Persistent organochlorine pesticide residues in freshwater systems and sediments from the Eastern Cape, South Africa

RO Awofolu[1] and OS Fatoki[2*]
[1]*Department of Chemistry, University of Fort Hare, Alice 5700, South Africa*
[2]*Research & Development Office, University of Venda for Science & Technology, P/Bag x5050, Thohoyandou 0950, South Africa*

Abstract

Persistent organochlorines such as ΣDDT, chlordane, hexachlorobenzene (HCB), heptachlor and endosulfan were determined in water and sediment samples of freshwater systems in the Eastern Cape Province of South Africa that receive runoff from agricultural lands and effluents from industries. The organochlorine pesticides (OCPs) in water and sediments were determined by liquid/liquid extraction and Soxhlet extraction methods, respectively. Percentage recoveries ranged from 71.03 ± 8.15 % (dieldrin) to 101.25 ± 2.17 % (α-BHC) in water and from 88.22 ± 7.85 % (endrin) to 109.63 ± 5.10 (β-BHC) in sediment. The OCP levels ranged from trace (2,4'-DDD) to 450 ± 0.0002 ng/ℓ (β-BHC) in water samples and from trace (aldrin and 2,4'-DDD) to 184 x 10^3 ± 0.7 ng/kg (β-BHC) in sediments for triplicate analyses. Some endocrine-disrupting OCPs such as 2,4'-DDT, 4,4'-DDT, 2,4'-DDE, heptachlor, endosulfan and the chlordanes were detected.

Keywords: organochlorine pesticides, water, sediments, GC-ECD

Introduction

The presence of organochlorine pesticides (OCPs) in the environment has been of great concern due to their persistent nature and chronic adverse effect on wildlife and humans. Despite the ban and restriction on the usage of OCPs in developed countries during the 1970s and 1980s, some developed countries are still using them for agricultural and public purposes because of their effectiveness in controlling various insects (Tanabe et al., 1994). The early spectacular success of dichlorodiphenyl-trichloroethane (DDT) for malaria control in some countries has seen the continuous use of this insecticide in developing countries. Studies have suggested that these compounds may affect the normal function of the endocrine system (Hileman, 1994). The ability of the prevalent isomer of the major and most persistent DDT derivative, 2,4*'*–dichlorodiphenyldichloro-ethylene (2,4*'*-DDE), to bind to the androgen receptor in male rats has been reported (Keice et al.,1995). OCPs have also been linked to human breast and liver cancers and to testicular tumors and lower sperm counts in humans (Davies and Barlow, 1995; Cocco et al., 1997).

The appearance of DDT and its metabolites in human tissues and its effect on wildlife (USEPA, 1975) triggered its determination in food (Doong and Lee, 1999), water (London et al., 2000) and human milk (Okonkwo et al., 1999). OCP residues have also been found in sediment (Naude et al., 1998) and wildlife (Heath and Claessen, 1999) at significant concentrations.

Water monitoring for OCPs in South Africa (Weaver, 1993; Grobler, 1994; Naude et al., 1998; London et al., 2000), developed European (Fernandez-Alba et al., 1998), Asian (Iwata et al., 1994) and American (Dorothea and Muir, 1991) countries, has shown a widespread occurrence of residues of these pesticides in environmental water systems, though they have been banned for decades. In developing countries such as South Africa, this group of chemicals is still used in agriculture, and it is believed to still be in use clandestinely under unknown trade names, due to their low cost. DDT is still used officially in malaria areas for malaria vector control applied by the Department of Health and Welfare. However, there is still a paucity of data on OCP residues in the South African water environment.

Liquid/liquid extraction (LLE) is a common method used for the determination of organic pollutants in water (USEPA, 1984; Tan, 1992; Hernandez et al., 1993; Powell, 1995). The study by Tan (1992) has shown this method as more reliable than solid phase extraction. The use of commercial solid phase extraction cartridges during sample preparation has been shown to render interferences, especially when gas chromatography-electron capture detection is used for analysis. Extraneous peaks, which appear in the gas chromatograms, have been attributed to phthalate esters contained in the housing materials of these cartridges. The liquid/liquid extraction method was evaluated in this study using 15 OCPs in water from freshwater sources using dichloromethane (DCM) as solvent. This study indicated that the liquid/liquid extraction method for sample enrichment of OCPs in the environmental water samples would render to more reliable data.

Soxhlet extraction (SE) is an established technique that has been used for the extraction of organic pollutants from marine sediment and soil samples (USEPA, 1990; Snyder et al., 1992). In this study, a Soxhlet extraction method for the determination of 15 OCPs in sediment was evaluated.

The methods – liquid/liquid extraction and Soxhlet extraction were applied to monitor for OCP residues in freshwater systems. The study areas selected were the Buffalo, Keiskammahoek, Tyume and Swartkops Rivers as well as the Sandile Dam, in the Eastern Cape Province of South Africa.

The objectives of this work were to use the liquid/liquid extraction and Soxhlet extraction methods that would be evaluated to determine the levels of OCPs in freshwater and sediment from the Eastern Cape and to assess whether the levels detected in water and sediment pose cause for concern.

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* To whom all correspondence should be addressed.
☎+2715 962 8504; fax: +2715 962 8493; e-mail: Fatoki@univen.ac.za
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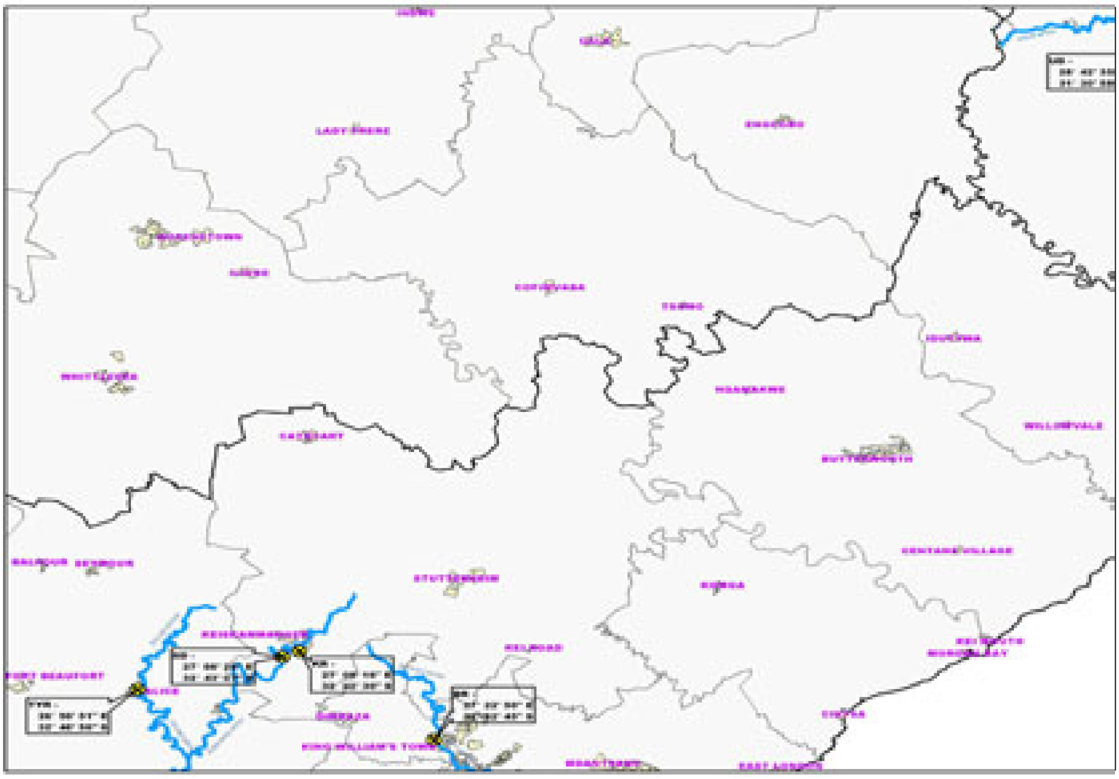

Figure 1

Map of the sample sites.

BR = Buffalo River, KR = Keiskamma River, SD = Sandile Dam, TYR = Tyume River, UD = Umtata Dam, UR = Umtata River

Experimental

Apparatus

Analyses were done using a Perkin Elmer AutoSystem XL gas chromatograph fitted with an electron-capture detector. A Quadrex Corporation, New Haven CT, USA bonded-phase fused silica capillary column, methyl 5% phenyl silicone (30m x 0.53mm i.d. x 2 µm) was used. A glass injector liner (8cm x 3mm), manually packed with silanised glass wool and supplied by Perkin Elmer Instrument Pty, Johannesburg, South Africa was attached to the injector end of the column.

Reagents

All the solvents used, n-hexane, dichloromethane (DCM), light petroleum, acetone and distilled water were of analytical grade. OCP standards were purchased from Sigma-Aldrich (Germany). All standard solutions were prepared by preparing a stock solution of 1 000 mg/ℓ in hexane, which was kept in a fridge. These solutions were further diluted as required.

Determination of response factors

The response factor (RF) of the standard pesticides relative to a (pentachloronitrobenzene) internal standard (I.S), was determined by injecting 1.0 mℓ of a mixture of the organochlorine standard pesticides and the internal standard at a concentration range of 60 to 400 ng/ℓ. The response factor was calculated based on the equation below:

$$\text{Response factor} = \frac{\text{Peak area of the pesticide standard}}{\text{Peak area of the internal standard}}$$

Liquid/liquid extraction (LLE)

All glassware used was washed with liquid soap and rinsed properly with distilled water, and then with pure acetone (analytical grade). They were then baked in an oven at 100°C for 24 h and 1 ℓ volume of pre-extracted river water was fortified with a pesticide standard mixture, at varying concentrations (between 60 ng/ℓ and 400 ng/ℓ) to investigate the potential effect of the matrix on extraction efficiency. The fortified mixture was extracted with 3 x (15 mℓ) of dichloromethane. The extracts were combined, dried with anhydrous sodium sulphate and concentrated to about 2 mℓ using Buchi rotary vacuum evaporator for chromatographic clean-up.

Blank extraction of non-fortified ultra-pure distilled water (prepared by passing doubly distilled water through a Milli-Q purifier system) was carried out using a dichloromethane extraction and chromatographic clean-up method as described below.

Silica gel column chromatography (clean-up)

A chromatographic column (20 cm x 8 mm I.D.) was slurry-packed with 5.0g of activated analytical grade silica gel, made into a slurry with about 1.2% v/m water-adsorbent in distilled water and stirred before use. Approximately 0.5 mℓ of anhydrous sodium sulphate was placed at the top of the column to absorb any water in the sample. The column was pre-eluted with 15 mℓ of light petroleum and prior to the exposure of the sodium sulphate layer to air, the reduced extract from the earlier LLE process was placed in the column and allowed to sink below the sodium sulphate layer. OCPs were then eluted with 2 x (10 mℓ) portions of the extracting solvent. The eluate was collected, dried with anhydrous sodium sulphate and evaporated to dryness using a Buchi vacuum rotary evaporator. Internal standard (Pentachloronitrobenzene) was added and the residues were re-constituted with 2 mℓ of the extracting solvent for gas chromatographic (GC) analysis.

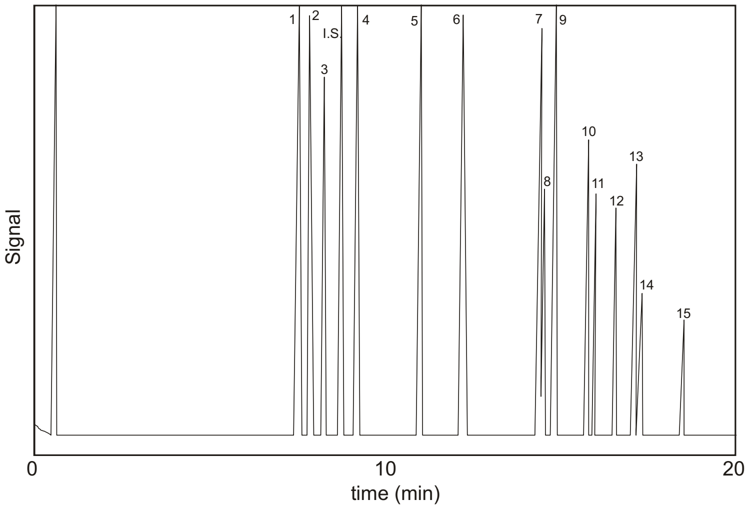

Figure 2
Gas chromatogram of organochlorine pesticide standards. (1) α-BHC, (2) HCB, (3) β-BHC (I.S.), internal standard (pentachloronitrobenzene), (4) δ-BHC, (5) Heptachlor, (6) Aldrin, (7) γ-Chlordane, (8) 2.4'-DDE, (9) Endosulfan, (10) Dieldrin, (11) 2.4'-DDD, (12) Endrin, (13) 4.4'-DDD, (14) 2.4'-DDT, (15) 4.4"=DDT

Soxhlet extraction (SE)

Ten grams of dried, sieved and pre-extracted sediment sample was weighed into a pre-extracted Whatman extraction thimble fortified with pesticide standards in the range of 30 x 10^3 ng/kg to 300 x 10^3 ng/kg and then extracted for 10 h with 120 mℓ of dichloromethane. The extract was allowed to cool, filtered and then concentrated at 40°C to about 2 mℓ on a vacuum rotary evaporator. The reduced extract was then carried through the column chromatographic clean-up process as described above prior to GC analysis.

Analyses of freshwater and sediment samples

Approximately 2.5 ℓ grab water samples were collected in triplicates in clean Winchester bottles from midstream Buffalo River at King William's Town, midstream Keiskamma River at Keiskammahoek, midstream Tyume River at Alice and downstream Swartkops River at Port Elizabeth between January and April 2002. The samples were collected from these sites on the rivers because they were the most accessible. The samples were immediately preserved by adding 5 mℓ of concentrated H_2SO_4 and stored at 4°C in a refrigerator until analysed. Sediment samples were collected from the 0 to 5 cm sediment layers from the same sites as water samples into clean wide-mouth plastic containers and covered immediately after sampling. Samples were kept cool during transportation to the laboratory. At the laboratory, they were frozen at -18°C prior to sample preparation. Sediment samples were air-dried in a circulating air oven at approximately 30°C for 2 to 3 d and sieved.

Ten grams of dried, sieved and pre-extracted sediment sample was weighed into a pre-extracted Whatman extraction thimble and treated as described previously for SE with DCM as extracting solvent. The reduced extract was then carried through the column chromatographic clean-up process as described above prior to GC analysis. Triplicate analyses of the same sediment sample from each site were done.

One litre of an acidified water sample was extracted with dichloromethane as described above. The dichloromethane extract was concentrated to approximately 2 mℓ and put through the silica gel column chromatographic clean-up as described earlier. Triplicate analyses of the same water sample from each site were done.

Quality control

Quality control was internal in this study and the measures implemented for this included performing blank analysis of doubly distilled water, assessing recoveries from pre-extracted and fortified river water and sediment samples and performing triplicate analyses of samples from each sampling site per sampling date.

Capillary gas chromatographic analysis

One microlitre each of processed sample was injected into the GC (split mode - 1 min) for analyses. The injector and detector temperatures were maintained at 250°C and 350°C respectively. The oven temperature was initially maintained at 120°C, and then programmed to increase at 20°C/min to 150°C and ramped to 250°C at 5°C. 99.999% ultra-pure helium and nitrogen gases purchased and supplied by Afrox Limited, South Africa were used as the carrier and make-up gases respectively. The carrier gas flow rate was 2 mℓ/min while the make-up gas flow was set at 28 mℓ/min for optimum performance.

Results and discussion

The gas chromatogram of a mixture of the 15 organochlorine (OC) pesticide standards plus the internal standard is shown in Fig. 2. The 15 pesticides were well resolved and eluted within 22 min. Table 1 shows the retention times and the response factors for the OCPs used.

The mean percentage recoveries of the 15 OCPs from fortified pre-extracted river water by LLE with dichloromethane ranged from 71.03% ± 0.11 to 101.25% ± 0.02 (Table 2), which were judged acceptable, hence the choice of the solvent for use in the LLE method for the analyses of environmental river water samples. The results obtained with dichloromethane extraction were comparable to those reported using the USEPA Test Method 608 for organochlorine pesticides via solvent extraction with the same solvent (USEPA, 1984).

The percentage recoveries of OCPs from fortified sediment by Soxhlet extraction method with the same solvent are shown in Table 3. The recoveries of the pesticides ranged from 88.22 % ± 0.09 to 109.63 % ± 0.05, which were judged acceptable for organochlorine pesticide residue analysis in environmental sediment samples collected.

The results of the analyses of organochlorine pesticide residues in environmental river water samples collected from the Buffalo, Tyume, Keiskamma and Swartkops Rivers and from Sandile Dam are shown in Tables 4 to 7. The identities of the OCPs in sample extracts were confirmed by comparing their retention times with those of OCP standards and concentrations were determined by computer calculation making use of both the response factors of the OCPs and the internal standard. Results for the analyses of sediments

TABLE 1
[a]Retention times ± CV and [a]response factors ± CV of organochlorine pesticide standards

OCPs	Retention time(min)	Response factor
α-BHC	8.18 ± 0.002	1.48 ± 0.05
HCB	8.55 ± 0.005	1.17 ± 0.08
β-BHC	8.97 ± 0.003	1.42 ± 0.06
δ-BHC	9.98 ± 0.004	1.57 ± 0.05
Heptachlor	11.93 ± 0.003	1.24 ± 0.07
Aldrin	13.23 ± 0.001	0.90 ± 0.09
γ-Chlordane	15.57 ± 0.001	1.12 ± 0.10
2,4-DDE	15.70 ± 0.001	1.93 ± 0.08
Endosulfan	16.06 ± 0.001	0.88 ± 0.13
Dieldrin	17.04 ± 0.002	0.63 ± 0.30
2,4´-DDD	17.24 ± 0.001	1.67 ± 0.11
Endrin	17.83 ± 0.001	1.81 ± 0.11
4,4´-DDD	18.47 ± 0.001	1.73 ± 0.11
2,4´-DDT	18.63 ± 0.001	1.33 ± 0.17
4,4´-DDT	19.91 ± 0.001	1.28 ± 0.29
Pentachloro nitrobenzene	9.49 ± 0.21	--

[a]Values are mean of 6 injections
CV - Coefficient of variation

TABLE 2
[a]Mean % recoveries of organochlorine pesticide standards added to pre-extracted river water by LLE with dichloromethane as the extracting solvent

Organo-chlorine pesticides	Spiked at (ng/ℓ)	% Recovery[a] +CV	Limits of Detection† (ng/ℓ)
α-BHC	60	101.25 ± 0.02	18
HCB	200	93.50 ± 0.12	18.6
β-BHC	200	93.37 ± 0.71	7.7
δ-BHC	200	100.13 ± 0.03	15
Heptachlor	140	89.29 ± 0.03	12
Aldrin	160	85.00 ± 0.04	7.5
γ-Chlordane	160	78.13 ± 0.04	20.6
2,4´-DDE	400	83.94 ± 0.03	7.7
Endosulfan	140	78.69 ± 0.07	18.5
Dieldrin	160	71.03 ± 0.11	5.7
2,4´-DDD	400	83.78 ± 0.10	5.5
Endrin	400	91.46 ± 0.03	14.7
4,4´-DDD	400	80.79 ± 0.08	13.4
2,4´-DDT	400	77.16 ± 0.12	6.0
4,4´-DDT	400	80.42 ± 0.14	18.9

[a]Values are mean of triplicate analyses.
† Calculated from the linear regression equation of the calibration curve of each organochlorine pesticide standard (Miller and Miller, 1998)
CV = Coefficient of variation

TABLE 3
[a]Mean % recoveries of organochlorine pesticide standards added to pre-extracted sediment by Soxhlet extraction with dichloromethane as extracting solvent

OCPs	Spiked at (ng/kg)	% Recovery[a] ±CV
α-BHC	30 x 10^3	96.09 ± 0.01
HCB	150 x 10^3	98.87 ± 0.11
β-BHC	150 x 10^3	109.63 ± 0.05
δ -BHC	75 x 10^3	98.48 ± 0.08
Heptachlor	100 x 10^3	98.88 ± 0.02
Aldrin	120 x 10^3	97.12 ± 0.05
γ -Chlordane	150 x 10^3	96.89 ± 0.01
2,4-DDE	300 x 10^3	96.03 ± 0.05
Endosulfan	100 x 10^3	97.55 ± 0.09
Dieldrin	200 x 10^3	96.17 ± 0.04
2,4-DDD	300 x 10^3	100.61± 0.05
Endrin	300 x 10^3	88.22 ± 0.09
4,4-DDD	300 x 10^3	97.84 ± 0.03
2,4-DDT	300 x 10^3	99.14 ± 0.09
4,4-DDT	300 x 10^3	90.19 ± 0.02

[a]Values are mean of triplicate analyses
CV = Coefficient of variation

TABLE 4
[a]Organochlorine pesticide levels (ng/ℓ ± CV) in fresh-water samples

Sampling date	10/01/2002	10/01/2002	10/01/2002
OCPs	$^{b}(BR)_1$	$^{b}(BR)_2$	$^{b}(BR)_3$
α-BHC	Trace	20 ± 0.001	50 ± 0.0002
HCB	Trace	100 ± 0.0002	80 ± 0.0004
β-BHC	200 ± 0.0002	30 ± 0.0003	450 ± 0.0002
δ-BHC	100 ± 0.0004	80 ± 0.004	140 ± 0.0004
Heptachlor	Trace	200 ± 0.0001	171 ± 0.0008
Aldrin	Trace	20 ± 0.002	120 ± 0.0002
γ-Chlordane	Trace	100 ± 0.0005	120 ± 0.0003
2,4’-DDE	Trace	100 ± 0.0003	240 ± 0.0003
Endosulfan	Trace	100 ± 0.0004	50 ± 0.0004
Dieldrin	Trace	100 ± 0.0002	60 ± 0.0007
2,4’-DDD	Trace	30 ± 0.001	180 ± 0.0003
Endrin	Trace	40 ± 0.0005	30 ± 0.002
4,4’-DDD	Trace	100 ± 0.0005	210 ± 0.0001
2,4’-DDT	100 ± 0.0002	100 ± 0.0002	260 ± 0.0006
4,4’-DDT	140 ± 0.0004	20 ± 0.003	160 ± 0.0003

[a]Mean of triplicate analyses, [b]Buffalo River
CV = Coefficient of variation
Trace = < Detection limit
$(BR)_1$, $(BR)_2$ and $(BR)_3$ = samples from different locations but around the same site

are shown in Tables 8 to 11. Levels of OCPs ranged from trace (2,4'-DDD) ng/ℓ to 450 ng/ℓ (β-BHC) in the Buffalo River, from trace (2,4'-DDE) to 180 ng/ℓ (β-BHC) in the Keiskamma River and from trace (2,4'-DDT) to 130 ng/ℓ (HCB) in the Tyume River. The concentration of pesticides in the Swartkops River varied between trace (2,4'-DDT) and 100 ng/ℓ (2,4'-DDE). Our values are much higher than those reported by Grobler et al. (1994) for Olifants River and those reported by Weaver (1993) for Hex River where no OCP was detected but much lower than those reported by London et al. (2000) for Hex. Piketburg and Grabouw/Vyeboom Rivers in the Western Cape Province (OCPs, 50 ng/ℓ to 1 000 ng/ℓ). 37% of the samples analysed by London et al. (2000) were detected above the EU limit of 100 ng/ℓ for endosulfan. 100% of the samples analysed in this study were detected below the EU limit for endosulfan (European Community, 1980). Among the OCPs detected at levels > 100 ng/ℓ in our study were HCB, β-BHC, δ-BHC, heptachlor and ΣDDT. In the river sediments, the levels of OCPs ranged from trace (2,4'-DDT) to 184 x 10^3 ng/kg (heptachlor) in the Buffalo River, from trace (2,4'-DDT, dieldrin) to 16 x 10^3 ng/kg (γ-chlordane) in the Keiskamma River and from trace (2,4'-DDT, dieldrin) to 19 x 10^3 ng/kg (2,4'-DDD) in the Tyume River. The residues pesticides in the Swartkops River varied between trace (2,4'-DDT, 2,4'-DDD, dieldrin) and 30 x 10^3 ng/kg (β-BHC). These levels of OCPs were significantly lower than the levels found in river sediment from the Olifants River by Grobler et al. (1994). The residues detected in this study were also of lower values than those detected in sediment by Naude et al. (1998), which ranged from 8.7 x 10^3 ng/kg to 320 x 10^3 ng/kg for DDT, from 12 x 10^3 ng/kg to 374 x 10^3 ng/kg for DDD and from 23.5 x 10^3 ng/kg to 346 x 10^3 ng/kg for DDE.

TABLE 5
[a]Organochlorine pesticide levels (ng/ℓ ± CV) in freshwater samples

Sampling date	12/03/02	12 /03/02	12 /03/02	12 /03/02	12 /03/02
OCPs	[b](BR)	[c](SD)	[d](KR)	[e](TYR)	[f](SKR)
α-BHC	70 ± 0.0001	50 ± 0.0006	40 ± 0.002	40 ± 0.0008	90 ± 0.0002
HCB	150 ± 0.0001	20 ± 0.001	30 ± 0.0003	20 ± 0.003	30 ± 0.002
β-BHC	30 ± 0.0007	50 ± 0.0004	180 ± 0.002	85 ± 0.0007	40 ± 0.002
δ-BHC	20 ± 0.003	20 ± 0.003	110 ± 0.0005	10 ± 0.004	20 ± 0.001
Heptachlor	20 ± 0.001	30 ± 0.0003	50 ± 0.0002	20 ± 0.004	70 ± 0.0006
Aldrin	25 ± 0.0004	70 ± 0.0009	80 ± 0.001	90 ± 0.001	10 ± 0.002
γ-Chlordane	40 ± 0.0005	50 ± 0.0004	40 ± 0.0003	50 ± 0.0008	90 ± 0.0006
2,4'-DDE	20 ± 0.0005	20 ± 0.003	30 ± 0.001	40 ± 0.003	100 ± 0.0008
Endosulfan	10 ± 0.005	80 ± 0.001	Trace	Trace	Trace
Dieldrin	30 ± 0.001	30 ± 0.001	10 ± 0.002	60 ± 0.001	10 ± 0.003
2,4'-DDD	30 ± 0.0003	40 ± 0.0003	40 ± 0.0005	120 ± 0.001	30 ± 0.001
Endrin	20 ± 0.0005	20 ± 0.001	30 ± 0.0003	20 ± 0.002	10 ± 0.002
4,4'-DDD	20 ± 0.002	20 ± 0.0005	20 ± 0.0005	30 ± 0.003	30 ± 0.002
2,4'-DDT	40 ± 0.002	20 ± 0.001	30 ± 0.0007	50 ± 0.001	20 ± 0.001
4,4'-DDT	50 ± 0.0008	20 ± 0.001	80 ± 0.0008	50 ± 0.0006	30 ± 0.0003

[a]Mean of triplicate analyses, [b]Buffalo River, [c]Sandile Dam, [d]Keiskamma River, [e]Tyume River and [f]Swartkops River
CV = coefficient of variation
Trace = < detection limit.

TABLE 6
[a]Organochlorine pesticide levels (ng/ℓ ± CV) in freshwater samples

Sampling date	26/03/02	26 /03/02	26 /03/02	26 /03/02	26 /03/02
OCPs	[b](BR)	[c](SD)	[d](KR)	[e](TYR)	[f](SKR)
α-BHC	60 ± 0.0005	20 ± 0.002	40 ± 0.0008	70 ± 0.0007	20 ± 0.002
HCB	20 ± 0.002	20 ± 0.003	20 ± 0.002	60 ± 0.002	60 ± 0.0003
β-BHC	20 ± 0.001	40 ± 0.002	40 ± 0.002	30 ± 0.003	10 ± 0.003
δ-BHC	70 ± 0.0007	20 ± 0.003	20 ± 0.002	120 ± 0.001	Trace
Heptachlor	Trace	40 ± 0.004	Trace	50 ± 0.0006	Trace
Aldrin	30 ± 0.0003	20 ± 0.003	70 ± 0.0004	20 ± 0.003	Trace
γ-Chlordane	Trace	60 ± 0.002	70 ± 0.002	10 ± 0.004	Trace
2,4'-DDE	40 ± 0.003	Trace	Trace	Trace	Trace
Endosulfan	Trace	20 ± 0.004	Trace	Trace	20 ± 0.002
Dieldrin	30 ± 0.002	10 ± 0.005	10 ± 0.004	50 ± 0.0008	20 ± 0.004
2,4'-DDD	30 ± 0.002	20 ± 0.003	20 ± 0.004	20 ± 0.001	40 ± 0.0008
Endrin	Trace	Trace	Trace	70 ± 0.003	70 ± 0.002
4,4'-DDD	20 ± 0.005	Trace	20 ± 0.005	30 ± 0.001	Trace
2,4'-DDT	40 ± 0.0005	Trace	10 ± 0.003	Trace	30 ± 0.002
4,4'-DDT	30 ± 0.002	Trace	50 ± 0.001	20 ± 0.004	30 ± 0.0003

[a]Mean of triplicate analyses, [b]Buffalo River, [c]Sandile Dam, [d]Keiskamma River, [e]Tyume River and [f]Swartkops River
CV = Coefficient of variation

The highest residue concentration detected in river water (β-BHC, 450 ng/ℓ) was found in the Buffalo River. The highest residue concentration detected in sediment (heptachlor, 184 x 10^3 ng/kg) was also found in the same river. Residues of DDT and its metabolites ranged from trace to 260 ng/ℓ in the rivers with the highest value detected in the Buffalo River (Tables 4 to 7). High levels of β-BHC were also detected in the Keiskamma, Keiskammahoek (180 ng/ℓ) and the Tyume (130 ng/ℓ) Rivers though the highest value for the OCP (200 ng/ℓ) was detected in the Buffalo River. In addition the highest concentrations of (140-ng/ℓ) δ-BHC and HCB (150 ng/ℓ) were detected in Buffalo River though relatively high value of HCB (130 ng/ℓ) was also detected in the Tyume River. For sediment the highest levels of

TABLE 7
[a]Organochlorine pesticide levels (ng/ℓ ± CV) in freshwater samples

Sampling date	26/04/02	26/04/02	26/04/02	26/04/02	26/04/02
OCPs	[b](BR)	[c](SD)	[d](KR)	[e](TYR)	[f] (SKR)
α-BHC	50 ± 0.0004	Trace	Trace	20 ± 0.002	Trace
HCB	20 ± 0.003	Trace	40 ± 0.0008	130 ± 0.0009	20 ± 0.003
β-BHC	60 ± 0.003	30 ± 0.002	30 ± 0.0007	Trace	50 ± 0.002
δ-BHC	70 ± 0.0007	30 ± 0.003	50 ± 0.002	20” 0.003	40 ± 0.003
Heptachlor	25 ± 0.002	40 ± 0.001	70 ± 0.0006	Trace	30 ± 0.001
Aldrin	10 ± 0.005	Trace	10 ± 0.004	40 ± 0.001	Trace
γ-Chlordane	60 ± 0.001	Trace	80 ± 0.0004	Trace	Trace
2,4’-DDE	Trace	20 ± 0.02	Trace	30 ± 0.003	20 ± 0.003
Endosulfan	20 ± 0.003	Trace	30 ± 0.002	Trace	Trace
Dieldrin	10 ± 0.003	Trace	10 ± 0.003	20 ± 0.002	10 ± 0.006
2,4’-DDD	20 ± 0.004	Trace	30 ± 0.005	20 ± 0.004	40 ± 0.001
Endrin	Trace	Trace	Trace	40 ± 0.004	30 ± 0.0007
4,4’-DDD	Trace	Trace	Trace	30 ± 0.0003	Trace
2,4’-DDT	Trace	Trace	40 ± 0.002	40 ± 0.001	Trace
4,4’-DDT	Trace	Trace	Trace	20 ± 0.001	Trace

[a]Mean of triplicate analyses, [b]Buffalo River, [c]Sandile Dam, [d]Keiskamma River, [e]Tyume River and [f]Swartkops River
CV = Coefficient of variationCV = Coefficient of variation
Trace = < Detection limit

TABLE 8
[a]Organochlorine pesticide levels (ng/kg ± CV) in sediment samples

Sampling date	10/01/2002	10/01/2002	10/01/2002
OCPs	[b](BR)$_1$	[b](BR)$_2$	[b](BR)$_3$
α-BHC	90 x 10^3 ± 0.3	19.1x 10^3 ± 4.2	23 x 10^3 ± 1.3
HCB	34 x 10^3 ± 0.6	30 x 10^3 ± 1.7	24.6 x 10^3 ± 1.2
β-BHC	81.5 x 10^3 ± 0.5	72.7 x 10^3 ± 0.1	75.3 x 10^3 ± 0.9
δ-BHC	56 x 10^3 ± 0.4	74.3 x 10^3” 0.4	177 x 10^3 ± 0.3
Heptachlor	36.7 x 10^3 ± 1.4	95 x10^3 ± 0.1	184 x 10^3 ± 0.7
Aldrin	70.2 x 10^3 ± 2.6	Trace	30.7 x 10^3 ± 2.0
γ-Chlordane	92 x 10^3 ± 0.8	Trace	117 x 10^3 ± 0.3
2,4’-DDE	Trace	Trace	20.6 x 10^3 ± 0.17
Endosulfan	92 x 10^3 ± 0.9	Trace	72 x 10^3 ± 8.3
Dieldrin	Trace	Trace	60 x 10^3 ± 0.2
2,4’-DDD	94 x 10^3 ± 1.1	Trace	39.5 x 10^3 ± 1.5
Endrin	100 x 10^3 ± 0.5	Trace	38.4 x 10^3 ± 0.5
4,4’-DDD	Trace	Trace	47.7 x 10^3 ± 0.2
2,4’-DDT	Trace	Trace	109 x 10^3 ± 0.4
4,4’-DDT	110 ± 0.2	Trace	33.6 x 10^3 ± 1.8

[a]Mean of triplicate analyses, [b]Buffalo River.
CV = Coefficient of deviation
Trace = < Detection limit

α-BHC (90 x 10^3 ng/kg), β-BHC (81.5 x 10^3 ng/kg), δ-BHC (177 x 10^3 ng/kg) and heptachlor (184 x 10^3 ng/g) were detected in the Buffalo River. Similarly the highest values of aldrin, γ-chlordane, endosulfan, and ΣDDT were detected in the same river. Generally, the levels of OCPs were relatively lower in the Swartkops River. This river flows through Port Elizabeth and commercial agricultural areas. The Buffalo, Tyume and Keiskamma Rivers pass through agricultural lands in the Eastern Cape where rural agriculture is prevalent. Thus high levels of some pesticide residues in them are probably due to illegal use of some OCPs in the rivers’ catchment areas by rural farmers. OCPs such as endosulfan and chlordane (the latter only used for termite control in structures) are still legally being used in South Africa, however, the low concentrations of these pesticides in the rivers suggests their not common use in the study areas. The sources of OCPs such as heptachlor, β-BHC and δ-BHC in the water systems are probably from diffuse sources such as runoff from agricultural lands. All the rivers pass through agricultural areas in the province. β-BHC and δ-BHC could also have industrial sources especially in the Buffalo River, which receives some industrial effluents from the King William’s Town area. The presence of DDT and some of its degradation residues in the water systems can be attributed to their wide usage before their banning (the use of DDT is still strictly controlled in South Africa) (Van Dyk et al., 1982; Davies and Randall, 1989). Since they are persistent enough and degrade slowly and easily accumulate, the transportation of these pesticides both sorbed onto solids and dissolved in the surface water can be expected (Aydin and Yurdin, 1999).

Results of analyses of samples collected from the rivers showed that the concentrations of most of the OCP residues detected in water were below the maximum acceptable concentration of 100 ng/ℓ value set by the European Union (EU) for the protection of human health (European Community, 1980). However, some elevated levels of 450 ng/ℓ, 200 ng/ℓ, 260 ng/ℓ, 210 ng/ℓ and 240 ng/ℓ were detected in β-BHC, heptachlor, 2,4´-DDT, 4,4’-DDD and 2,4´-DDE respectively in the Buffalo River. These elevated concentrations give cause for concern. In many rural areas, drinking water is sourced directly from the contaminated rivers and this could expose some of the primary users of water from these rivers to these residues with potential health effects. Some of the residues detected in the water sources like chlordane, heptachlor, 2,4’-DDT, 4,4’-DDT, 2,4’-DDE and endosulfan are known to have synergistic and cumulative effects on the endocrine systems (Soto et al., 1994; Safe, 2001). Thus the population and the environment in the study area could probably be at risk if the trend is not checked.

Standards to protect aquatic ecosystems are far lower than those for human health. The South African Target Water Quality guidelines to protect aquatic ecosystems are aldrin 10 ng/ℓ, chlordane25 n/ℓ, DDT 1.5 ng/ℓ, dieldrin 5 ng/ℓ, endosulfan 3 ng/ℓ, endrin 2 ng/ℓ and heptachlor 5 ng/ℓ (DWAF, 1996). The levels detected in some of the water samples were higher than these guideline values and may thus affect the fitness of species in the river in terms of health, reproduction and behaviour (DWAF, 1996).

In the Sandile Dam, levels of OCPs ranged from trace (2,4'-DDT) to 80 ng/ℓ (endosulfan). The Sandile Dam is situated on the Keiskamma River. Water from this dam is treated to supply the Keiskammahoek local government area and the Middledrift district with tapped drinking water. The presence of OCPs in this impoundment gives cause for concern, especially the presence of endocrine disrupting (ED) pesticides such as endosulfan, which may have health implications for the rural communities who are secondary users of water from the dam. Water treatment in general does not remove pesticides.

TABLE 9

^{a}Organochlorine pesticide levels (ng/kg ± CV) in sediment samples

Sampling date	**12/03/02**	**12 /03/02**	**12/03/02**	**12/03/02**
OCPs	**^{b}(BR)**	**^{d}(KR)**	**^{e}(TYR)**	**^{f}(SKR)**
α-BHC	5.0 x 10^{3} ± 6.0	2.0 x 10^{3} ± 20.0	3.0 x 10^{3} ± 10.0	5.0 x 10^{3} ± 6.0
HCB	9.0 x 10^{3} ± 6.7	6.0 x 10^{3} ± 23.3	4.0 x 10^{3} ± 35.0	5.0 x 10^{3} ± 12.0
β-BHC	11 x 10^{3} ± 4.5	6.0 x 10^{3} ± 3.3	8.9 x 10^{3} ± 6.7	30 x 10^{3} ± 2.7
δ-BHC	3.0 x 10^{3} ± 50	8.0 x 10^{3} ± 6.3	7.8 x 10^{3} ± 5.1	Trace
Heptachlor	Trace	2.0 x 10^{3} ± 30.0	6.0 x 10^{3} ± 16.7	Trace
Aldrin	5.0 x 10^{3} ± 8.0	5.0 x 10^{3} ± 6.0	9.0 x 10^{3} ± 8.9	2.0 x 10^{3} ± 25.0
γ-Chlordane	Trace	16.0 x 10^{3} ± 2.5	Trace	Trace
2,4'-DDE	Trace	Trace	4.0 x 10^{3} ± 5.0	21.0 x 10^{3} ± 3.3
Endosulfan	3.0 x 10^{3} ± 6.7	Trace	Trace	15.3 x 10^{3} ± 10.5
Dieldrin	18.0 x 10^{3} ± 3.3	6.0 x 10^{3} ± 28.3	Trace	Trace
2,4'-DDD	2.0 x 10^{3} ± 10.0	15.0 x 10^{3} ± 8.7	19.0 x 10^{3} ± 6.8	Trace
Endrin	1.0 x 10^{3} ± 70.0	8.0 x 10^{3}” 5.0	17.0 x 10^{3} ± 3.5	Trace
4,4'-DDD	12 x 10^{3} ± 2.5	5.0 x 10^{3} ± 14.0	6.0 x 10^{3} ± 3.3	Trace
2,4'-DDT	11 x 10^{3} ± 4.5	Trace	3.0 x 10^{3}” 16.7	Trace
4,4'-DDT	19 x 10^{3} ± 6.8	3.0 x 10^{3} ± 16.7	4.0 x 10^{3} ± 5.0	Trace

^{a}Mean of triplicate analyses, ^{b}Buffalo River, ^{c}Sandile Dam, ^{d}Keiskamma River, ^{e}Tyume River and ^{f}Swartkops River
CV = Coefficient of variation
Trace = < Detection limit

TABLE 10

^{a}Organochlorine pesticide levels (ng/kg ± CV) in sediment samples

Sampling date	**26/03/02**	**26/03/02**	**26/03/02**	**26/03/02**
OCPs	**^{b}(BR)**	**^{d}(KR)**	**^{e}(TYR)**	**^{f}(SKR)**
α-BHC	4.0 x 10^{3} ± 45.0	5.0 x 10^{3} ± 14.0	4.2 x 10^{3} ± 11.9	2.8 x 10^{3} ± 14.3
HCB	2.0 x 10^{3} ± 20.0	4.0 x 10^{3} ± 7.5	2.5 x 10^{3} ± 16.0	12.0 x 10^{3} ± 6.7
β-BHC	24.0 x 10^{3} ± 2.1	3.0 x 10^{3} ± 13.3	2.0 x 10^{3} ± 20.0	9.0 x 10^{3} ± 14.4
δ-BHC	5.0 x 10^{3} ± 16.0	Trace	2.1 x 10^{3} ± 66.7	Trace
Heptachlor	2.0 x 10^{3} ± 35.0	Trace	2.0 x 10^{3} ± 15.0	Trace
Aldrin	Trace	2.1 x 10^{3} ± 28.6	Trace	Trace
γ-Chlordane	Trace	3.4 x 10^{3} ± 14.7	Trace	Trace
2,4'-DDE	5.0 x 10^{3} ± 8.0	Trace	3.5 x 10^{3} ± 22.9	1.2 x 10^{3} ± 66.7
Endosulphan I	Trace	3.0 x 10^{3} ± 6.7	3.0 x 10^{3} ± 40.0	Trace
Dieldrin	Trace	2.0 x 10^{3} ± 35.0	Trace	Trace
2,4'-DDD	8.0 x 10^{3} ± 3.8	5.0 x 10^{3} ± 16.0	Trace	Trace
Endrin	Trace	Trace	2.0 x 10^{3} ± 35.0	Trace
4,4'-DDD	Trace	2.0 x 10^{3} ± 25.0	Trace	Trace
2,4'-DDT	3.0 x 10^{3} ± 6.7	Trace	Trace	Trace
4,4'-DDT	8.0 x 10^{3} ± 15.0	Trace	Trace	2.5 x 10^{3} ± 52.0

^{a}Mean of triplicate analyses, ^{b}Buffalo River, ^{c}Sandile Dam, ^{d}Keiskamma River, ^{e}Tyume River and ^{f}Swartkops River
CV = Coefficient of variation
Trace = < Detection limit

Conclusion

This study showed that solvent extraction with DCM is an accurate and reliable method for OCP residue analyses in environmental water samples. It also showed SE extraction with DCM to be a reliable method for OCP determination in sediments. Several OCPs were detected in the water systems including some endocrine disrupting compounds such as endosulfan, heptachlor, 2,4'-DDT, 4,4'-DDT and 2,4'-DDE.

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TABLE 11

[a]Organochlorine pesticide levels (ng/kg ± CV) in sediment samples

Sampling date	26/04/02	26/04/02	26/04/02	26/04/02
OCPs	**[b](BR)**	**[d](KR)**	**[e](TYR)**	**[f](SKR)**
α-BHC	$3.4 \times 10^{3} \pm 23.5$	$3.0 \times 10^{3} \pm 6.7$	$2.0 \times 10^{3} \pm 35.0$	Trace
HCB	Trace	$2.8 \times 10^{3} \pm 53.6$	$5.0 \times 10^{3} \pm 6.0$	$5.4 \times 10^{3} \pm 3.7$
β-BHC	$6.0 \times 10^{3} \pm 8.3$	$5.0 \times 10^{3} \pm 10.0$	$9.0 \times 10^{3} \pm 15.6$	$3.0 \times 10^{3} \pm 26.7$
δ-BHC	$4.5 \times 10^{3} \pm 28.9$	$1.9 \times 10^{3} \pm 15.8$	$3.0 \times 10^{3} \pm 26.7$	Trace
Heptachlor	Trace	Trace	$2.0 \times 10^{3} \pm 20.0$	$5.0 \times 10^{3} \pm 8.0$
Aldrin	Trace	$2.0 \times 10^{3} \pm 20.0$	Trace	$1.2 \times 10^{3} \pm 25.0$
γ-Chlordane	Trace	Trace	Trace	Trace
2,4'-DDE	$3.0 \times 10^{3} \pm 3.3$	$3.5 \times 10^{3} \pm 28.6$	$5.0 \times 10^{3} \pm 30.0$	Trace
Endosulfan	Trace	Trace	Trace	Trace
Dieldrin	Trace	Trace	Trace	$1.0 \times 10^{3} \pm 30.0$
2,4'-DDD	$4.0 \times 10^{3} \pm 7.5$	$6.0 \times 10^{3} \pm 5.0$	Trace	$8.0 \times 10^{3} \pm 21.3$
Endrin	$2.0 \times 10^{3} \pm 15.0$	Trace	Trace	Trace
4,4'-DDD	Trace	$4.0 \times 10^{3} \pm 12.5$	Trace	Trace
2,4'-DDT	Trace	Trace	Trace	Trace
4,4'-DDT	Trace	$3.0 \times 10^{3} \pm 13.3$	$5.0 \times 10^{3} \pm 8.0$	Trace

[a]Mean of triplicate analyses, [b]Buffalo River, [c]Sandile Dam, [d]Keiskamma River, [e]Tyume River and [f]Swartkops River
CV = Coefficient of variation
Trace = < Detection limit

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