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Organochlorine (OC) pesticide residues in soils of major cocoa plantations in Ondo State, Southwestern Nigeria

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Organochlorine compounds were extracted from soils of major cocoa plantations in Ondo State of Nigeria by supercritical fluid extraction and their concentrations were determined by electron capture detector – gas chromatography. The percentage recoveries for the optimized extraction temperatures were 89.99 ± 0.05 to 105.24 ± 0.04 at 60°C and 63.88 ± 1.12 to 93.33 ± 0.15 at 80°C while the analytes were not detected at 50 and 100°C. The extraction pressure was also optimized and percentage recoveries were 54.13 ± 5.03 to 87.98 ± 10.56 and 89.99 ± 0.05 to 105.24 ± 0.04 at 200 and 300 Bar, respectively. Results of routine analysis using the optimized conditions (60°C, 300 Bar) showed that soils of the study area are contaminated by organochlorine compounds (OCCs) in varied degree which ranged from ND to 40.55 ±1.54 µg/g which may be due to pesticide application on cocoa plantations for the control of insect pests and diseases in the study area.

Key words: Organochlorine pesticides (OCPs), soil, supercritical fluid extraction, electron capture detector – gas chromatography (ECD-GC).

INTRODUCTION

Pesticides are substances that protect plants against moulds, fungi, and insects, and hence reduce the percentage of crop loss for harvest and potential loss. Organochlorine (OC) pesticides and polychlorinated biphenyls (PCBs) have been used extensively in agriculture and various industries in the last century. The OCPs are highly resistant to degradation by biological, photochemical or chemical means. They are also toxic, hazardous and bioaccumulate in the environment (Erickson, 1997; Mackay and Shiu, 1997). Their persistence in the environment still makes them to be detected in different environmental matrices such as soil and sediments despite the fact that their use has been banned (Katsoyiannis and Samara, 2004; Okoya et al., 2013). Also some developing countries still use them extensively on large farms (Mathews et al., 2003) as in Cameroon and for vector control purposes in Tanzania (Colombo et al., 1990; Mwevura et al., 2002).

Chemical analysis sometimes requires separation of the analytes from the sample matrix to avoid substances that may interfere with the analysis in the matrix and also to preconcentrate the analytes into the operating ranges of some techniques (Field, 1997). Supercritical fluid extraction (SFE) has proved useful in achieving either role. In addition SFE is advantageous and more environment friendly than other conventional techniques

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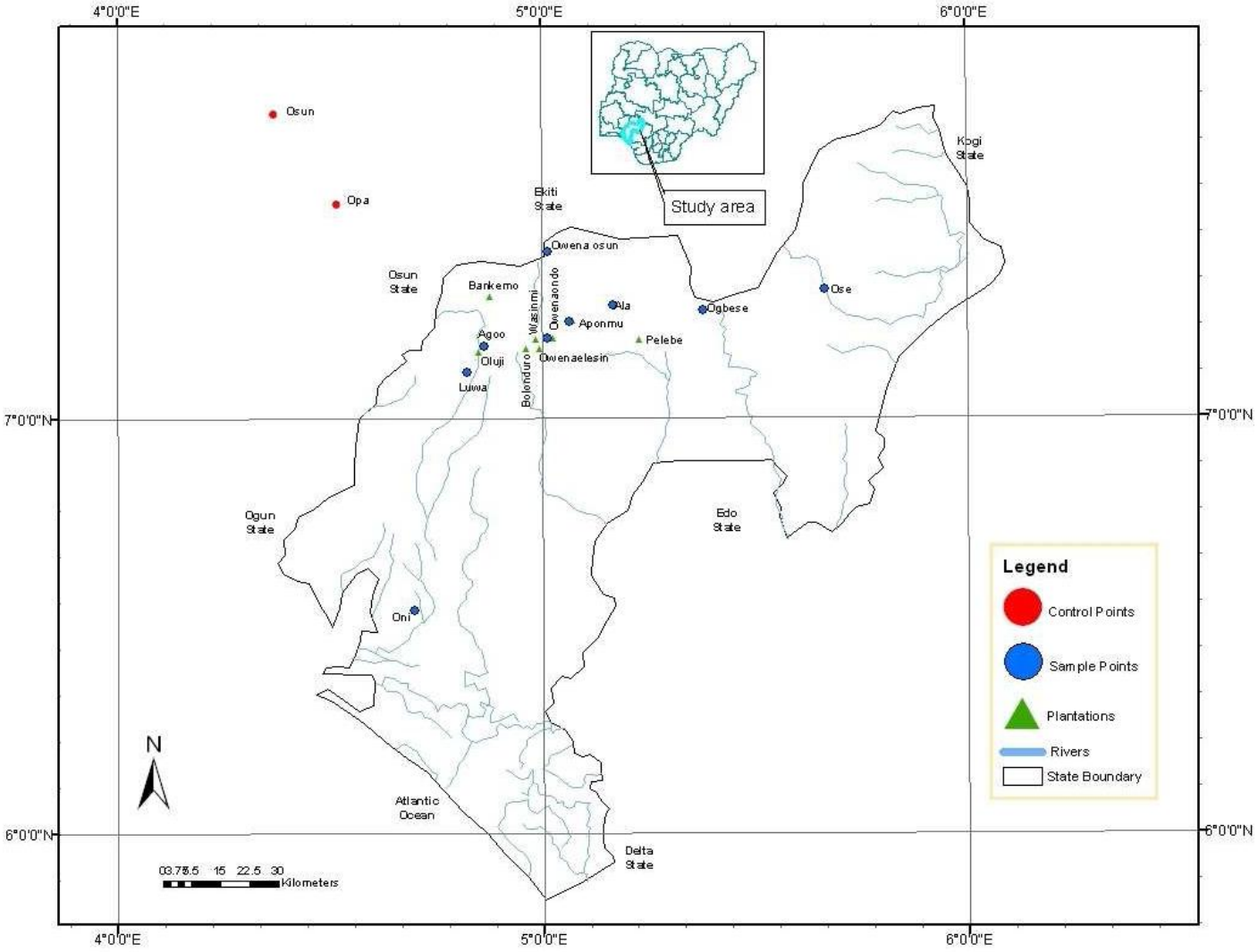

Figure 1. Map of the study area showing the geographical locations of sampling points.

because it does not involve large volumes of hazardous and flammable liquid organic solvents with potential toxic emissions. It is also not time consuming ((Naude et al., 1998; Akinlua et al., 2008). However results obtained with SFE are matrix dependent. Langenfeld et al. (1995) reported that great discrepancies exist between the SFE rates of spiked analytes and incurred analytes. Moreover, certain pesticides that are extracted successfully from foods may be difficult, or require different experimental conditions, for removal from soils. This has also being experienced by researchers when using other sample preparation methods (King, 1997; Haleem, 2001; Torto et al., 2007). There is therefore a need for an approach in SFE where methods are developed directly on contaminated real soil samples.

Hence it becomes necessary to optimize the extraction parameters and assess the performance of SFE on the soils of the major cocoa plantation of Ondo State, Southwestern Nigeria in the determination of some organochlorine compounds for which no such information has been established in the study area.

EXPERIMENTAL

Sampling location and collection of samples

Soil samples from 0 to 5 cm layer were collected randomly from the major cocoa plantation area of Ondo State. These cocoa plantations are located at Oluji, Bamkemo, Bolorunduro, Wasinmi, Owena Elesin, Owena Ondo, Aponmu and Pelebe. Figure 1 shows the geographical locations of the sampling sites and the control. On each cocoa plantation, ten random samples were composited and homogenized. The homogenized soil samples were wrapped up in aluminium foil and then put in a polyethylene bag. Samples were kept cool during transportation to the laboratory.

Chemicals

High purity solvents (Rochelle Chemicals, Ultrafine Limited),

analytical grade chemicals and pesticide standards (Riedel - de Haen, Sigma - Aldrich, Chem Service and Supelco), SFE grade liquid CO_2 and N_2 gas (99.999%) were used for the study as purchased from the manufacturers.

Sample preparation

Soil samples were air dried at ambient temperature. The composite dried soil samples were processed through 2.0 mm stainless steel sieve (Shelton and Capel, 1994; Awofolu and Fatoki, 2003). The less than 63 µm soil samples were prepared using the 63 µm stainless steel sieve prior to analysis. Extraction of each sample was done in triplicate and blank experiments were carried out to establish blank levels.

Supercritical fluid extraction

Applied separations Speed SFE extraction chamber model 7070 (SFE-2, 120VAC) available at the Department of Chemistry, University of Botswana, Gaborone, Botswana was used for SFE. The sample cell of SFE chamber was packed with some glass wool, after which 3 g soil sample fortified with pesticide standards in the concentration range of 1 to 50 ppm and with 500 µl modifier (methanol/acetone mixture ratio 2:3) spiked onto the soil samples were introduced and glass wool was further added to fill the cell completely. The cell was pressurized to 200 bar at 50°C with Supercritical-CO_2 (density = 0.872 g/ml). The pressure was maintained for 20 min (static extraction) and dynamic extraction was carried out for another 30 min. The extract was collected into a glass tube containing 5 ml acetone and then concentrated to about 2 ml on a vacuum rotary evaporator. The same extraction procedure as above was repeated using varied temperatures (60, 80 and 100°C) and pressures (300 and 400 Bar).

Finally, after the extraction was completed for each temperature and pressure condition, the extraction chamber was depressurized according to the equipment manual. The reduced extract was analysed using optimized gas chromatograph – electron capture detector (GC-ECD). The extraction efficiencies at the different temperatures and pressures were determined by comparison of the peak areas of the spiked samples with those of the pesticide standard mixture. The procedure described above was used on the soils from the different cocoa plantations from the study area.

Gas chromatographic analysis

One microlitre each of processed samples was injected into the GC-ECD (Autosystem XL Perkin Elmer (Norwalk, CT, USA) available at the Department of Chemistry, University of Botswana, Gaborone, Botswana in a splitless mode and equipped with a ^{63}Ni electron capture detector. The column used was Zebron ZB 35 fused silica capillary column 30 × 0.25 mm × 0.25 µm (film thickness). The injector and detector temperatures were maintained at 250 and 300°C, respectively. The oven temperature was initially maintained at 50°C (hold 1 min), ramped to 200°C at 40°C/min (hold 2 min), and later ramped to 240°C at 4°C/ min (hold 1 min). This was finally ramped to 270°C at 4°C /min (hold 5 min). The carrier gas was 99.99% nitrogen gas and was maintained at the flow rate of 14 ml/min for optimum performance. Quantitation of the compounds from the samples was by the use of internal standard (Methoxychlor).

Statistical analysis of the data

The various data obtained were subjected to statistical analyses using the New Duncan Multiple Range Tests.

RESULTS AND DISCUSSION

Table 1 shows the retention times and response factors of the twenty two organochlorine (OC) pesticides and polychlorinated biphenyl (PCB) standards plus the internal standard. The compounds were eluted within a reasonable time of less than 25 min under the optimized gas chromatograph – electron capture detector (GC-ECD) conditions.

The results of supercritical fluid extraction of pesticide standards from spiked soil samples carried out at different temperatures and pressures respectively are presented in Tables 2 and 3 as percentage recoveries of organochlorine pesticide standards after extraction of the spiked soil samples. The percentage recovery of the pesticide standards at different temperatures (50, 60, 80 and 100°C) and pressures (200, 300 and 400 Bar) clearly showed that the extraction could best be accomplished at pressures approaching 300 Bar and temperature of 60°C, where the recoveries of the OCPs and PCBs were maxima. It was observed from the results (Table 2) that the extraction of the OCPs and PCBs was not feasible at 50°C whereas the optimum extraction temperature was 60°C. However, the fact that the compounds were no longer detected with the GC-ECD after SFE at 100°C could be due to decomposition of the analytes to residues which may not be detectable either at the extraction temperature (100°C) or with the detector being used.The percentage recoveries ranged from 71.42 ± 0.22% (Aldrin) to 97.03 ± 0.38% (p, p′, DDE) for triplicate analyses. Table 4 shows the concentration of OCPs and PCBs in the soil samples of the cocoa plantations considered for this study. The concentration levels of all the analytes in the soil samples from cocoa plantation in Bolorunduro arequite high except for o,p′- DDD and p,p′ - DDD that were not detected. Almost all the analytes were detected in the samples from Oluji cocoa plantation, although the levels detected are not as high as those from the cocoa plantation at Bolorunduro. The cocoa plantation atWasinmi was young at the period of sampling which may account for why only few of the analytes were detected at relatively low concentrations since very few pesticide applications have been carried out. The concentrations of most of the analytes from the study sites are high relative to the maximum acceptable concentration of 0.1 µg/L value set by the European Union (EU) for water. The maximum allowable limits for these compounds in soil were not available to us at the time of this study. With this background information, the levels of the organochlorine compounds detected in soils of the study area are quite high and may give cause for concern since the residues could find their ways into nearby streams via surface runoff and the effects could be deleterious to aquatic biota and man, as humans are at the top of food chain.

Table 1. Retention times and response factors of organochlorine pesticides and polychlorinated biphenyl standards.

S/N	Standards	Retention time (min)	Response factor
1	PCB#8	8.31	0.41
2	HCB	8.31	0.41
3	α - BHC	8.58	0.48
4	β - BHC	9.74	0.56
5	γ - BHC	9.52	0.54
6	Heptachlor	10.37	0.66
7	Aldrin	10.52	0.96
8	Trans - chlordane	11.37	0.66
9	Cis - chlordane	11.51	1.07
10	α - Endosulfan	13.82	0.45
11	B -Endosulfan	14.07	1.10
12	p,p´-DDE	14.59	0.60
13	o,p´-DDD	14.59	0.60
14	p,p´-DDD	15.41	0.68
15	p,p´-DDT	15.83	1.03
16	Dieldrin	16.38	0.81
17	Endrin	17.16	1.08
18	PCB#8	17.72	0.80
19	PCB#31	18.12	1.05
20	PCB#52	19.09	0.86
21	PCB#95	19.63	0.73
22	PCB#156	21.34	1.03
23	PCB#183	22.96	-

ND = Not detected.

Table 2. Mean % recoveries of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in spiked soil samples by supercritical extraction under 300 Bar pressure at different temperatures.

S/N	Standards	50°C	60°C	80°C	100°C
1	HCB	ND	100.05 ±2.15	75.89±0.01	ND
2	α - BHC	ND	90.46 ±0.01	70.01±0.05	ND
3	β - BHC	ND	93.33 ±2.21	77.37±2.16	ND
4	γ - BHC	ND	99.11 ±6.31	79.52±0.93	ND
5	Heptachlor	ND	89.99 ±0.05	78.11±4..67	ND
6	Aldrin	ND	96.05 ±0.07	80.03±6.01	ND
7	Trans - chlordane	ND	99.65 ±1.03	80.11±4.89	ND
8	Cis - chlordane	ND	98.45 ±2.13	75.87±4.13	ND
9	α - Endosulfan	ND	87.42 ±0.06	70.02±3.01	ND
10	B -Endosulfan	ND	95.19 ±0.02	77.76± 0.54	ND
11	p,p´-DDE	ND	90.96 ±1.02	80.21±7.13	ND
12	o,p´-DDD	ND	105.24 ±0.04	93.33±0.15	ND
13	p,p´-DDD	ND	99.17 ±0.01	76.04±4.01	ND
14	p,p´-DDT	ND	103.22 ± 0.05	80.57±8.07	ND
15	Dieldrin	ND	90.13 ± 0.08	77.47±2.01	ND
16	Endrin	ND	90.01 ±0.01	78.71±5.02	ND
17	PCB#8	ND	93.44 ±0.02	66.05±9.53	ND
18	PCB#31	ND	106.57 ±0.04	68.01±6.63	ND
19	PCB#52	ND	100.25 ±0.01	69.23±4.59	ND

Table 2. Contd.

20	PCB#95	ND	104.09 ±1.34	63.88±1.12	ND
21	PCB#156	ND	96.02 ±2.02	70.01±0.09	ND
22	PCB#183	ND	99.69 ±3.03	74.56±5.99	ND

ND = Not detected.

Table 3. Mean % recoveries of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in spiked soil samples by supercritical extraction at 60°C with different pressures

Standards	200 Bar	300 Bar	400 Bar
HCB	70.01±2.02	100.05 ±2.15	ND
α - BHC	75.67±2.89	90.46 ±0.01	ND
β - BHC	60.54±7.02	93.33 ±2.21	ND
γ - BHC	62.82±4.05	99.11 ±6.31	ND
Heptachlor	64.16±9.07	89.99 ±0.05	ND
Aldrin	60.19±9.43	96.05 ±0.07	ND
Trans - chlordane	72.69±2.53	99.65 ±1.03	ND
Cis - chlordane	78.11±8.07	98.45 ±2.13	ND
α - Endosulfan	73.01±5.12	87.42 ±0.06	ND
B -Endosulfan	79.46±4.85	95.19 ±0.02	ND
p,p´-DDE	54.13±5.03	90.96 ±1.02	ND
o,p´-DDD	63.09±3.88	105.24 ±0.04	ND
p,p´-DDD	70.87±3.98	99.17 ±0.01	ND
p,p´-DDT	87.98±10.56	103.22 ± 0.05	ND
Dieldrin	74.25±4.01	90.13 ± 0.08	ND
Endrin	75.72±5.78	90.01 ±0.01	ND
PCB#8	79.96±5.01	93.44 ±0.02	ND
PCB#31	83.44±0.98	106.57 ±0.04	ND
PCB#52	78.11±4.78	100.25 ±0.01	ND
PCB#95	80.79±5.37	104.09 ±1.34	ND
PCB#156	68.59±2.51	96.02 ±2.02	ND
PCB#183	77.03±9.02	99.69 ±3.03	ND

ND = Not detected.

The concentrations of these compounds in the soil samples of the control site (Osogbo) (Table 4) were either generally lower or not detected compared to those from cocoa plantations of Ondo State. The results of the Duncan multiple range tests for the compounds studied reveal that the mean concentrations of some of the analytes within each cocoa plantation followed by the same alphabet in the same column are not significantly different from one another (Table 4).

Some of the pesticide residues found in the soil samples from the cocoa plantations, such as Chlordane, Heptachlor, DDT, DDE and Endosulfan are known to have implications in a broad range of adverse human health effects including endocrine disrupting properties, reproductive failures and birth defects, immune system malfunction, Parkinson's disease and cancers (Garabrant et al., 1992; Fleming et al., 1994; Mckinnney and Waller, 1994; Afful et al., 2010), which may ultimately impact the bio-diversity of the aquatic ecosystem through surface runoffs. The presence of DDT and some of its degradation residues in the matrix can also be attributed to their wide usage in the study area, more so that they are persistent enough and degrade slowly and easily accumulate in the soil.

Conclusions

A procedure was described for the determination of organochlorine compounds in soil samples from some cocoa plantations. The optimized temperature and pressure for supercritical fluid extraction of these compounds from the soils of the major cocoa plantations of Ondo State, Western Nigeria were determined. Soils of

Table 4. Mean concentration (µg / g) of OCPs and PCBs in soils of some cocoa plantations in Ondo State.

Analyte	Wasinmi	Bamkemo	Aponmu	Bolorunduro	Pelebe	Owena- Elesin	Control	Ile - Oluji
HCB	1.88±1.41^{b}	0.25±0.24^{c}	0.21±0.03^{d,c}	3.26±1.23^{a}	0.24±0.02^{c}	0.18±0.07^{d,c}	ND	0.13±0.03^{d}
α - BHC	0.52±0.07^{b}	0.16±0.08^{c}	0.08±0.06^{e}	15.15±0.05^{a}	0.01±0.01^{f}	ND	ND	0.13±0.11^{d}
β - BHC	0.70±0.20^{b}	0.35±0.15^{c}	0.10±0.01^{e}	12.28±5.56^{a}	0.07±0.03^{f}	ND	ND	0.20±0.02^{d}
γ - BHC	ND	0.45±0.05^{b}	0.07±0.03^{d}	5.67±1.93^{a}	0.05±0.03^{e}	ND	ND	0.09±0.03^{c}
Heptachlor	ND	0.14±0.06^{b}	0.05±0.02^{c}	3.88±2.22^{a}	0.05±0.02^{d}	ND	ND	ND
Aldrin	ND	0.27±0.07^{b}	0.01±0.01^{e}	5.06±1.05^{a}	0.03±0.01^{c}	ND	ND	0.01±0.01^{d}
*Trans - c*hlordane	ND	ND	0.02±0.01^{c}	1.66±1.08^{a}	ND	ND	ND	0.03±0.02^{b}
*Cis- c*hlordane	ND	ND	0.01±0.01^{b}	0.05±0.01^{a}	ND	ND	ND	ND
α - Endosulfan	ND	ND	0.01±0.01^{b}	0.05±0.02^{a}	ND	ND	ND	ND
B-Endosulfan	ND	ND	0.06±0.02^{b}	9.15±0.06^{a}	0.03±0.02^{c}	0.01±0.01^{e}	ND	0.02±0.01^{d}
p,p′- DDE	ND	0.26±0.01^{c}	0.34±0.04^{c}	36.42±1.05^{a}	0.32±0.19^{c}	0.13±0.02^{d}	0.01±0.01^{d}	0.94±0.01^{b}
o,p′- DDD	0.75±0.27^{b}	ND	0.04±0.01^{c}	ND	0.01±0.01^{d}	ND	ND	0.94±0.01^{a}
p,p′- DDD	ND	ND	0.10±0.01^{a}	ND	ND	ND	ND	0.05±0.01^{b}
p,p′- DDT	ND	ND	0.15±0.03^{c}	40.55±1.54^{a}	0.17±0.01^{c}	0.05±0.01^{d}	0.01±0.01^{d}	0.27±0.02^{b}
Dieldrin	ND	0.16±0.02^{b}	0.41±0.15^{a}	0.42±0.03^{a}	0.45±0.15^{a}	0.08±0.02^{c,b}	0.02±0.01^{c}	0.37±0.28^{a}
Endrin	ND	ND	0.30±0.09^{a}	0.01±0.01^{c}	0.05±0.03^{b}	ND	ND	0.05±0.02^{b}
PCB#8	1.88±1.53^{b}	0.10±0.04^{g}	0.21±0.02^{e}	3.02±1.23^{c}	0.24±0.05^{d}	0.18±0.01^{f}	ND	0.33±0.08^{a}
PCB#31	ND	0.41±0.13^{b}	0.05±0.01^{e}	25.29±1.01^{a}	0.13±0.01^{d}	ND	ND	0.25±0.06^{c}
PCB#52	ND	0.34±0.03^{b}	0.08±0.03^{e}	9.40±0.01^{a}	0.22±0.02^{d}	ND	ND	0.26±0.03^{c}
PCB#95	ND	0.06±0.02^{d,c}	.03±0.01^{d,e}	13.49±5.33^{a}	0.09±6.64^{c}	ND	ND	0.45±0.15^{b}
PCB#156	ND	ND	0.16±0.13^{d}	51.19±5.69^{a}	0.24±0.03^{c}	0.02±7.58^{f}	0.12±0.01^{e}	0.49±0.18^{b}
PCB#183	2.85±0.05^{b}	0.14±0.03^{d}	0.14±0.06^{d}	47.16±5.02^{a}	0.07±0.01^{e,d}	0.02±0.01^{e}	0.09±0.04^{e,d}	0.66^{c}±0.57

Data in the column followed by the same alphabets are not significantly different at α = 0.05 using the new Duncan multiple range test. ND = Not detected.

cause for concern. the study area were contaminated with toxic organochlorine compounds in varied degrees and give

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