3 (5°28′20″ N 6°1′5″ E), WAR1 (5°34′07″ N 5°47′54″ E), WAR2 (5°33′23″ N 5°47′7″ E) and WAR3 (5°33′44″ N 5°47′12″ E). Others includes OLEH1 (5°28′49″ N 6°12′16″ E), OLEH2 (5°30′29″ N 6°13′27″ E), OLEH3 (5°28′49″ N 6°12′16″ E), OZO1 (5°28′59″ N 6°12′39″ E), OZO2 (5°32′44″ N 6°12′45″ E), OZO3 (5°32′10″ N 6°13′7″ E), PTN1 (5°28′41″ N 6°13′51″ E), PTN2 (5°28′43″ N 6°13′25″ E) and PTN3 (5°28′44″ N 6°13′32″ E), ASB1 (6°11′9″ N 6°43′12″ E), ASB2 (6°11′9″ N 6°43′1″ E), ASB3 (6°11′9″ N 6°43′14″ E), KWL1 (5°38′5″ N 6°24′5″ E), KWL2 (5°38′3″ N 6°24′5″ E), KWL3 (5°38′3″ N 6°24′4″ E), AGB1 (6°15′49″ N 6°14′5″ E), AGB2 (6°15′34″ N 6°11′16″ E) and AGB3 (6°16′0″ N 6°10′52″ E).
Reagents and chemicals: The n-hexane and acetone (HPLC-grade), copper powder, anhydrous sodium sulfate, dichloromethane (LC grade), silica gel, and alumina (100–300 mesh) purchased from Merck (Darmstadt, Germany) were used for the extraction of OCPs of interest A mixture of known concentrations of 20 OCPs: 4 hexachlorocyclohexane isomers (α-HCH, β-HCH, γ-HCH, δ-HCH, p), 3 dichlorodiphenyltrichloroethanes isomers (p' – DDE, p, p' – DDD, p, p' – DDT), chlordanes (α-chlordane, γ-chlordane, heptachlor, heptachlor epoxide, methoxychlor), endosulfans (α-endosulfan, β-endosulfan, endosulpfan sulfate, and drins (aldrin, dieldrin, endrin, endrin-aldehyde endrin-ketone) were purchased from AccuStandards (New Haven, CT, USA).
Sample extraction and instrumental analysis: The extraction of OCPs from the soil samples was done using a modified procedure of Tesi *et al*. (2020c). Summarily, 10 g of soil was soxlet extracted for 10 hrs with dichloromethane/hexane and the extract was concentrated to 4 mL. The extract was purified on a column packed from bottom to top with anhydrous Na_2SO_4, Florisil, acidified silica gel, and copper powder. The OCPs were eluted with 20 mL each of hexane and dichloromethane (DCM) into a 50 mL flask and concentrated to about 2 mL with a rotary evaporator. The concentrated extract was transferred into a tube and further evaporated to near dryness with a stream of N_2 gas, solubilized with 1.7 mL ethyl acetate, and transferred into an amber-colored 2 mL injection vial ready for analysis. The OCPs in the extract were quantified using a gas chromatograph (6890 N Agilent technologies) coupled with a Mass Selective Detector (Agilent 5975B) (GC–MS) fitted with an Agilent HP-5 − 60 to 325 °C GC column (30 m × 320 μm × 0.25 μm film thickness) was used in quantifying the Σ20OCPs concentrations in the sample extracts. The initial oven temperature was maintained at 100 °C for 2

min, ramp to 180 °C at a rate of 15 °C/min, and raised to 300 °C at a flow rate of 3 °C/min and held for 9 min. The carrier gas, helium, was operated at a flow rate of 0.8 mL/min. The volume of the concentrated sample injected in the splitless mode was 1 µL. The operation mode of the mass spectrometer was electron impact ionization with the use of automatic gain control. The storage window was programmed at full scan mode in the range of m/z 200–500, and the selected ion monitoring mode was employed in acquiring data by Agilent Chemstation software.

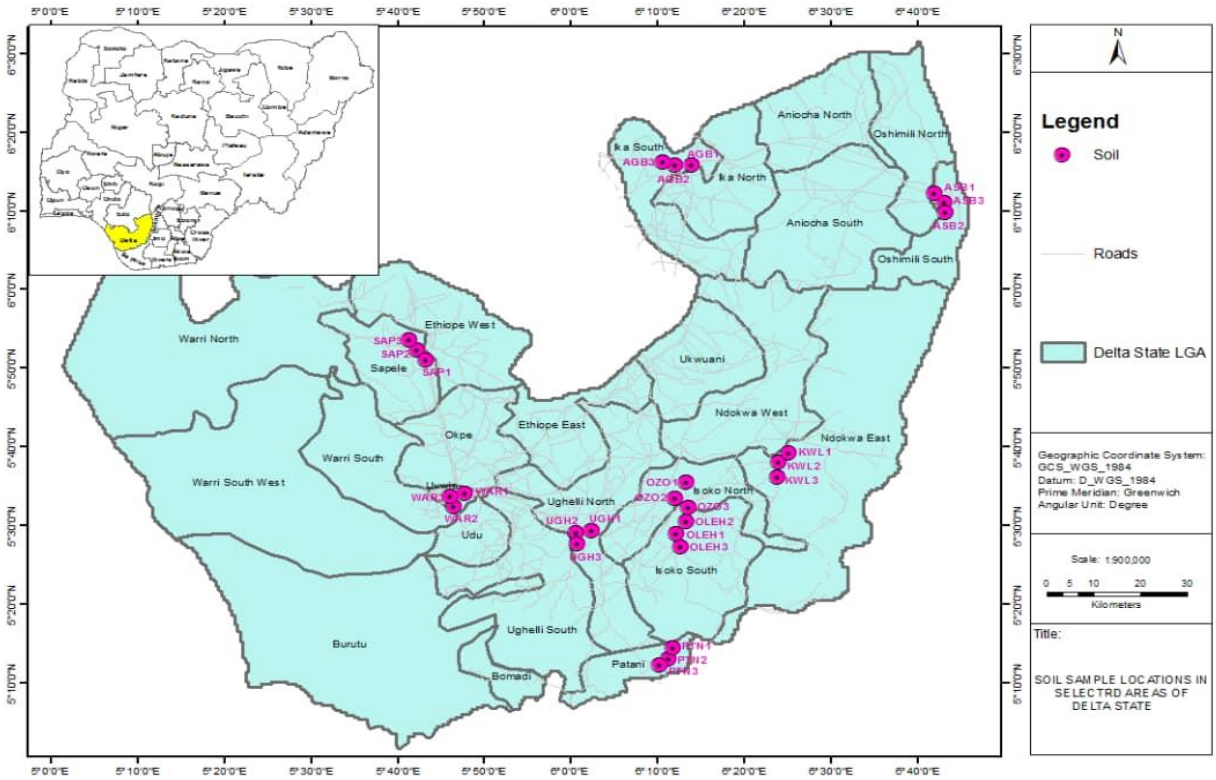

Figure 1: The map of Delta State showing sample sites

Quality assurance and control: All analytical techniques were monitored with strict quality control and assurance protocols. External calibration was done with five-point OCP standards between 10 µg/L and 100 µg/L, prepared by serial dilution of the stock standard. A spiked recovery sample was obtained by spiking blank samples with 2 µL of 20 µg/mL of OCP standard. During instrumental analysis, the GC-MS syringes were programmed to wash two times with ethyl acetate and hexane before and after injection. Both field and laboratory blanks were extracted and analyzed in the same manner as the samples and OCP residues were not detected in the blanks.

Statistical analysis: Statistical Package for the Social Sciences (SPSS, Inc., USA)) version 25 was used for all statistical evaluations. Analysis of variance (ANOVA) was used to determine if there was significant spatial variation in the concentrations of OCPs in the soils while t-test was used to determine if there was significant seasonal variation in the concentrations of OCPs in the soil.

Ecological risks of OCPs in the MSWD soils: The ecological risk of OCPs in the soils was assessed using the soil/sediment quality guideline quotient (SQGQs) which has been used by other researchers (Emoyan *et al.*, 2021; Wang *et al.*, 2016; Costa *et al.*, 2011; Long and MacDonald, 1998). The SQGQ is given by the equation:

$$\text{SQGQ} = \frac{\sum PELQ_i}{n} \quad (1)$$

But $$\text{PELQ}_i = \frac{C_i}{PEL} \quad (2)$$

where PELQ_i = PEL quotient for each OCP and n = number of analyzed OCPs with SQGs, C_i = observed concentration of each OCP and PEL is the probable effect level for each OCP. An SQGQ value < 0.1 = no effects, 0.1 ≤ SQGQ < 1 = moderate effect and SQGQ ≥ 1 = high adverse biological effect (Costa *et al.*, 2011).

Human health risk assessment of OCPs in the MSWD soils: The non-carcinogenic risk was assessed as hazard index (HI) while the carcinogenic risk was assessed as the total cancer risk (TCR). The inhalation route was not taken into consideration when computing the HI as inhalation reference doses for OCPs were not available. The HI was obtained using equations 3 to 6 and TCR was obtained using equations 7 to 10 (Tesi *et al.*, 2020c; USEPA, 1989).

$$\text{Hazard index (HI)} = \sum HQ = HQ_{ing} + HQ_{dermal} \quad (3)$$

$$HQ = \frac{CDInc}{RfD} \quad (4)$$

$$CDI_{ing\text{-}nc} = \frac{C \times IngR \times EF \times ED}{BW \times AT_{nc}} \times 10^{-6} \quad (5)$$

$$CDI_{dermal\text{-}nc} = \frac{C \times SA \times AF \times ABS \times EF \times ED}{BW \times AT_{nc}} \times 10^{-6} \quad (6)$$

$$\text{Total cancer risk} = Risk_{Ing} + Risk_{Inh} + Risk_{Dermal} \quad (7)$$

$$Risk_{ing} = \frac{C \times IngR \times EF \times ED \times CF \times SFO}{BW \times ATca} \quad (8)$$

$$Risk_{inh} = \frac{C \times Inh \times EF \times ED \times IUR}{PEF \times ATca} \quad (9)$$

$$Risk_{derm} = \frac{C \times SA \times AF \times ABS \times EF \times ED \times CF \times SFO \times GIABS}{BW \times ATca} \quad (10)$$

where CDI_{ing} and CDI_{Derm}= chronic daily intake = chronic daily intake via ingestion and dermal respectively.

$Risk_{ing}$, $Risk_{inh}$ and $Risk_{Derm}$ = risks via ingestion, inhalation and dermal contact respectively. The values of variables and definitions of terms in equations 3 to 10 can be found in Emoyan *et al*. (2021) and Tesi *et al*. (2020c). Usually, HI value above 1 shows that there is potential non-cancer risk while total cancer risk of 1×10^{-4} is the acceptable limit for cancer risk (USEPA, 2022).

Results

The summarized results of the OCPs concentrations in soils from the MSWD studied are shown in Table 1. The distribution pattern of $\sum_{20}$ OCPs concentrations and homologues in both seasons are displayed in Figures 2 and 3 respectively. Table 2 gives the computed ecological risk values while Tables 3 and 4 show the HI and TCR values respectively. The isomeric ratios for source identification are displayed in Tables 5 and 6.

Table 1: Summary statistics of OCPs in the dumpsites for the dry and wet seasons

	Dry Season						Wet Season					
	Mean	SD	Median	Min	Max	CV%	Mean	SD	Median	Min	Max	CV%
Alpha-BHC	0.29	0.27	0.28	ND	0.80	93	0.23	0.26	0.13	ND	1.15	113
Beta-BHC	0.32	0.39	0.25	ND	1.41	119	0.34	0.44	0.20	ND	1.76	129
Gamma-BHC	0.31	0.49	0.00	ND	1.49	160	0.20	0.33	0.00	ND	1.40	163
Delta-BHC	0.10	0.21	0.00	ND	0.81	212	0.18	0.28	0.00	ND	1.10	157
DDD	0.21	0.38	0.00	ND	1.31	182	0.17	0.41	0.00	ND	1.30	244
DDE	0.25	0.40	0.00	ND	1.22	158	0.07	0.12	0.00	ND	0.33	180
DDT	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Heptachlor	0.56	0.58	0.38	ND	1.82	102	0.31	0.50	0.16	ND	1.68	163
Heptachlor Epoxide	0.22	0.38	0.00	ND	1.50	168	0.30	0.46	0.00	ND	1.75	152
Alpha-Chlordane	0.79	0.58	0.77	ND	1.82	74	0.52	0.54	0.23	0.02	1.62	105
Gamma-Chlordane	0.35	0.58	0.00	ND	1.74	166	0.45	0.66	0.00	ND	1.86	148
Methoxychlor	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Endosulfan I	0.35	0.34	0.34	ND	1.07	98	0.27	0.48	0.00	ND	1.50	180
Endosulfan II	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Endosulfan sulfate	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Aldrin	0.30	0.47	0.09	ND	1.55	153	0.27	0.26	0.15	ND	0.80	99
Dieldrin	0.19	0.30	0.00	ND	0.88	159	0.46	0.60	0.17	ND	1.77	130

	Dry Season						Wet Season					
	Mean	**SD**	**Median**	**Min**	**Max**	**CV%**	**Mean**	**SD**	**Median**	**Min**	**Max**	**CV%**
Endrin	0.05	0.11	0.00	ND	0.43	209	0.17	0.23	0.03	ND	0.63	139
Endrin aldehyde	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Endrin ketone	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TOTAL	**4.31**	**2.25**	**4.64**	**0.68**	**7.29**	**52**	**3.92**	**2.49**	**3.48**	**0.09**	**9.47**	**64**
∑BHC	1.02	0.79	0.91	ND	2.62	77	0.95	1.00	0.76	ND	3.62	106
∑DDTs	0.47	0.65	0.00	ND	1.75	139	0.23	0.51	0.00	ND	1.63	219
∑Chlordane	1.92	1.39	1.73	ND	4.49	72	1.58	1.77	0.89	0.09	5.98	113
∑Endosulfan	0.35	0.34	0.34	ND	1.07	98	0.27	0.48	0.00	ND	1.50	180
∑Drins	0.55	0.45	0.54	ND	1.55	82	0.90	0.74	0.94	ND	2.18	83

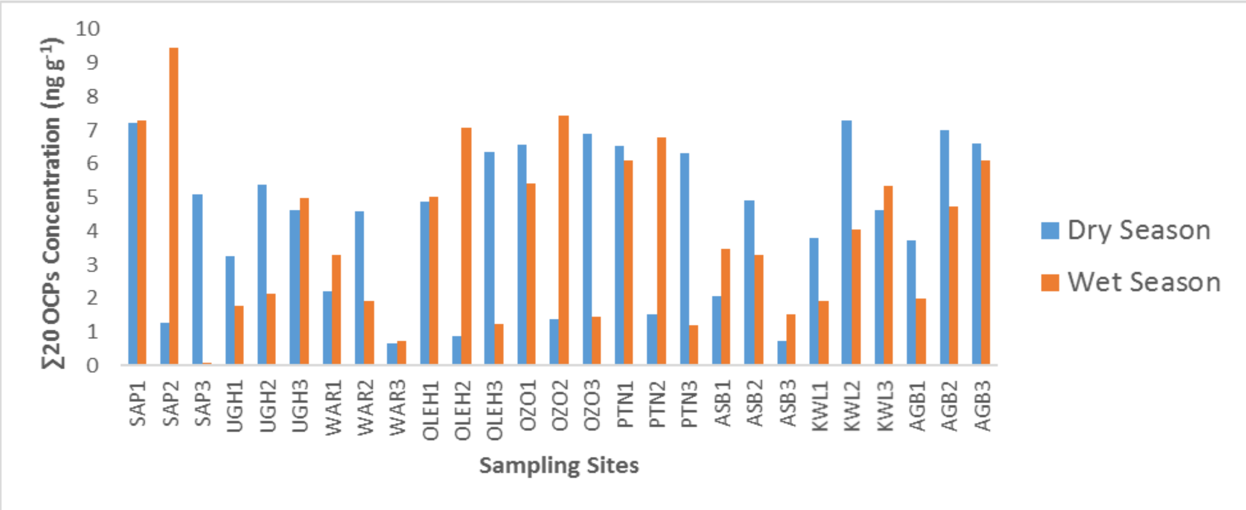

Figure 2: Seasonal variation of ∑20 OCPs in the MSWD soils

From Table 1 and Figure 2, the concentrations of the Σ_{20}OCPs in soil of the MSWD varied between 0.74 and 7.29 ng g^{-1} for the dry season and from 0.09 to 9.47 ng g^{-1} for the wet season. The highest and lowest Σ_{20}OCPs concentration was observed in KWL2 and ASB3 respectively for dry season and in SAP2 and SAP3 respectively for the wet season.

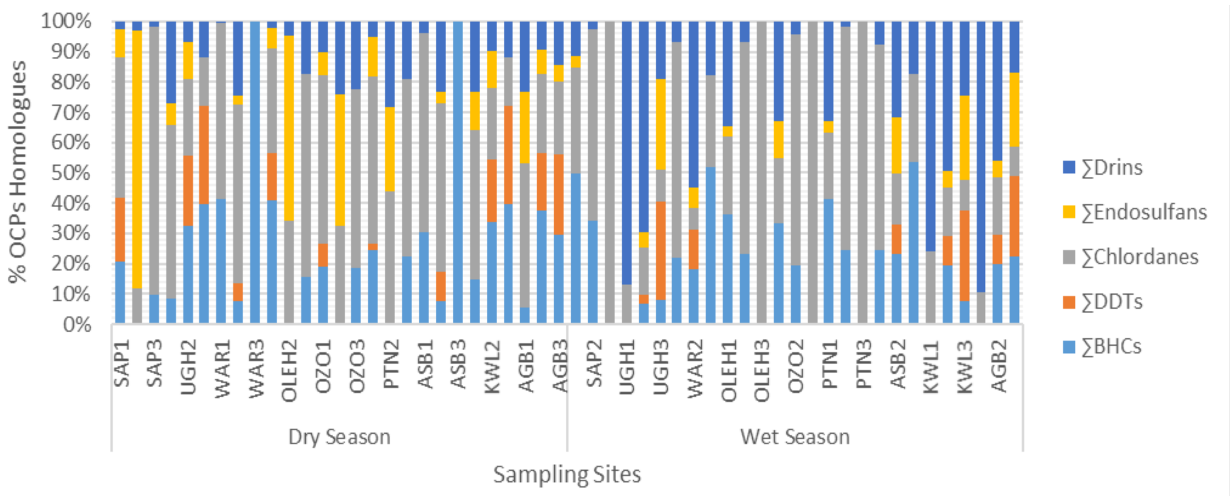

Figure 3: OCPs homologues distribution pattern in the MSWD soils

Figure 3 showed that the distribution pattern of OCPs homologues in the soils of the MSWD was in the order of ∑Chlordanes > ∑BHCs > ∑Drins > ∑DDTs > ∑Endosulfans for the dry season while for the wet season, the distribution pattern of OCPs in the MSWD followed the order: ∑Chlordanes > ∑BHCs > ∑Drins > ∑Endosulfans > ∑DDTs.

Table 2: SQGQs of OCPs in the MSWD soils

	Dry Season						**Wet Season**					
	PELQs						**PELQs**					
	γ-BHC	**DDD**	**DDE**	**DDT**	**Dieldrin**	**SQGQs**	**γ-BHC**	**DDD**	**DDE**	**DDT**	**Dieldrin**	**SQGQs**
SAP1	1.08	0.07	0.14	0.00	0.00	1.29	1.01	0.00	0.00	0.00	0.04	1.02
SAP2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SAP3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
UGH1	0.00	0.00	0.00	0.00	0.20	0.04	0.00	0.00	0.00	0.00	0.36	0.07
UGH2	0.72	0.02	0.16	0.00	0.03	0.91	0.02	0.01	0.00	0.00	0.12	0.06
UGH3	0.07	0.13	0.06	0.00	0.03	0.27	0.17	0.15	0.05	0.00	0.07	0.38
WAR1	0.00	0.00	0.00	0.00	0.00	0.00	0.28	0.00	0.00	0.00	0.03	0.29
WAR2	0.00	0.00	0.04	0.00	0.00	0.04	0.00	0.01	0.02	0.00	0.00	0.03
WAR3	0.22	0.00	0.00	0.00	0.00	0.22	0.00	0.00	0.00	0.00	0.00	0.00
OLEH1	1.04	0.04	0.07	0.00	0.00	1.15	0.51	0.00	0.00	0.00	0.28	0.56
OLEH2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
OLEH3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
OZO1	0.17	0.06	0.00	0.00	0.16	0.27	0.51	0.00	0.00	0.00	0.28	0.56
OZO2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
OZO3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PTN1	0.61	0.02	0.00	0.00	0.08	0.64	0.44	0.00	0.00	0.00	0.34	0.51
PTN2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PTN3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ASB1	0.00	0.00	0.00	0.00	0.00	0.00	0.15	0.00	0.00	0.00	0.04	0.16
ASB2	0.00	0.00	0.07	0.00	0.00	0.07	0.00	0.02	0.02	0.00	0.00	0.04
ASB3	0.25	0.00	0.00	0.00	0.00	0.25	0.00	0.00	0.00	0.00	0.00	0.00
KWL1	0.00	0.00	0.00	0.00	0.20	0.04	0.00	0.00	0.00	0.00	0.34	0.07
KWL2	0.74	0.03	0.18	0.00	0.07	0.97	0.23	0.02	0.03	0.00	0.23	0.33
KWL3	0.07	0.13	0.06	0.00	0.03	0.27	0.17	0.15	0.05	0.00	0.07	0.38
AGB1	0.00	0.00	0.00	0.00	0.20	0.04	0.00	0.00	0.00	0.00	0.41	0.08
AGB2	0.87	0.02	0.17	0.00	0.08	1.08	0.14	0.02	0.05	0.00	0.24	0.25
AGB3	0.14	0.15	0.07	0.00	0.13	0.39	0.34	0.15	0.05	0.00	0.07	0.56

From Table 2, the SQGQ values ranged from 0.04 to 1.29 for dry season and 0.04 to 1.02 for wet season.

Table 3: Hazard index and total cancer risk of OCPs in soils of MSWD

	Dry Season						**Wet Season**					
	CHILD			**ADULT**			**CHILD**			**ADULT**		
	HQING	**HQDERM**	**HI**	**HQING**	**HQDERM**	**HI**	**HQING**	**HQDERM**	**HI**	**HQING**	**HQDERM**	**HI**
SAP1	1.67E+00	4.51E-01	**2.12E+00**	2.09E-01	8.04E-02	**2.89E-01**	1.77E+00	4.82E-01	**2.25E+00**	2.21E-01	8.58E-02	**3.07E-01**
SAP2	7.80E-03	1.56E-03	**9.36E-03**	9.75E-04	2.77E-04	**1.25E-03**	1.93E+00	5.27E-01	**2.45E+00**	2.41E-01	9.39E-02	**3.35E-01**
SAP3	1.53E-01	2.79E-02	**1.81E-01**	1.91E-02	4.97E-03	**2.41E-02**	2.40E-03	2.69E-04	**2.67E-03**	3.00E-04	4.80E-05	**3.48E-04**
UGH1	2.74E-01	7.21E-02	**3.46E-01**	3.43E-02	1.28E-02	**4.71E-02**	4.00E-01	1.11E-01	**5.11E-01**	5.00E-02	1.98E-02	**6.97E-02**
UGH2	3.87E-01	9.69E-02	**4.84E-01**	4.84E-02	1.73E-02	**6.57E-02**	4.84E-01	1.35E-01	**6.20E-01**	6.06E-02	2.41E-02	**8.46E-02**
UGH3	3.15E-01	8.65E-02	**4.01E-01**	3.94E-02	1.54E-02	**5.48E-02**	2.85E-01	7.72E-02	**3.62E-01**	3.57E-02	1.37E-02	**4.94E-02**
WAR1	3.33E-02	3.82E-03	**3.72E-02**	4.17E-03	6.81E-04	**4.85E-03**	6.24E-01	1.64E-01	**7.88E-01**	7.80E-02	2.92E-02	**1.07E-01**
WAR2	7.17E-01	1.97E-01	**9.14E-01**	8.97E-02	3.50E-02	**1.25E-01**	2.84E-01	7.89E-02	**3.63E-01**	3.55E-02	1.40E-02	**4.95E-02**
WAR3	1.34E-02	1.50E-03	**1.49E-02**	1.67E-03	2.67E-04	**1.94E-03**	1.11E-02	2.19E-03	**1.33E-02**	1.39E-03	3.91E-04	**1.78E-03**
OLEH1	8.66E-01	2.29E-01	**1.10E+00**	1.08E-01	8.65E-05	**1.08E-01**	1.26E+00	3.47E-01	**1.61E+00**	1.58E-01	4.08E-02	**1.99E-01**
OLEH2	1.05E-02	1.66E-03	**1.22E-02**	1.32E-03	2.31E-02	**2.44E-02**	1.17E+00	3.18E-01	**1.49E+00**	1.47E-01	2.95E-04	**1.47E-01**
OLEH3	5.73E-01	1.47E-01	**7.20E-01**	7.17E-02	4.39E-04	**7.21E-02**	3.15E-02	3.52E-03	**3.50E-02**	3.93E-03	2.61E-02	**3.00E-02**
OZO1	1.17E+00	3.21E-01	**1.49E+00**	1.46E-01	1.65E-04	**1.46E-01**	1.09E+00	2.98E-01	**1.39E+00**	1.36E-01	5.71E-02	**1.93E-01**
OZO2	2.68E-02	5.58E-03	**3.24E-02**	3.36E-03	2.49E-02	**2.83E-02**	1.01E+00	2.69E-01	**1.28E+00**	1.26E-01	9.95E-04	**1.27E-01**
OZO3	7.64E-01	2.01E-01	**9.65E-01**	9.55E-02	5.61E-04	**9.61E-02**	3.73E-02	4.18E-03	**4.15E-02**	4.67E-03	3.58E-02	**4.05E-02**
PTN1	9.54E-01	2.57E-01	**1.21E+00**	1.19E-01	1.82E-04	**1.19E-01**	9.85E-01	2.68E-01	**1.25E+00**	1.23E-01	4.58E-02	**1.69E-01**
PTN2	3.64E-02	7.31E-03	**4.37E-02**	4.55E-03	3.07E-02	**3.53E-02**	6.20E-01	1.59E-01	**7.79E-01**	7.75E-02	1.30E-03	**7.88E-02**
PTN3	6.02E-01	1.57E-01	**7.59E-01**	7.53E-02	3.60E-04	**7.56E-02**	3.12E-02	3.49E-03	**3.47E-02**	3.90E-03	2.80E-02	**3.19E-02**
ASB1	3.79E-02	4.82E-03	**4.28E-02**	4.74E-03	1.22E-04	**4.86E-03**	6.31E-01	1.67E-01	**7.98E-01**	7.88E-02	8.59E-04	**7.97E-02**
ASB2	8.05E-01	2.22E-01	**1.03E+00**	1.01E-01	2.10E-03	**1.03E-01**	2.74E-01	7.45E-02	**3.49E-01**	3.43E-02	3.95E-02	**7.38E-02**
ASB3	1.49E-02	1.67E-03	**1.66E-02**	1.86E-03	1.93E-02	**2.12E-02**	2.23E-02	4.36E-03	**2.67E-02**	2.79E-03	2.98E-04	**3.09E-03**
KWL1	2.74E-01	7.19E-02	**3.46E-01**	3.42E-02	1.62E-04	**3.44E-02**	3.83E-01	1.05E-01	**4.88E-01**	4.78E-02	1.28E-02	**6.06E-02**
KWL2	7.09E-01	1.87E-01	**8.96E-01**	8.87E-02	1.34E-02	**1.02E-01**	5.75E-01	1.58E-01	**7.33E-01**	7.18E-02	3.33E-02	**1.05E-01**
KWL3	3.18E-01	8.73E-02	**4.05E-01**	3.97E-02	1.22E-04	**3.99E-02**	4.42E-01	1.21E-01	**5.63E-01**	5.52E-02	1.55E-02	**7.08E-02**
AGB1	2.67E-01	6.86E-02	**3.36E-01**	3.34E-02	1.55E-02	**4.89E-02**	4.58E-01	1.27E-01	**5.85E-01**	5.72E-02	1.22E-02	**6.95E-02**
AGB2	9.52E-01	2.55E-01	**1.21E+00**	1.19E-01	1.85E-02	**1.37E-01**	5.43E-01	1.49E-01	**6.93E-01**	6.79E-02	4.53E-02	**1.13E-01**
AGB3	4.51E-01	1.20E-01	**5.71E-01**	5.64E-02	1.29E-04	**5.65E-02**	3.26E-01	8.66E-02	**4.13E-01**	4.08E-02	2.14E-02	**6.22E-02**

From Table 3, the HI values ranged from 9.36×10^{-3} to 2.12 and 1.94×10^{-3} to 0.29 for child and adult for dry season and from 2.67×10^{-3} to 0.80 and 0.08 to 0.31 for child and adults for wet season.

From Table 4, the TCR of OCPs in the soils from the MSWD ranged from 9.17×10^{-4} to 1.25×10^{-4} and 6.89×10^{-6} to 1.07×10^{-7} for infants and adult for dry season and ranged from 7.27×10^{-6} to 1.55×10^{-4} and 5.22×10^{-7} to 1.15×10^{-5} for infants and adult for the wet season.

Table 4: Total cancer risk of OCPs in soils of MSWD

	Dry Season								Wet Season							
	CHILD				ADULT				CHILD				ADULT			
	RISKING	RISKINH	RISKDERM	Total Cancer Risk	RISKING	RISKINH	RISKDERM	Total Cancer Risk	RISKING	RISKINH	RISKDERM	Total Cancer Risk	RISKING	RISKINH	RISKDERM	Total Cancer Risk
SAP1	2.78E-04	4.39E-11	1.52E-04	**4.30E-04**	1.92E-05	8.78E-11	7.20E-06	**2.64E-05**	4.46E-04	7.04E-11	1.70E-04	**6.16E-04**	3.07E-05	1.41E-10	1.19E-05	**4.26E-05**
SAP2	6.53E-07	1.03E-13	7.32E-08	**7.27E-07**	4.50E-08	2.06E-13	7.19E-09	**5.22E-08**	4.86E-04	7.69E-11	2.26E-04	**7.11E-04**	3.35E-05	1.54E-10	1.31E-05	**4.66E-05**
SAP3	1.04E-04	1.66E-11	2.11E-05	**1.25E-04**	7.18E-06	3.32E-11	2.61E-06	**9.78E-06**	4.21E-07	6.63E-14	4.71E-08	**4.68E-07**	2.90E-08	1.33E-13	4.63E-09	**3.36E-08**
UGH1	2.52E-04	3.99E-11	6.97E-05	**3.22E-04**	1.74E-05	7.99E-11	6.85E-06	**2.42E-05**	3.16E-04	5.01E-11	8.83E-05	**4.04E-04**	2.18E-05	1.00E-10	8.68E-06	**3.05E-05**
UGH2	1.66E-04	2.63E-11	4.24E-05	**2.09E-04**	1.15E-05	5.26E-11	4.26E-06	**1.57E-05**	2.94E-04	4.67E-11	3.35E-05	**3.27E-04**	2.02E-05	9.33E-11	8.07E-06	**2.83E-05**
UGH3	2.09E-04	3.31E-11	5.11E-05	**2.60E-04**	1.44E-05	6.62E-11	5.71E-06	**2.01E-05**	1.20E-04	1.91E-11	3.62E-05	**1.57E-04**	8.30E-06	3.81E-11	3.24E-06	**1.15E-05**
WAR1	7.24E-05	1.14E-11	1.93E-05	**9.17E-05**	4.99E-06	2.28E-11	1.90E-06	**6.89E-06**	1.42E-04	2.24E-11	6.22E-05	**2.04E-04**	9.76E-06	4.47E-11	3.67E-06	**1.34E-05**
WAR2	3.70E-04	5.89E-11	4.57E-05	**4.16E-04**	2.55E-05	1.18E-10	1.01E-05	**3.57E-05**	1.50E-04	2.39E-11	4.69E-06	**1.55E-04**	1.04E-05	4.77E-11	4.12E-06	**1.45E-05**
WAR3	3.37E-05	5.31E-12	8.70E-06	**4.24E-05**	2.33E-06	1.06E-11	8.55E-07	**3.18E-06**	1.47E-05	2.35E-12	3.96E-06	**1.87E-05**	1.01E-06	4.70E-12	3.89E-07	**1.40E-06**
OLEH1	1.75E-04	2.77E-11	8.47E-05	**2.60E-04**	1.21E-05	5.53E-11	4.43E-06	**1.65E-05**	4.96E-04	7.86E-11	1.50E-04	**6.47E-04**	3.42E-05	1.57E-10	1.35E-05	**4.77E-05**
OLEH2	1.34E-06	2.12E-13	1.50E-07	**1.49E-06**	9.25E-08	4.23E-13	1.48E-08	**1.07E-07**	3.78E-04	6.00E-11	1.28E-04	**5.07E-04**	2.61E-05	1.20E-10	1.02E-05	**3.63E-05**
OLEH3	3.32E-04	5.29E-11	2.42E-05	**3.56E-04**	2.29E-05	1.06E-10	8.89E-06	**3.18E-05**	5.50E-06	8.67E-13	6.16E-07	**6.12E-06**	3.79E-07	1.73E-12	6.06E-08	**4.40E-07**
OZO1	4.00E-04	6.34E-11	1.67E-04	**5.68E-04**	2.76E-05	1.27E-10	1.09E-05	**3.85E-05**	4.76E-04	7.54E-11	1.34E-04	**6.10E-04**	3.28E-05	1.51E-10	1.29E-05	**4.57E-05**
OZO2	2.01E-06	3.17E-13	2.26E-07	**2.24E-06**	1.39E-07	6.35E-13	2.22E-08	**1.61E-07**	3.23E-04	5.12E-11	1.15E-04	**4.38E-04**	2.23E-05	1.02E-10	8.65E-06	**3.09E-05**
OZO3	4.38E-04	6.97E-11	2.60E-05	**4.64E-04**	3.02E-05	1.39E-10	1.18E-05	**4.20E-05**	6.53E-06	1.03E-12	7.32E-07	**7.27E-06**	4.50E-07	2.06E-12	7.19E-08	**5.22E-07**
PTN1	3.22E-04	5.09E-11	1.34E-04	**4.56E-04**	2.22E-05	1.02E-10	8.57E-06	**3.07E-05**	5.26E-04	8.34E-11	1.36E-04	**6.62E-04**	3.62E-05	1.67E-10	1.43E-05	**5.05E-05**
PTN2	3.00E-06	4.72E-13	3.36E-07	**3.33E-06**	2.07E-07	9.45E-13	3.30E-08	**2.40E-07**	2.27E-04	3.60E-11	8.17E-05	**3.09E-04**	1.57E-05	7.20E-11	5.99E-06	**2.16E-05**
PTN3	3.67E-04	5.84E-11	2.83E-05	**3.95E-04**	2.53E-05	1.17E-10	9.89E-06	**3.52E-05**	5.46E-06	8.60E-13	6.11E-07	**6.07E-06**	3.76E-07	1.72E-12	6.01E-08	**4.36E-07**
ASB1	4.33E-05	6.85E-12	1.11E-05	**5.44E-05**	2.99E-06	1.37E-11	1.09E-06	**4.08E-06**	1.56E-04	2.47E-11	6.68E-05	**2.23E-04**	1.08E-05	4.95E-11	4.12E-06	**1.49E-05**
ASB2	3.94E-04	6.27E-11	5.62E-05	**4.51E-04**	2.72E-05	1.25E-10	1.08E-05	**3.80E-05**	1.50E-04	2.39E-11	7.60E-06	**1.58E-04**	1.04E-05	4.78E-11	4.09E-06	**1.45E-05**
ASB3	3.63E-05	5.71E-12	9.35E-06	**4.57E-05**	2.50E-06	1.14E-11	9.18E-07	**3.42E-06**	3.27E-05	5.22E-12	8.82E-06	**4.15E-05**	2.25E-06	1.04E-11	8.67E-07	**3.12E-06**
KWL1	2.74E-04	4.34E-11	7.58E-05	**3.50E-04**	1.89E-05	8.68E-11	7.45E-06	**2.63E-05**	2.99E-04	4.74E-11	8.33E-05	**3.82E-04**	2.06E-05	9.47E-11	8.18E-06	**2.88E-05**
KWL2	3.11E-04	4.93E-11	8.16E-05	**3.93E-04**	2.15E-05	9.86E-11	8.25E-06	**2.97E-05**	4.06E-04	6.44E-11	7.37E-05	**4.79E-04**	2.80E-05	1.29E-10	1.11E-05	**3.90E-05**
KWL3	2.11E-04	3.34E-11	5.14E-05	**2.62E-04**	1.45E-05	6.69E-11	5.76E-06	**2.03E-05**	2.01E-04	3.19E-11	3.61E-05	**2.37E-04**	1.39E-05	6.38E-11	5.46E-06	**1.93E-05**
AGB1	2.18E-04	3.46E-11	6.00E-05	**2.78E-04**	1.50E-05	6.92E-11	5.90E-06	**2.09E-05**	3.63E-04	5.76E-11	1.01E-04	**4.65E-04**	2.50E-05	1.15E-10	9.97E-06	**3.50E-05**
AGB2	3.24E-04	5.13E-11	1.08E-04	**4.32E-04**	2.24E-05	1.03E-10	8.58E-06	**3.09E-05**	4.08E-04	6.47E-11	8.19E-05	**4.90E-04**	2.81E-05	1.29E-10	1.12E-05	**3.93E-05**
AGB3	2.94E-04	4.65E-11	7.43E-05	**3.68E-04**	2.03E-05	9.31E-11	7.96E-06	**2.82E-05**	1.69E-04	2.67E-11	4.47E-05	**2.14E-04**	1.16E-05	5.34E-11	4.51E-06	**1.62E-05**

Table 5: Computed ratios of parent OCPs and their metabolites in the MSWD soils

Seasons	Samples	α-BHC/ γ-BHC	γBHC/ ∑BHC	β-BHC/ γBHC	DDD/ DDE	(DDD+DDE) /∑DDTs	α-Chlordane/ γ-Chlordane	Heptachlor Epoxide /Heptachlor	Endrin/ Dieldrin	Dieldrin/ Aldrin
Dry	SAP1	0.00	1.00	0.00	0.65	1.21	0.00	3.19	0.00	0.00
	SAP2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	SAP3	0.00	0.00	0.00	0.00	0.00	1.09	0.00	0.00	0.00
	UGH1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	UGH2	0.31	0.57	0.25	0.13	1.03	0.00	1.06	0.00	0.71
	UGH3	7.50	0.05	5.70	2.78	1.37	0.35	0.39	1.55	0.41
	WAR1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	WAR2	0.00	0.00	0.00	0.00	1.00	3.57	0.11	0.00	0.00
	WAR3	1.16	0.46	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	OLEH1	0.16	0.72	0.23	0.64	0.91	0.00	3.13	0.00	0.00
	OLEH2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	OLEH3	0.00	0.00	0.00	0.00	0.00	0.87	0.00	0.00	0.00
	OZO1	2.33	0.19	1.83	0.00	0.51	0.00	0.61	0.00	0.00
	OZO2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	OZO3	0.00	0.00	0.00	0.00	0.00	1.47	0.00	0.00	0.00
	PTN1	0.49	0.53	0.40	0.00	0.15	0.00	0.42	0.00	0.00
	PTN2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	PTN3	0.00	0.00	0.00	0.00	0.00	0.94	0.00	0.00	0.00
	ASB1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	ASB2	0.00	0.00	0.00	0.00	1.00	2.48	0.16	0.00	0.00
	ASB3	1.11	0.47	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	KWL1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	KWL2	0.61	0.41	0.46	0.23	1.09	0.00	1.06	0.00	0.71
	KWL3	7.50	0.05	5.70	2.78	1.37	0.35	0.39	1.55	0.41
	AGB1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	AGB2	0.43	0.46	0.31	0.15	1.05	0.00	1.74	0.00	1.03
	AGB3	2.85	0.10	1.85	2.98	1.56	1.02	0.42	0.24	2.12
Wet	SAP1	0.33	0.39	0.47	0.00	0.00	0.05	4.41	0.35	0.29
	SAP2	0.00	0.00	0.00	0.00	0.00	0.81	1.32	0.00	0.00
	SAP3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	UGH1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	UGH2	1.00	0.21	2.67	3.00	0.35	0.00	0.00	0.36	0.63
	UGH3	0.48	0.58	0.00	4.03	1.49	3.00	0.81	2.00	3.63
	WAR1	0.64	0.54	0.21	0.00	0.00	0.21	0.00	0.00	1.67
	WAR2	0.00	0.00	0.00	0.86	0.68	0.00	0.00	0.00	0.00
	WAR3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	OLEH1	0.33	0.39	0.47	0.00	0.00	0.05	4.44	0.02	2.47
	OLEH2	0.00	0.00	0.00	0.00	0.00	1.04	0.57	0.00	0.00
	OLEH3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	OZO1	0.33	0.39	0.47	0.00	0.00	0.15	3.12	0.07	2.47
	OZO2	0.00	0.00	0.00	0.00	0.00	0.95	0.45	0.00	0.00
	OZO3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	PTN1	0.18	0.24	2.03	0.00	0.00	0.03	1.30	0.03	2.92
	PTN2	0.00	0.00	0.00	0.00	0.00	0.87	0.43	0.00	0.00
	PTN3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	ASB1	1.48	0.25	1.57	0.00	0.00	0.21	0.00	0.00	1.89
	ASB2	0.00	0.00	0.00	1.13	0.64	0.00	0.00	0.00	0.00
	ASB3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	KWL1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	KWL2	0.97	0.41	0.50	0.73	0.74	0.00	0.00	0.36	1.56
	KWL3	0.48	0.58	0.00	4.03	1.49	2.57	0.81	2.00	0.64
	AGB1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	AGB2	2.68	0.20	1.26	0.44	0.84	0.00	0.00	0.61	1.98
	AGB3	0.70	0.35	0.00	3.94	1.50	1.50	0.81	2.03	1.93

Table 6: Ratios of parent OCPs and metabolites with their interpretations in relations to the sources of OCPs in the soils

Isomeric ratios	Values	Sources	Dry season	Wet season
α-BHC/γ-BHC	> 3	Inputs from technical BHC	UGH3, KWL3	-
	< 3	Fresh/Recent input of γ-BHC	UGH2, WAR3, OLEH1, OZO1, PTN1, ASB3, KWL2, AGB2, AGB3	SAP1, UGH2, UGH3, WAR1, OLEH1, OZO1, PTN1, ASB1, KWL2, KWL3, AGB2, AGB3
γ-BHC/∑BHC	> 1	Historical/aged input	SAP1,	-
	< 1	Inputs from technical BHC	UGH2, UGH3, WAR3, OLEH1, OZO1, PTN1, ASB3, KWL2, KWL3,AGB2, AGB3	SAP1, UGH2, UGH3, WAR1, OLEH1, OZO1, PTN1, ASB1, KWL2, KWL3, AGB2, AGB3
β-BHC/γ-BHC	> 1	Historical/aged input	UGH3, OZO1, KWL3, AGB3	UGH2, AGB2, PTN1, ASB1
	< 1	Fresh/Recent input	UGH2, OLEH1, PTN1, KWL2, AGB2	SAP1, WAR1, OLEH1, OZO1, KWL2
p, p'- DDD/ p, p'- DDE	> 1	DDD is the principal DDT degraded product	UGH3, KWL3, AGB3	UGH2, UGH3, ASB2, KWL3, AGB3
	< 1	DDE is the principal DDT degraded product	SAP1, UGH2, OLEH1, KWL2, AGB2	WAR2, KWL2, AGB2
(p, p'- DDD+ p, p'- DDE)/∑DDT	> 0.5	Long term weathering of historical/aged DDTs	SAP1, UGH2, UGH3, WAR2, ASB2, KWL2, KWL3, AGB2, AGB3, OLEH1, OZO1	UGH3, WAR2, ASB2, KWL2, KWL3, AGB2, AGB3
	< 0.5	Fresh/Recent input	PTN1	UGH2
α-Chlordane/γ-Chlordane	> 1	Historical/aged input	SAP3, WAR2, OZO3, ASB2, AGB3	UGH3, OLEH2, KWL3, AGB3
	< 1	Fresh/Recent input	UGH3, OLEH3, PTN3, KWL3	SAP1, SAP2, WAR1, OLEH1, OZO1, OZO2, PTN1, PTN2, ASB1,
Heptachlor Epoxide/Heptachlor	> 1	Historical/aged input	SAP1, UGH2, OLEH1, KWL2, AGB2	SAP1, SAP2, OLEH1, OZO1, PTN1
	< 1	Fresh/Recent input	UGH3, WAR2, OZO1, PTN1, ASB2, KWL3, AGB3	UGH3, OLEH2, OZO2, PTN2, KWL3, AGB3
Endrin/Dieldrin	> 1	Degradation process	UGH3, KWL3	UGH3, KWL3, AGB3
	< 1	Fresh input of dieldrin	AGB3	SAP1, UGH2, OLEH1, OZO1, PTN1, KWL2, AGB2
Dieldrin/Aldrin	> 1	Fresh input of dieldrin	AGB2, AGB3	UGH3, WAR1, OLEH1, OZO1, PTN1, ASB1, KWL2, AGB2, AGB3
	< 1	Degradation process	UGH2, UGH3, KWL2, KWL3	SAP1, UGH2, KWL3,

Discussion

Distribution of OCPs in the MSWD soils: There were significant ($p < 0.05$) spatial and seasonal variations in the OCPs concentrations in the soils from the MSWD. This significant spatial and seasonal variations could be caused by the physicochemical characteristics of the soil of MSWD and various OCPs source inputs; degradation rates of OCPs (Emoyan *et al.,* 2021; Tesi *et al*. 2020c; Bai *et al.* 2015). The soil quality guideline standard of China classified OCPs in soil into Grade I (HCHs ≤ 50 and DDTs = 50 ng g^{-1}) as negligible pollution, Grade II (HCHs ≤ 500 and DDT = 500 ng g^{-1}) as low pollution, Grade III (HCH ≤ 1000 and DDT = 1000 ng g^{-1}) as moderate pollution and Grade IV (> 1000 ng g^{-1}) as high pollution (Gereslassie *et al*., 2019). Based on this classification, the studied soils of MSWD are negligible polluted with OCPs. The occurrence profiles of the OCPs in these soils are shown in Figure 2. The ∑chlordane is the predominant OCP homologue in the soil of MSWD. The ∑Chlordane concentrations varied from 0.15 to 4.49 ng g^{-1} for dry season and 0.09 to 5.98 ng g^{-1} for the wet season and constitute 11.9 to 84.9 % and 7.3 to 100 % of the Σ_{20}OCPs for dry and wet season respectively. The highest and lowest concentration of ∑Chlordane were obtained in SAP2 and SAP3 for dry season and SAP3 and SAP2 for wet season respectively. The ∑Chlordane obtained in this study were similar to those reported for dumpsite soils from Vietnam and Cambodia (Minh *et al*., 2006) but lower than those reported for dumpsite soils in Ethiopia (Nigatu and Hussen, 2022). The ∑BHC levels in the soils of the MSWD for dry season varied from 0.21 to 2.62 ng g^{-1} and 0.14 to 3.62 ng g^{-1} for the wet season. The ∑BHC constituted 5.6 to 100 % and 6.6 to 53.6 % of the Σ_{20}OCPs for dry and wet seasons. The ∑BHCs obtained in this study were similar to those reported for dumpsite soils from Vietnam and Cambodia (Minh *et al*., 2006) but lower than those reported for dumpsite soils in Ethiopia (Nigatu and Hussen, 2022) and Pakistan (Sultan *et al*., 2019), landfill in Greece (Chrysikou *et al*., 2008) and Slovak republic (Veningerová *et al*., 1997). The highest and lowest concentrations of ∑DDTs in the soils of MSWD were 0.15 and 1.75 ng g^{-1} and constituted 2.3 to 32.5 % of the Σ_{20}OCPs for dry season while for the wet season the concentration ranged from 0.07 to 1.63 ng g^{-1} and constituted 3.3 to 32.2 % of the Σ_{20}OCPs. The levels of ∑DDTs obtained in this study were lower than those reported for soils of dumpsites from Vietnam, India and Cambodia (Minh *et al*., 2006) and Greece (Chrysikou *et al*., 2008). The ∑Endosulfan concentrations in the soil of the MSWD ranged from 0.01 to 1.07 ng g^{-1} and constituted 0.2 to 84.9 % of the Σ_{20}OCPs for dry season and ranged from 0.11 to 1.50 ng g^{-1} and constituted 3.4 to 29.8 % of the Σ_{20}OCPs for the wet season. The highest and lowest concentrations of the ∑Endosulfan were found in SAP2 and UGH3 and KWL3 for dry season while for the wet season the highest and lowest concentrations were found in AGB3 and UGH2. The ∑Endosulfans obtained in this study lower than those reported for dumpsite soils from Jordan (Jiries *et al*., 2002) The concentrations of ∑Drins ranged from 0.01 to 1.55 ng g^{-1} and constituted 0.5 to 28.1 % of the Σ_{20}OCPs for dry season and ranged from 0.12 to 2.18 ng g^{-1} and constituted 1.8 to 89.4 % of the Σ_{20}OCPs for the wet season. The highest concentration of the ∑Drins were found in OZO3 and lowest concentration was found in WAR1 for dry season while for the wet season the highest and lowest concentrations of ∑Drins were found in AGB2 and PTN2 respectively.

Ecological risks of OCPs in the soils: The SQGQs concentrations for the OCPs for dry and wet seasons were generally < 1 indicating no adverse biological health effects on soils organisms in the soils of the MSWD. However, the SQGQs for sites SAP1, OLEH1 and AGB2 for dry season and SAP1 for the wet season were greater than 1 suggesting severe biological health effects of soil organism upon exposure in these four sites (Emoyan *et al.,* 2021). The potential ecological risk posed by OCPs to the MSWD soil was also assessed by comparing the OCPs in the MSWD soils with soil quality standard guidelines (SQSGs). The Netherland SQSG for OCPs in unpolluted soils is 2.5 ng g^{-1} (Zhang *et al*., 2016; Qu *et al*., 2015). The concentrations of OCPs found in this study were lower than the Netherland standard indicating no adverse ecological risk for soil organism in the study area. The concentrations of ∑HCHs and ∑DDTs in the soil of the MSWD were lower than the NOAA ∑BHCs and ∑DDTs TEL values of 11 ng g^{-1} for birds and 10 ng g^{-1} for soil biological communities (Bai *et al*., 2015). This suggested that there is no ecological risk from the OCPs in the MSWD soils.

Human health risk: The hazard quotient (HQ) for both children and adults were such that HQ via ingestion was higher than HQ via dermal contact for both season. The HI values for infants were seven (7) times higher than those of adults for both the wet and dry season. Its shows that infants are at more at risk of OCPs exposure than adults in the MSWD soils. The HI values for infants and adults were < 1 for both season except SAP1, SAP2, OLEH1, OZO1, PTN1, ASB2, AGB2 for dry season and SAP1, SAP2, OLEH1, OLEH2, OZO1, OZO2, PTN1 for wet season. This suggests there is no adverse non-carcinogenic risk for human exposure to OCPs in the MSWD soils. However, for SAP1, SAP2, OLEH1, OZO1, PTN1, ASB2, AGB2 in dry season and SAP1, SAP2, OLEH1, OLEH2, OZO1, OZO2, PTN1 in wet season for infant exposure there is non-carcinogenic risk to infants.

The levels of risk of OCPs in the MSWD soils follows the order of RiskIng > RiskDerm > RiskInh for both season for infants and adults. The RiskIng and RiskDerm values for infants were greater than those of adults. This could be due to the smaller body weight of infants and as well as their high physical contacts with soil. However, the RiskInh for adults were greater than those of infants which could be as a result of longer exposure duration for adults (Emoyan *et al*., 2021; Tesi *et al*., 2020c). The TCR values for infants' exposure were thirteen (13) times higher than those of adults, indicating that infants are at a greater exposure risk than adults from the OCPs exposure in the soils of the MSWD. The values of the TCR obtained were within the acceptable TCR value of 1×10^{-4}, suggesting no adverse carcinogenic risk to infants and adults exposed to the soils from the MSWD.

Source Identification of OCPs: The ratios of parent OCPs and their metabolites were used to identified and categorized the sources of OCPs in this study into fresh or historical usage (Emoyan *et al*., 2021; Tesi *et al*., 2022; Tesi *et al*., 2020c; Tang *et al*., 2018). Tables 4 and 5 clearly indicated that the main source of OCPs in the soils of the MSWD are recent and historical usage of OCPs. The ratios of α-Chlordane/β-Chlordane and heptachlor epoxide/heptachlor from were generally >1 for both seasons and indicated shistorical inputs in the soils of the MSWDs. The ratio of endrin/dieldrin was generally <1 and ranged from 0.24 to 1.55 for dry season and 0.02 to 2.03 for the wet season. While the ratio of dieldrin/aldrin was generally >1 and ranged from 0.41 to 2.12 for dry season and from 0.29 to 3.63 for the wet season respectively, suggesting fresh and recent inputs of dieldrin in the MSWD soils. Also, the ratio of α-BHC/γ-BHC in this study were generally < 3 and ranged from 0.16 to 7.50 for dry season and 0.18 to 2.68 for the wet season. This indicated fresh/recent input of γ-BHC. The ratio of γ-BHC/ ΣBHC were all <1 for both season except SAP1 and indicated inputs from technical BHC. The ratio of β-BHC/γ-BHC indicated both fresh and historical inputs. The ratio of p, p'- DDD/ p, p'- DDE indicated that DDE is the principal DDT degraded product during the dry season while DDD is the principal DDT degraded product during the wet season. The ratios of (p,p′-DDD + p,p′-DDE)/ ΣDDTs were mostly > 0.5 for both season and ranged from 0.15 to 1.56 and 0.35 to 1.50 respectively. This ratio indicates long term weathering of historical/aged DDTs in soils of the MSWD.

Conclusion

This study provides information on spatial and seasonal variations, potential risks and sources of OCPs in MSWD soils from Delta State, Nigeria. The study revealed that there was negligible pollution of OCPs in the MSWD soils. The distribution pattern of OCPs homologues in the soils of the MSWD was in the order of ∑Chlordanes > ∑BHCs > ∑Drins > ∑DDTs > ∑Endosulfans for the dry season and ∑Chlordanes > ∑BHCs > ∑Drins > ∑Endosulfans > ∑DDTs for the wet season. The SQGSs indicated that there is no adverse ecological risk of OCPs in the MSWD soils. The HI and TCR values indicated that there are no associated non-carcinogenic and carcinogenic risks with the OCPs exposure in these soils. The isomeric ratios indicated that the sources of OCPs in the MSWD soils include recent and historical pesticide usage.

References

Abdus-Salam N, Ibrahim MS, Fatoyinbo FT: Dumpsite in Lokoja Nigeria, a silent pollution zone for underground water. J Environ Sci, 3(2): 21-30. 2011.

Amos-Tautua BMW, Onigbinde AO, Ere D: Assessment of some heavy metals and physicochemical properties in surface soils of municipal open waste dumpsite in Yenagoa, Nigeria. Afr J Environ Sci Technol, 8(1): 41-47. 2013.

Aralu CC, Okoye PC, Akpomie KG, Chukwuemeka-Okorie HO, Abugu HO: Polycyclic aromatic hydrocarbons in soils situated around solid waste dumpsite in Awka, Nigeria. Toxin Rev, 42(1): 122-131. 2021.

Ayoola EO, Enwemiwe VN, Oluwagbemi EB, Obi CC, Okushemiya JU, Ufoegbune H, Egwenum J: Determination of polychlorinated biphenyls (PCBs) levels in the soil and water from electronic waste dumpsite at Alaba, Lagos State, Nigeria. FJS 7(3): 133 - 145. 2023.

Bai J, Lu Q, Zhao Q, Wang J, Gao Z, Zhang G: Organochlorine pesticides (OCPs) in wetland soils under different land uses along a 100-year chronosequence of reclamation in a Chinese estuary. Sci Rep, 5: 17624. 2015.

Chrysikou L, Gemenetzis P, Kouras A, Manoli E, Terzi E, Samara C: Distribution of persistent organic pollutants, polycyclic aromatic hydrocarbons and trace elements in soil and vegetation following a large scale landfill fire in northern Greece. Environ Int, 34: 210–225. 2008.

Costa PM, Neuparth TS, Caeiro S, Lobo J, Martins M, Ferreira AM, Caetano M, Vale C, DelValls TA, Costa MH: Assessment of the genotoxic potential of contaminated estuarine sediments in fish peripheral blood: Laboratory versus *in situ*, studies. Environ Res, 111 (1): 25–36. 2011.

Edjere O, Otolo SE, Asibor IG, Adebayo AA, Akande N, Adeigbe A: PCB levels in soil at e-waste dumpsite, Alaba International market, Ojo, Lagos. Scientia Africana, 18(1): 25-27. 2019.

Emoyan OO, Peretiemo-Clarke BO, Tesi GO, Ohwo E: Occurrence, origin, ecological and human health risks of organochlorine pesticides in soils from selected urban, suburban and rural storm water reservoirs. Soil Sediment Contam, https://doi.org/10.1080/15320383.2021.1913993. 2021.

Gereslassie T, Workineh A, Atieno OJ, Wang J: Determination of occurrences, distribution, health impacts of organochlorine pesticides in soils of Central China. Int J Environ Res Public Health, 16: 146. 2019.

Jiries AG, Al Nasir FM, Beese F: Pesticide and heavy metals residue in wastewater, soil and plants in wastewater disposal site near Al-Lajoun Valley, Karak/Jordan. Water Air Soil Pollut, 133: 97–107. 2002.

Lateef TA, Eluwole AB, Adewa DJ: Geoelectrical assessment of the impact of the Iloku dumpsite, Ado-Ekiti South Western Nigeria, on surrounding ground water aquifers. Int Lett Nat Sci, 40: 41-47. 2015.

Long ER, Macdonald DD: Recommended uses of empirically derived, sediment quality guidelines for marine and estuarine ecosystems. HERA, 4(5):1019–39. 1998.

Minh N, Minh TB, Kajiwara N, Kunisue T, Subramanian A, Iwata H, Tana TS, Baburajendran R, Karuppiah S, Viet PH, Tuyen BC, Tanabe S: Contamination by persistent organic pollutants in dumping sites of Asian developing countries: implication of emerging pollution sources. Arch Environ Contam Toxicol, 50: 474–481. 2006.

Nigatu G, Hussen A: Obsolete pesticide residue level analysis and toxicological risk evaluation from Hadya zone dump site, Ethiopia. Bull Chem Soc Ethiop, 36(2), 329-337. 2022.

Ogbeibu AE, Chukwurah NA, Oboh IP: Effects of open waste dump-site on its surrounding surface water quality in Ekurede-Urhobo, Warri, Delta State, Nigeria. Nat Environ, 1: 1-16. 2013.

Okechukwu VU, Omokpariola DO, Onwukeme VI, Nweke EN, Omokpariola PL: Pollution investigation and risk assessment of polycyclic aromatic hydrocarbons in soil and water from selected dumpsite locations in Rivers and Bayelsa States, Nigeria. Environ Anal Health Toxicol, 35(4): e2021023. 2021.

Olayinka OO, Adedeji OH, Ipeaiyeda AR: Determination of polycyclic aromatic hydrocarbons (PAHs) on selected dumpsites in Abeokuta metropolis, SW, Nigeria. Appl Environ Res, 37(3): 33-48. 2015.

Onojake L, Emoyan OO, Tesi JN, Ohwo E: Polychlorinated biphenyls in soils around municipal solid waste dumpsites in selected areas of Delta State, Nigeria. NJSE, 21(1): 42-62. 2023.

Qu C, Qi S, Yang DS, Huang H, Zhang J, Chen W, Yohannes HK, Sandy EH, Yang J, Xing X: Risk assessment and influence factors of organochlorine pesticides (OCPs) in agricultural soils of the hill region: a case study from Ningde, southeast China. J Geochem Explor, 149:43–51. 2015.

Sultan M, Waheed S, Alia U, Sweetman AJ, Jones KC, Malik RN: Insight into occurrence, profile and spatial distribution of organochlorine pesticides in soils of solid waste dumping sites of Pakistan: Influence of soil properties and implications for environmental fate. Ecotoxicol Environ Saf, 170: 195-204. 2019.

Tang J, Feng J, Li G, Liang M, Wang R, Cai C: Occurrence and possible sources of organochlorine pesticides in soils of Ningbo, East China. Earth Environ Sci Trans R Soc Edinb, 109(3-4): 495-500. 2018

Tesi GO, Obi-Iyeke GE, Ossai JC, Ogbuta AA, Ogbara EF, Olorunfemi DI, Agbozu IE: Human exposure to organochlorine pesticides in vegetables from major cities in south-south Nigeria. Chemosphere, 303 (Part 3): 135296. 2022.

Tesi GO, Ojegu JO, Akporido SO: Chemical speciation and mobility of heavy metals in soils of refuse dumpsites in some urban towns in the Niger Delta of Nigeria. Ovidius Univ Ann Chem, 31(2): 66-72. 2020b.

Tesi GO, Ojegu JO, Akporido SO: Distribution and risk of metals in soils of refuse dumpsites in some urban towns in Delta State, Nigeria. Afr Scientist, 21(1): 211-224. 2020a.

Tesi JN, Tesi GO, Ossai JC, Agbozu IE: Organochlorine pesticides (OCPs) in agricultural soils of southern Nigeria: Spatial distribution, source identification, ecotoxicological and human health risks assessment. Environ Forensics, https://doi.org/10.1080/15275922.2020.1850570 2020c.

USEPA: Regional screening levels (RSL) summary tables. http://www.epa.gov/risk/risk-based-screening-table-generic-tables (accessed on 12 December, 2023).

USEPA: Risk assessment guidance for Superfund, Vol. I: Human health evaluation manual. Office of Solid Waste and Emergency Response EPA/540/1-89/002. 1989.

Veningerová M, Prachar V. Kovacicova J, Uhnak J: Analytical methods for the determination of organochlorine compounds: application to environmental samples in the Slovak Republic. J Chromatogr, A 774, 333–347. 1997.

Wang Y, Hu J, Lin W, Wang N, Li C, Luo P, Hashmi MZ, Wang W, Su X, Chen C, Liu Y, Huang R, Shen C: Health risk assessment of migrant workers' exposure to polychlorinated biphenyls in air and dust in an e-waste recycling area in China: Indication for a new wealth gap in environmental rights. Environ Int, 87:33–41. 2016.

Zhang J, Liu J, Yu R, Liu Q, Wang Y: Pollution assessment of organochlorine pesticides in urban agricultural soils of Jilin City, China. Hum Ecol Risk Assess Int J, 22:792- 801. 2016.