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ORGANOCHLORINE PESTICIDES ASSESSMENT IN SEDIMENT SAMPLES FROM VAAL RIVER BY ACCELERATED SOLVENT EXTRACTION TECHNIQUE

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ABSTRACT

The excessive use of pesticides has become a global concern owing to the great adverse effect exerted on human health and the environment. The application of Soxhlet extraction (SE) and accelerated solvent extraction (ASE) techniques to the analysis of 15 organochlorine pesticides (OCPs) in sediment samples was described. Sediment samples were obtained from the Vaal River, the largest tributary of the Orange River in South Africa. The method detection limit (MDL) is in the range of 0.01 to 0.25 mg/L, and the average recoveries were in the range 63.2 %-96.0% with standard deviations in the range 3 %-12.5 %. The total OCPs are in the values of 0.352 µg/L, 0.352 µg/L, and 0.212 µg/L in the sediments from Vereeniging, Barrage, and Parys respectively using the ASE method. Higher values of 4,4′-DDE, 4,4′-DDD, and 4,4′-DDT were found in samples collected from Vereeniging and Barrage locations within the range 0.068-0.095 µg/L and 0.063-0.089 µg/L respectively. The mean concentrations of OCPs residues in the sediment samples follows the order: endosulfan I > 4,4′-DDT > 4,4′-DDE > 4,4′-DDD > α-HCH > β-HCH > heptachlor epoxide > trans-chlordane > γ-HCH heptachlor. It was revealed that the ASE was the optimal technique for the analysis of OCPs in sediments. It can be concluded that the accelerated solvent extraction (ASE) is an effective extraction technique for the analysis of organochlorine pesticides from sediment matrices within a short period, and consumes less solvent.

Keywords: Organochlorine Pesticides, Vaal River, Accelerated Solvent Extraction, Soxhlet Extraction, Environment, Sediment

INTRODUCTION

The increasing use of pesticides such as organochlorine in the domestic industry and agriculture activities for controlling pests is polluting the environment daily.[1-6] Pesticides are a collection of substances used for the annihilation of insects, bacteria, fungi, weeds, and others; hence, they are commonly termed insecticides, herbicides, bactericides, rodenticides or fungicides.[7-9] Environmental adulteration due to the disproportionate use of pesticides possesses a great adverse effect on human health and the environment.[7,10-13] The excessive use of pesticides to control the crop-destroying insects have gained momentum in the last two to three decades, which can be linked to rapid urbanization, hence, the need to meet up with the world's population demand. Most OCPs are categorized as persistent organic pollutants (POPs) because they are not broken down easily and/ or can remain in the environs long after application.[2,4,5,7,10,13,14] OCPs vary in their mechanisms of toxicity, chemical structures and persistence in the environment.[14-16] They possess hydrophobic and lipophilic nature, hence; they are likely to accumulate in the fatty tissues of marine and wildlife species.[2,15] Concerning their widespread usage, different media such as air, soil, and groundwater are easily contaminated. These compounds after product usually remain in the soil, thereby decreasing the biodiversity in the soil, and also finds their

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ways into the groundwater by eroding soil.[10,17] The use of these pesticides have been banned in most developed countries owing to their potential neurological effects on humans and the biota. In the same manner, in many developing countries, the use of OCPs has been banned because they are not readily broken down. They contaminate the river, air, soil, lakes, and marine ecosystem via bioaccumulation processes,[7,15,18] also these compounds have been prohibited from use due to their toxic effects.[7,19]

Sample preparation for environmental examination is usually time-consuming and encompasses expensive processes that aim at isolating target analytes. In pesticide residue analysis, extraction is often the most time-consuming step. Comprehensive methods like soxhlet extraction (SE) require the use of long-time cycles (8 - 24 h). Substitute methods like solvent-shake extraction are highly labor-intensive since the use of multiple extraction steps is required unless a machinelike system is employed.[20] Treatment and readiness of samples in these methods are typically low and cost expensive because of the intensive human treatment. Also, large quantities of solvents are often required therefore, the cost of treatment and waste removal often increases the overall cost of sample investigation. In recent times, various new extraction techniques have surfaced, one of which is accelerated solvent extraction (ASE). The principle of ASE is similar to that of SE, with the exception to the elevated temperatures and pressures that are used within the enclosed vessels,[21,22] that allows extraction with a small amount of solvent (< 50 mL), in a very short time (< 20 min) to be completed. Excess use or misuse of organochlorine pesticides has contributed to adverse impacts on environmental healthiness as well as to ecosystem services. Also, pesticides have been reported to affect numerous terrestrial and aquatic species. Such life in aquatic ecosystems like microorganisms, fishes, invertebrates, and plants are severely affected by OCPs.[7,23,24]

In this study, the outcome ASE conditions on the recovery of OCPs residues in sediment from Vaal River, South Africa was evaluated, and the extraction efficiency of ASE and the SE methods correlated.

EXPERIMENTAL

Material and Methods

Every reagent utilized for this study were of analytical and HPLC grade (Merck, South Africa). 99.5% pure of anhydrous sodium sulphate, was deactivated by drying at 400 °C for 3 h in the muffle furnace before use. Each solvent was subjected to three times distillation before use and ranged from 99.0 to 99.5% pure. OCPs standards were obtained from the department of water and sanitation (DWS) research laboratory in Pretoria, South Africa. Kieselgel Merck Typ 77754, 70 to 230 mesh 100 μm was purchased from Sigma-Aldrich, South Africa. Pesticarb was supplied by SMM Instruments (Pty) South Africa and all the gases used were 99.9% pure acquired from Afrox, South Africa.

Sampling Site

Sediment samples were obtained from the Vaal River, the main tributary of the Orange River in South Africa (Fig.-1). The river has its source in the east of Johannesburg, Drakensberg Mountains in Mpumalanga; also, about 240 km from the Ocean and about 30 km north of Ermelo. The river flows westwards to its unification with the Orange River Southwest of Kimberley in the Northern Cape. In length, the river is about 1,120 km and forms the border between Mpumalanga, Gauteng, and North West Provinces on its North bank, and Free State on it is South.[25] It is categorized by high-level pollution mainly by effluent discharges from industries and wastewater treatment works, contaminated stormwater run-off, sewage systems, and leachates from old landfill sites. Three sampling points were selected alongside the Vaal River within Vereeniging and Parys. Sediment samples were collected between June 2015 and October 2016. Samples for this study were collected along the stretch of the Vaal River with the help of geographical information systems (GIS). At every point, three sediment samples were collected, two from the banks, and one from the middle of the River.

Sediment Sampling

Sediment samples were collected below the surface with stainless grab at a depth of 0 – 5 cm into beforehand cleaned wide mouth 500 ml bottles swathed with aluminum foil. Samples were transported to the laboratory in cooler boxes after collection and kept frozen at -5 °C for a maximum of seven days

before analysis. Samples were air-dried in a fume hood at room temperature for 3 days on glass plates. Dried and caked sediment was finely ground in a mortar, and foreign objects such as sticks, leaves, rocks, and glass were discarded.

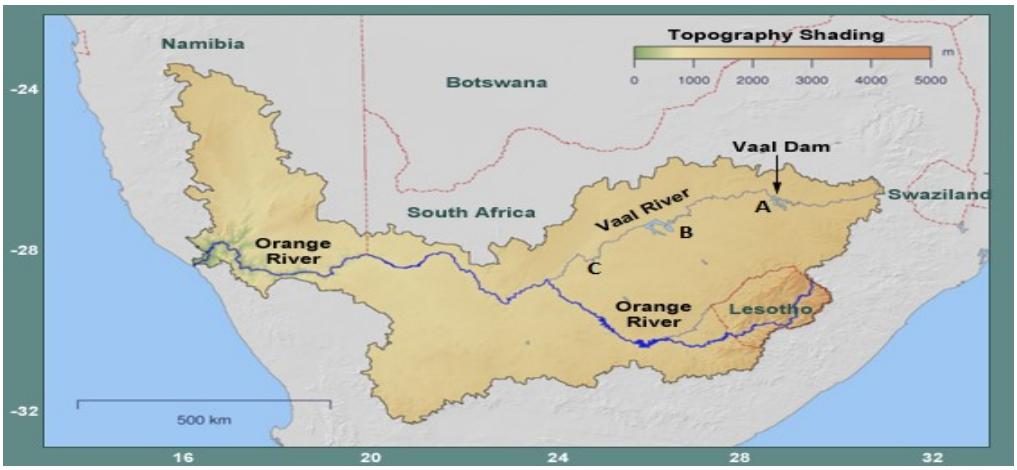

Fig.-1: Vaal River Map along with the Sampling Points: Vereeniging (A), Vanderbijlpark (B), and Parys (C).

Method Development

Sediment extraction was carried out with an accelerated solvent extractor (ASE 350-Dionex, Sunnyvale, CA, USA) equipped with 34-ml stainless-steel cells. The extraction method followed a slightly modified[26] method 3545A. Pre-cleaned (n-hexane was heated in the oven at 200 °C for 1 hour) stainless steel cells were loaded by placing a cellulose filter at the bottom of a tightly screwed cell and followed in the order. 5 g of washed sand, 4.5 g of silica gel, 0.6 g of pesticarb (clean up material), a mixture of 10 g of sample, 10 g of washed and 5 g of sodium sulphate, and another cellulose filter was placed at the top. Cells were tightly screwed and loaded into the instrument at the following condition; temperature- 120 °C, pressure- 11 MPa, heating time- 5 min, cycles- 2, flush volume- 90%, and purged time- 90 s with nitrogen on the one hand for condition 1 and clean-up material (2 g acidic silica, 1 g basic silica and 2 g neutral silica), 150 °C, pressure- 1500 MPa, heating time- 7 min, static state- 8 min and 3 cycles for extraction with condition 2. The solvent used was 60 mL and 100 mL n-hexane/acetone (1:1, v/v) respectively, and this was collected in 100 mL bottles with Teflon septa. Sediment samples were spiked with 1 mL of 0.3 ng/µL of OCPs standard dissolved in acetone. Collected extracts were concentrated to 1 mL under a gentle stream of nitrogen and exchanged solvent to hexane before the injection of an aliquot of 1 µL into the GC-MS for analysis. Each sediment extraction was carried out in duplicates.

Soxhlet Extraction

The authentication of the SE method was performed by spiking dried, sieved and pre-extracted sediment sample with OCP standards in a pre-extracted Whatman extraction thimble (35 mm x 150 mm, Schleicher & Schuell, Germany) and extracted for 16 h with 150 mL of hexane /acetone (1: 1). The extracts were allowed to cool, filtered, and then concentrated at 40 °C to about 2 mL on the vacuum rotary evaporator (Buchi RE-Ill, Switzerland). A comparison of the two extraction techniques is presented in Table-1. The remaining extract was carried through the column chromatographic clean-up process by a silica gel cartridge before GC-MS analysis.

Instrumental Analysis

Sediment extracts were analyzed using a gas chromatograph coupled with a mass spectrometer, 1 µL was injected on-column. The GC was equipped with a 2 m × 0.53 mm deactivated fused-silica precolumn and a 30 m × 0.32 mm capillary column (film thickness 0.25 µm). The flow velocity of helium was regulated at 50 cm/s. Temperature programming was performed as follows: 1 min at 60 to 250°C at 10 °C/min, and 4 min at 250°C. The GC-MS interface temperature was programmed to 300°C. Detection was accomplished in the electron impact ionization mode and single-ion monitoring (SIM). Correct

identification and quantification of a given analyte were ascertained via two compound-specific ions, and a mass ratio similar to the one determined with calibration (variation < 10%).

Table-1: Comparison of Soxhlet Extraction (SE) and Accelerated Solvent Extraction (ASE) techniques

Parameter	Accelerated Solvent Extraction (ASE)	Soxhlet Extraction (SE)
Extraction time	20 min	16h
Volume of solvents	20-30 ml	150ml
Automation	Automatic	Manual
Cost of solvent	Low	High
Recovery of analyte	High	High
Analyte loss	Lower	Higher

RESULTS AND DISCUSSION

Amongst the most widely used pesticides in developing countries, organochlorine insecticides like DDT, Aldrin, Hexachlorocyclohexane (HCH), and Dieldrin are chief, and this could be due to their low cost and their requirement against various pests.[27] The application of SE and ASE) techniques to the investigation of 15 OCPs in sediment samples obtained from the Vaal River, South Africa was evaluated in this study. The results obtained from the ASE technique were compared with the results obtained from the conventional SE technique, as presented in Table-2.

To confirm that the developed method is appropriate for the proposed use, and achieve the purpose of this study, the validation process was carried out. The quantification of OCPs was obtained using a matrix calibration curve with an internal standard. The SE showed recoveries in the range 62.2-92.5% (Table-2), and the standard deviations were in the range of 4.0-15.0%. The only exception was Dichlorodiphenyltrichloroethane (4,4′-DDT), which had an average standard deviation of 21.1%. This observation could be due to the chemical conversion reactions or other losses that might have taken place during the long extraction procedure.[22]ASE recoveries were in the range 63.0 – 96.0% with standard deviations in the range of 3.0-12.5% (Fig.-2). The highest recoveries were observed for 4,4′-DDT and Dichlorodiphenyldichloroethylene (4,4′-DDE) with 91% and 96%, respectively by ASE method, and 92.5% for 4,4′-DDE by SE method.

Overall recoveries found from the two techniques were quite close. However, ASE showed a better reproducibility compared to the other method SE. The data presented in Table-2 indicate that the ASE system provides excellent recovery and precision for the extraction of organochlorine compounds from sediment samples. Also, ASE is essentially equivalent to classical extraction procedures like Soxhlet for the extraction of OCPs from environmental matrices. In addition to being equivalent to Soxhlet, ASE can execute the extractions in a fraction of the time, utilizing less solvent. These results also indicated the high accuracy of the ASE method over SE as investigated. The MDLs for OCP for ASE and SE was found to be in the range 0.01-0.23 mg/L and 0.01-0.18 mg/L, respectively. Low and high values of MDLs (Fig.-3) enable the detection and quantitation of the various OCPs in sediments at low concentrations.

MDLs for many of the components were less than 0.20 mg/L, except for 4,4′-DDT, trans-chlordane and heptachlor where it is 0.23, 0.21, 0.23 mg/l by ASE method, while trans-chlordane showed the highest MDLs value of 0.18 mg/L, followed by 4,4′-DDT with a value of 0.15 mg/L by SE method (Fig.-3). The detection limit increasing trend for ASE was found in the order: 4,4'-DDT = heptachlor > trans-chlordane > aldrin = δ-HCH > γ-HCH > β-HCH > 4,4′-DDE > 4,4′-DDD > heptachlor-epoxide > α-HCH > endosulfan i > endrin = dieldrin = methoxychlor. MDLs reached by the developed method for 4,4′-DDT and heptachlor is 0.23 mg/L, which is 23 times higher than Endrin, Dieldrin, and Methoxychlor. Time, analyte loss, and solvents consumption in the current method was reduced by the application of ASE technique instead of SE, the same was observed in other studies.[28,29] Miller and Miller[30] recommended the comparison of different procedures to find reliable detection limit values.

Application of ASE Technique to Sediment Samples

Statistical handling of data from three locations along the Vaal river: Vereeniging, Barrage and Parys were conducted on the fifteen (15) OCP residues namely α-HCH, β-HCH, γ-HCH (lindane), δ-HCH, aldrin, heptachlor, heptachlor epoxide, trans-chlordane, 4,4′-DDE, 4,4′-DDT, 4,4′-DDD, endrin, dieldrin,

and methoxychlor. As the sediment samples were extracted three times, the statistical implication of the extraction technique via the LSD approach was assessed. Ten of them (excluding δ-HCH, Aldrin, Dieldrin, Endrin, and Methoxychlor) were detected and quantified in sediment samples (Tables-3) with concentrations ranging below MDLs to 0.352 µg/L dry weight. From the statistical analysis examined, the mean concentrations of the studied organochlorine pesticide residues in sediments from the three different sampling sites along the Vaal river did not differ significantly. The mean concentrations of OCPs residues (Fig.-4) found in the sediment samples from the Vaal river follows the order: endosulfan I > 4,4′-DDT > 4,4′-DDE > 4,4′-DDD > α-HCH > β-HCH > heptachlor epoxide > trans-chlordane > γ-HCH > heptachlor. According to the presented results in Table-3, it was observed that the content of total OCPs is in the order: 0.352 µg/L in the sediments from Vereeniging, 0.354 µg/L in sediments from Barrage, 0.212 µg/L in the sediment collected from Parys.

Table-2: Recovery and MDL of OCPs Determinations in Sediment Samples

Compound Name	Accelerated Solvent Extraction (ASE)			Soxhlet Extraction (SE)		
	MDLs (mg/L)	% RSD	% Recoveries	MDLs (mg/L)	% RSD	% Recoveries
α- HCH	0.06	9.8	79	0.04	12.2	70
β - HCH	0.13	10.6	88	0.082	11.9	79
γ- HCH	0.16	4.6	77	0.077	6.3	72
δ- HCH	0.18	4.1	82	0.11	5.8	77
Trans-Chlordane	0.21	3.9	85	0.18	5.9	81
4,4′-DDD	0.11	12.1	87	0.03	14.6	83
4,4′-DDE	0.124	10.8	96	0.05	13.8	92.5
4,4′-DDT	0.23	12.3	91	0.15	21.1	85
Dieldrin	0.01	8.2	68	0.01	9.3	63
Endosulfan I	0.02	6.1	84	0.01	8.3	80
Endrin	0.01	3.3	65.3	0.01	5.4	62.2
Methoxychlor	0.01	3.2	68.1	0.01	4.2	63.2
Heptachlor-epoxide	0.09	5.6	77	0.02	7.1	70
Heptachlor	0.23	5.3	64	0.09	6.9	62
Aldrin	0.18	8.6	71	0.11	10.5	63

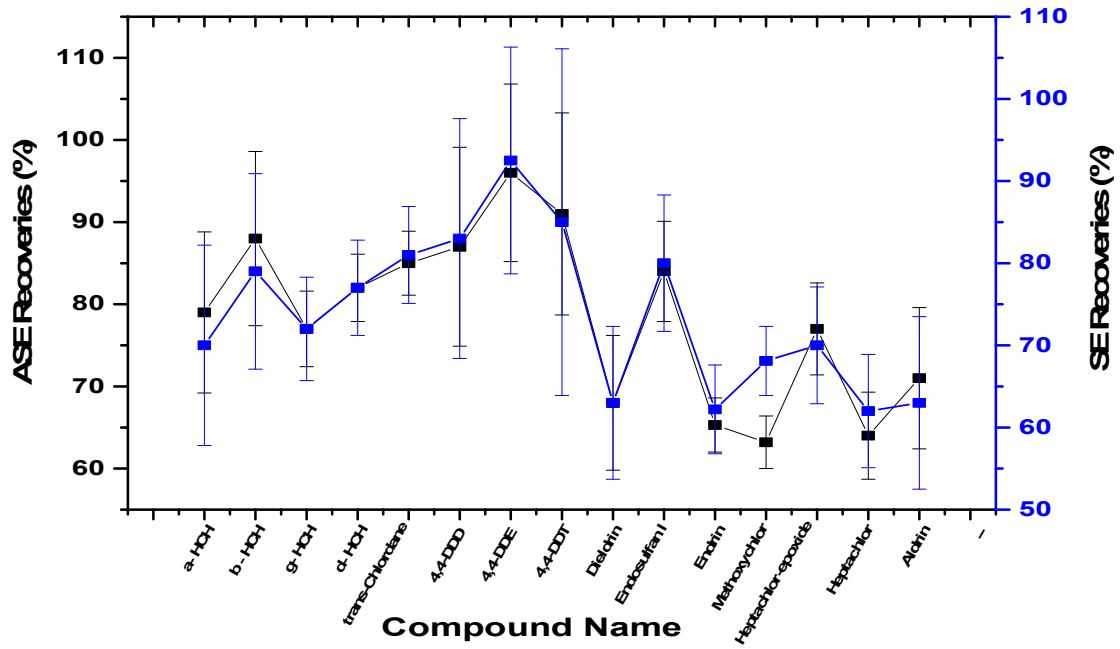

Fig.-2: Recoveries of Organochlorine Pesticides (OCPs) in Sediment Samples using ASE and SE Methods

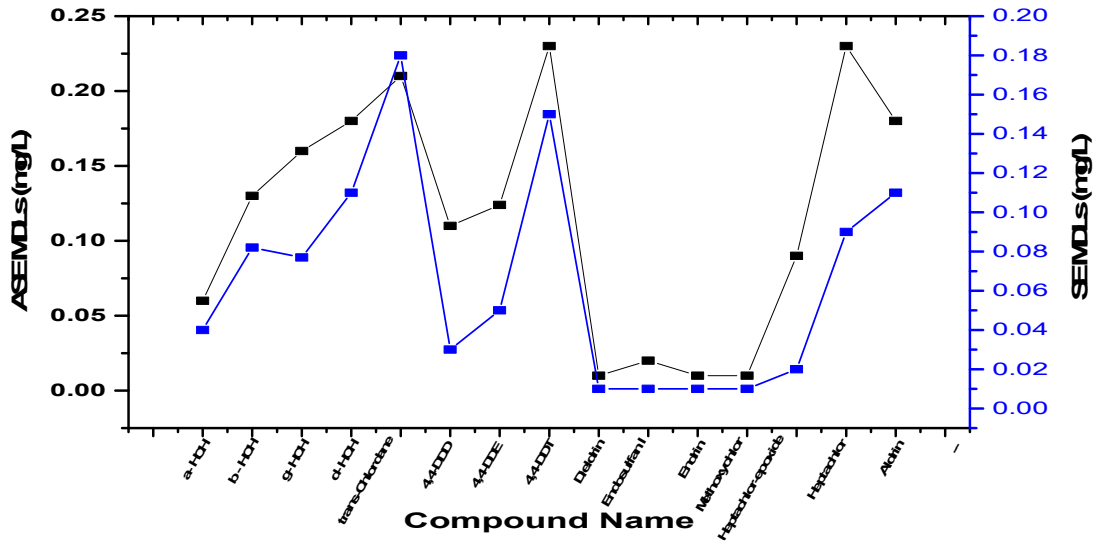

Fig.-3: Method Detection Limit (MDLs) of OCPs in Sediment Samples using ASE and SE

Of all detected OCPs in the sediment, the lowest values were detected in Parys, a region characterized by rock bottom, while the highest values were found in Barrage sediment, a region characterized by mainly muddy consistency with the presence of organic waste in a phase of disintegration. In similar studies, a positive correlation was perceived for exposure to some OCPs in human beings within the U.S. population.[31] Potential neurotoxic effects of OCPs were reported on early psychomotor growth even at low dosages.[32] A potential risk factor for gallstone disease in humans around Xiamen has been associated with exposure to OCP residues.[33] Interference with neonatal thyroid hormone status has been reported to be associated with early exposure to certain environmental compounds, particularly organochlorine compounds, exhibiting endocrine disruption action in newborn from Southern Spain.[34] Sarah and co-workers in 2011, reported that grasscutter (*Thryonomys swinderianus*), a good source of protein for the people of Ghana in Africa, is also a potential carrier of OCP residues.[35]

Table-3: Mean Concentrations of OCPs Residues in Sediment Samples (µg/L) from Rivers

Compound Name	Vereeniging	Barrage	Parys
α- HCH	0.009	0.008	0.002
β - HCH	0.005	ND	ND
γ- HCH	0.002	0.002	0.001
δ- HCH	ND	ND	ND
ΣHCHs	0.016	0.01	0.003
Heptachlor	ND	0.002	ND
Aldrin	ND	ND	ND
Heptachlor-epoxide	0.003	0.005	ND
Trans-Chlordane	0.002	0.004	ND
Endosulfan I	0.10	0.11	0.06
4,4′-DDT	0.095	0.089	0.06
4,4′-DDE	0.077	0.063	0.051
4,4′-DDD	0.068	0.071	0.038
ΣDDTs	0.0231	0.223	0.149
Dieldrin	ND	ND	ND
Endrin	ND	ND	ND
Methoxychlor	ND	ND	ND
ΣCyclodienes	0.105	0.121	0.06
ΣOCPs	0.352	0.354	0.212

*ND (not detected)

It has been well established that as pesticide age in samples like sediments, their extraction efficiency decreases.[36] The highest extraction quantities of the six OCPs obtained by the ASE method could be ascribed to the crucial role of the extraction pressure and temperature when extracting pollutants from sediment samples. Contact years between OCPs and sediments cause some pesticides or their transformed products to bind strongly to the organic matter or clay mineral fractions available in the sediments leading to the formation of a complex known as sediment-bound pesticide residues.[7,37]

The prevalent OCP residues in sediment samples were α-HCH, γ-HCH, endosulfan I, 4,4′-DDD, 4 4,4′-DDE, and 4′-DDT (Fig.-4). The total HCH's found in the sediment samples from the Vaal river follow the order: Vereeniging > Barrage > Parys; total cyclodienes follows the order: Barrage > Vereeniging > Parys; total DDTs follows the order: Vereeniging > Barrage > Parys. It is interesting to note that the content of total cyclodienes was found higher in Barrage followed by Vereeniging with 0.121 and 0.105 µg/L, respectively. This could be due to the constant anthropogenic activities around these sampling sites. Owing to the shift from rural to urban living, industrialized economies in Africa and developing countries, the release of contaminants into water, soil, and air have been amplified. These contaminants including pesticides, like organochlorine, heavy metals, toxic industrial chemicals, and other hazardous wastes, have been reported to obstruct the neonatal thyroid hormone status in human beings owing to their endocrine-disruption activity.[34,38,39]

Total endosulfan exhibited an analogous distribution as total HCH and showed the lowest value of 0.003 µg/L in the samples from Parys, and the highest value of 0.016 µg/L was measured in Vereeniging samples (Fig.-4). Technical endosulfan comprises of α- and β-isomers, and it is one of the few cyclodienes pesticides that are still in use all over the world extensively to control several insects and pests on crops.[15] Because the contamination with endosulfan is evidenced in the environment even in substantial distances from the source of its application,[40,41] many authors have detected its presence in the atmosphere, soils, estuaries, sediments, rainwater, surface, and foodstuffs.[14,15,42-45] Endosulfan is usually retained in the environment for a longer period and thus, bio-accumulates in plants and animals, thereby leading to the adulteration of humans consumed food.[46] Oxidation of cyclic sulphite group of endosulfan gives rise to endosulfan sulphate, or it's hydrolysis in aquatic systems to form endosulfan diol that is persistent in the environment than its parent form.[15,44, 47] The biochemical effects of endosulfan in humans include the adverse effects on the humoral and cell-mediated immune system, macrophage migration, and a decrease in the white blood cell count. Endosulfan can also affect the spermatogonial cells, quality of semen, sperm count, the morphology of sperm in male sex hormones leading to DNA mutation and damage.[7,15]

The mean concentrations of β-HCH and δ-HCH quantified in sediment samples ranged from 0.001 to 0.005 µg/L; this value is higher than the average of HCH concentrations reported by Gbeddy et al.[15] in sediment samples from the Volta Lake. Studies on OCPs have revealed that HCB, β-HCH, and DDT remain bio-accumulate in maternal and cord sera, from maternal blood, they can be conveyed via the placenta. It affects new-born babies thyroid hormone levels[48] and has also caused a decrease in birth weight of infants as reported by a study conducted in China.[49] The obtained results clearly showed that γ-HCH is evidenced with the lowest contents in the sediment of all researched locations in comparison with the other OCPs. This opposes the report by Gbeddy et al.[15] that γ-HCH (lindane) was not detected in any of the analyzed sediment samples from Volta Lake, Ghana. Although the values of this pesticide are below the detection limit, the low values can be explained by the fact that γ-HCH is characterized by higher solubility compared to the rest of the pesticides.[50] Pesticides detected in the sediment samples, including chlordane, DDT, heptachlor, endosulfan, and DDE are known to possess estrogenic and endocrine-disrupting features, that may significantly impact on the aquatic ecosystem biodiversity.[7,15,22,37]

Heptachlor epoxide and trans-chlordane concentrations were detected present only in sites: Vereeniging and Barrage (Table-3) within 0.002 to 0.005 µg/L. OCP heptachlor has been described to induce mitochondria-mediated cell death through electron transport chain complex III impairing. This compound acts as a neurotoxicant with a possible relationship to Parkinson's disease.[51,52] Amongst the French Caribbean women, chronic exposure to chlordecone has been reported to have caused hypertensive disorders in gestational diabetes mellitus and pregnancy.[53] The existence of DDT and some of its degradation residues in the matrixes can be accredited to their wide usage before banning.[54,55] Since these

compounds are persistent and easily get accumulated in the soil, they can be transported as those adsorbed on solids and later solubilized by the surface water down to the water sources.[14] A wide variety of acute and chronic effects on human fitness such as increased diabetes, risk of breast cancers, endocrine disruptor chemicals, and liver disease are associated with exposure to DDT.[45,52,56,57] The persistent half-life of DDT in the aquatic environment has been recommended to be approximately 5 years,[7] 10–20 years projected from studies in bivalves.[58,59] As different DDT metabolites persist for a long time in the environment, their gradual disintegration takes place under aerobic conditions as DDE and DDD.[14,45] The presence of the banned OCP residues in sediment samples from the study river is an indication that these chemicals are still being used, illegally, either on the farmlands around the river for pests or insect control. Therefore, routine monitoring of pesticide residues in the study area is essential for prevention, control, and reduction of environmental pollution, thereby leading to minimize associated health risks. Likewise, the need to create awareness to the farmers on safe pesticide use as a way to reducing the levels of pesticide residues in soils, drinking water, and aquatic biotas around the study area and other environs.

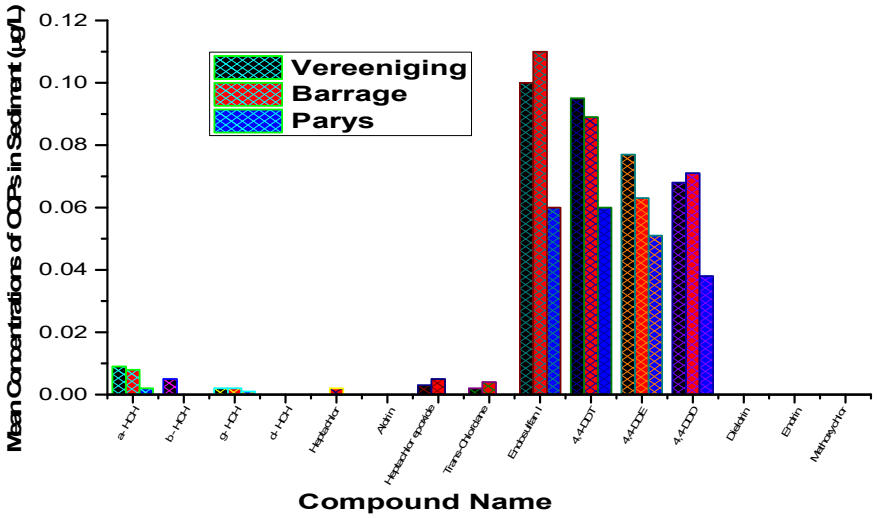

Fig.-4: Mean Concentrations of OCPs Residues in Sediment Samples

CONCLUSION

The extraction of 15 OCPs using SE and ASE techniques were evaluated, with a mind to finding the technique that offers the ability to detect the lowest amount of analyte. It was observed that the ASE is an effective extraction technique for analysis of OCPs from complicated sediment matrices in a short period, and it is less solvent-consuming and capable of high automation. The ASE technique used for the extraction of OCPs with hexane/acetone (1:1) in sediment samples was successful for the extraction of organochlorine compounds. The method makes available comparable or even better results than the SE, with OCPs recoveries in the range of 63 - 96%. High or low recoveries of the analytes of interest are therefore accredited to random or systematic errors in the clean-up extracts steps or the quantification step using GC-MS.

This study thus shows a reduced trend on the environmental burden of OCPs in the aquatic ecosystem of the Vaal River, South Africa. Thus, the necessity to sensitize farmers and agriculturists on the safe use of pesticides. This is imperative to decreasing the levels of pesticide residues in sediments, soils and drinking water around the studied river system, the largest tributary of the Orange River. The study, therefore, advocates routine monitoring of pesticide residues in the area of study, an essential matter for the prevention, control, and reduction of environmental pollution towards minimizing associated health risks.

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