Investigating the temporal trends in PAH, PCB and OCP concentrations in Hartbeespoort Dam, South Africa, using semipermeable membrane devices (SPMDs)

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ABSTRACT

The seasonal variability of persistent organic pollutants in Hartbeespoort Dam, South Africa, was investigated using semipermeable membrane devices (SPMDs) as passive samplers. Freely dissolved waterborne polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) were sampled to investigate seasonal changes in their concentrations. Exposure of the passive samplers was done for 14 days at the same sampling site in each of the four seasons of the year, in 2011. The SPMD-derived analyte amounts enabled the calculation of time-weighted averages of free dissolved waterborne levels of the contaminants. Concentrations ranged from 30.0 ng·ℓ^{-1} to 51.5 ng·ℓ^{-1} for PAHs, 38 pg ℓ^{-1} to 150 pg·ℓ^{-1} for PCBs, 9.2 to 10.4 ng·ℓ^{-1} for HCHs and 0.3 to 0.8 ng·ℓ^{-1} for DDTs, respectively. It was also noted that the winter season generally exhibited higher contaminant concentrations for most compounds studied, which likely reflects the seasonality of their atmospheric deposition. An attempt was also made to identify possible sources of PAH contaminants in the dam by examining PAH ratios. These diagnostic ratios were inclined towards pyrogenic sources of pollution, except for the winter season where both pyrogenic and petrogenic sources likely contribute to the contamination pattern.

Keywords: Hartbeespoort dam, persistent organic pollutants, semipermeable membrane devices, water-dissolved concentrations, temporal trends.

INTRODUCTION

Globally, huge quantities of organic pollutants, including persistent organic pollutants (POPs), are released into the environment. Due to their ubiquitous nature, hydrophobic organic compounds such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) have been identified as environmental contaminants in almost every compartment of the global system (ATSDR, 2009). As byproducts of incomplete combustion of organic compounds, pyrosynthesis or pyrolysis of hydrocarbons, PAHs are released to the environment by both natural and anthropogenic sources (Levinson et al., 2008). PAHs may also reach water systems through oil spills and direct industrial effluent discharges. PCBs and OCPs, on the other hand, are POPs of anthropogenic origin. Chemically stable, strongly lipophilic and considerably toxic, OCPs have slow degradation rates and tend to bioaccumulate in lipid-rich tissues (Tiemann, 2008) of living organisms. PAHs, PCBs and OCPs are of particular interest because of their potential toxicity, carcinogenicity, possible mutagenicity as well as tendency to bioaccumulate. They are present in the aquatic environment both as truly dissolved and particle-bound. The easily bioavailable fraction, which corresponds to the free dissolved fraction, is of primary interest for risk assessment (Sabaliunas and Sodergren, 1997). It is generally assumed that particle- and colloid-bound compounds cannot cross biological membranes, bioconcentrate and cause biological effects (Landrum et al., 1985). The concentration of freely-dissolved POPs in the water column is directly proportional to their chemical activity and fugacity in the water phase and is an important parameter in modelling their fate in the environment (Mayer et al., 2003).

Due to their characteristically high hydrophobicity and very low solubility in water, these compounds are adsorbed onto finely-dispersed colloids and particulates. Thus, their free dissolved concentrations in water are often several orders of magnitude lower than the total concentrations. Indeed, the water-dissolved concentrations are generally low (ng·ℓ^{-1} to pg·ℓ^{-1} range) and insufficient for reliable quantitative chemical analysis by conventional methods. Consequently, proper analysis of free dissolved PAHs and PCBs in natural water is not easy and many sampling problems are encountered.

A viable alternative to a grab sampling approach is to use passive samplers. These devices usually combine sampling, selective analyte isolation, pre-concentration and, in some cases, speciation preservation, in one step (Vrana et al., 2005). The long accumulation period by the samplers allows for detection of very low concentrations of target analytes (Sabaliunas and Sodergren, 1997), which would otherwise be impractical to achieve. By providing time-weighted average (TWA) values that take into account episodic fluctuations in pollutant concentrations, these devices are better suited for long-term monitoring of contaminants in an environmental compartment (Kot et al., 2000). Among passive sampler devices (PSDs), semipermeable membrane devices (SPMDs) have been widely applied to estimate the concentrations of hydrophobic contaminants in the water phase (Huckins et al. 2006; Verweij et al., 2004; Huckins

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et al., 1993). These passive samplers are composed of a triolein-receiving phase for contaminant accumulation enclosed in a low-density polyethene membrane (LDPE). Contaminant residues sequestered by the SPMDs represent an estimation of the dissolved or readily bioavailable concentration of hydrophobic contaminants in water, which is not provided by most analytical approaches (Vrana et al., 2001). Sampling rates (R_s) for highly hydrophobic compounds are influenced by the environment's hydrodynamic conditions (Booij et al., 2007), such as water turbulence, biofouling and temperature at the sampling site. Through incorporation of performance reference compounds (PRCs) during SPMD fabrication, differences in environmental exposure conditions between deployment sites, times and different monitoring programmes can be adjusted for by studying the dissipation of these compounds (Huckins et al., 2002; Booij et al., 1998). PRCs are non-native, non-interfering compounds characterised by moderate to high fugacities, usually added to the lipid of the SPMD during sampler construction, prior to field exposure. Information on the rate of PRC dissipation during field exposure of samplers can then be applied to estimate the in-situ sampling rates of the compounds of interest (Booij et al., 2010).

Although South Africa is a signatory of the Stockholm Convention and also has a relatively strong industrial presence, information on pollution by POPs remains scanty. Unlike the Northern Hemisphere countries which experience moderate climatic conditions and where most of the studies on POPs have been conducted, South Africa's climate is characterised by high temperatures, little precipitation and long summers (Quinn et al., 2009). Thus, findings from Northern Hemisphere studies cannot be reliably applied to the South African situation. Nevertheless, studies on POPs in South African, such as Nieuwoudt et al. (2011), Das et al. (2008), Bouwman (2003) and Bouwman et al. (1990), among others, have been documented in the literature, but are not adequate to fully describe the South African situation. Apart from a recent study by Degger et al. (2011) on the use of SPMDs to determine POPs in some South African marine environments, very little other information on application of passive sampling in South Africa is available in the literature.

This study was aimed at determining the water-dissolved concentrations of the 16 US EPA priority PAHs, PCBs and OCPs in Hartbeespoort Dam, South Africa, using SPMDs. Specifically, temporal trends in POP concentrations in the dam were investigated.

MATERIALS AND METHODS

Chemicals and reagents

The PAH standard mixture containing the 16 US EPA priority PAHs (all > 97% pure) was purchased from Sigma-Aldrich Chemie GmbH, Steinheim, Germany. Performance reference compounds – D_{10}-acenaphthene, D_{10}-fluorene, D_{10}-phenanthrene and D_{10}-pyrene – were sourced from Dr Ehrenstorfer GmbH, Augsburg, Germany. D_8-Naphthalene, D_{10}-anthracene, D_{12}-fluoranthene, D_{12}-benzo(a)anthracene, D_{12}-benzo(k)fluoranthene, D_{12}-benzo(g,h,i)pyrene, PCB 30, PCB 185 and d_6-gamma HCH (Dr Ehrenstorfer GmbH, Augsburg, Germany) were used as recovery standards. PCB 121 and terphenyl (Dr Ehrenstorfer GmbH, Augsburg, Germany) were used as internal standards for PCB and PAH instrumental analysis, respectively. Pesticide residue analysis grade n-hexane, dichloromethane, trichloromethane and all other solvents

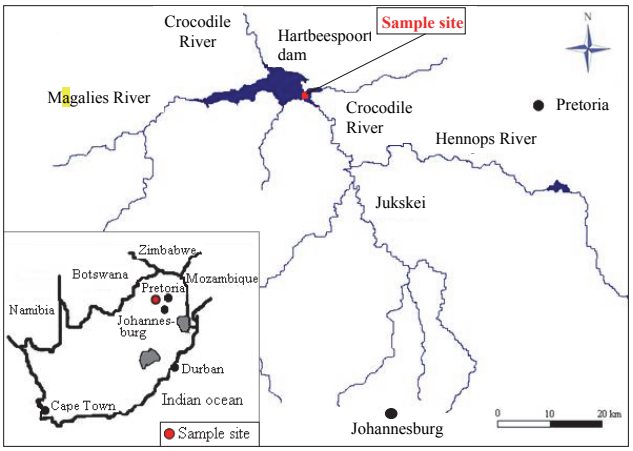

Figure 1
Map showing the sampling site in the Hartbeespoort Dam, South Africa

(all > 97% pure) used were purchased from Sigma-Aldrich (Prague, Czech Republic). Milli-Q water (18MΩ·cm) was obtained from the Millipore Simplicity 185 system (Millipore, Bedford, MA, USA).

Sampling site

The sampling site was located in the Hartbeespoort Dam, 25°45′09.97″S, 27°53′04.39″E, about 37 km west of Pretoria and on the Crocodile River in North West Province, South Africa (Fig. 1). The dam is a 20.7 km^2 water reservoir sandwiched between the Magalies mountain range in the Highveld region of northern South Africa (Nyoni et al., 2011). The dam reservoir receives water from a catchment area of about 4 100 km^2, via the Jukskei and Hennops rivers that flow into the Crocodile River (Harding et al., 2004). The five catchment basins of the dam are, from west to east: the Magalies/Skeerpoort, the Crocodile, the Juskei, the Hennops and the Swartspruit basin (Van Rei, 1987). The Crocodile River accounts for about 90% of the dam's water supply with rainwater being the major source in summer. This scenario dramatically changes during the dry season (winter) as 50% of the water received by the dam then comprises treated wastewater from urbanised areas upstream (Harding et al., 2004), which creates environmental challenges for the water body. Although the origins of the Crocodile River system can be traced to the north of the city of Johannesburg, extensive rural crop farming is still carried out within the dam's drainage area, using its water. Considerable urban development is also present along the shorelines of the basin, and a portion of the impounded water from the dam is utilised for domestic supply, both within the riparian community and in downstream urban centres (DWA, 2012).

Monitoring of the water body for PAHs, PCBs and OCPs using SPMDs was done in each of the four seasons of the year: winter, spring, summer and autumn, as described in Table 1.

Sampling procedure

At the deployment site, the samplers, including the field controls, were unpacked from the metal cans and placed on clean aluminium foil. The samplers were then mounted onto the deployment devices (protected by a steel casing). Once ready, they were quickly immersed in the water at between 1 and 1.5 m depth below the water surface. The steel cages housing

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TABLE 1 Deployment periods and some water quality parameters				
	Sampling period	Water temperature (°C)	pH	Dissolved oxygen (mg·ℓ$^{-1}$)
Winter	19-04-2011 to 04-05-2011	11.6	8.0	5.01
Spring	19-08-2011 to 02-09-2011	14.2	8.2	5.23
Summer	18-11-2011 to 02-12-2011	25.5	9.0	6.04
Autumn	24-02-2012 to 09-03-2012	19.7	8.6	5.75

the samplers were tied using ropes and anchored firmly to buoys. Finally, the field blanks were placed in airtight tin cans and transported in portable ice chests ('cool boxes') to the laboratory, where they were stored at –20°C.

SPMD sampler preparation and deployment

SPMDs (dimensions: 2.5 × 91.4 cm, 460 cm^2 external surface area, and a wall thickness of 70 µm) were prepared from LDPE layflat tubing (Brentwood Plastics, MO, USA) and filled with 1 mℓ of high purity triolein (1,2,3-tri(cis-9-octadecenoyl)glycerol) (99% pure) which had previously been spiked with performance reference compounds, namely, fluorene-d_{10}, acenaphthene-d_{10}, anthracene-d_{10}, phenanthrene-d_{10} and pyrene-d_{10}, to yield a nominal concentration of 2 µg·g^{-1} triolein. Prepared samplers were stored in airtight sealed metal cans under freezing temperatures (–20°C) awaiting deployment. SPMDs were deployed in the water body in triplicates for a 14-day period. On retrieval, samplers were placed in airtight metal containers and quickly transported to the laboratory where they were stored at –20°C until processing.

SPMD processing

After removing particulates and biofouling from the surface of affected SPMDs using a soft brush and tap water, they were briefly immersed in diluted (10%) hydrochloric acid to rid them of adsorbed carbonates acquired during field deployment. The samplers were again flushed with sufficient amounts of tap water, and dried using acetone and a soft paper tissue. Each sampler was transferred into a pre-cleaned, empty 250 mℓ glass bottle with a ground joint stopper and 100 mℓ of HPLC grade n-hexane added. Each sampler was then spiked with surrogate standard solutions, namely, naphthalene-d_8, fluoranthene-d_{12}, benzo(a)anthracene-d_{12}, benzo(k)fluoranthene-d_{12}, benzo(g,h,i) pyrene-d_{12}, PCB 30 and 85, and d_6-gamma HCH, and extraction done twice for 24 h in the dark at room temperature. The extracts were combined and reduced to about 10 mℓ using a rotary evaporator (Heidolph Laborata4000, Germany) at 40°C before concentrating further to about 0.5 mℓ. Finally, the extracts were reconstituted in 1 mℓ of pesticide residue analysis-grade trichloromethane.

Removal of lipids that diffused into the extract during dialysis was achieved using a gel permeation chromatography (GPC) system equipped with a high pressure pump (HPP5001) and a fraction collector (ECOM, Prague, Czech Republic). A gel 5 µm 50 Å, 7.5 x 300 mm, high performance size exclusion chromatography column (Agilent PL) was used to fractionate the extracts with chloroform as the mobile phase at a flow rate of 0.6 mℓ·min^{-1}. Analytes were collected from 18 min 20 s to 41 min 40 s and reduced to the last drop using a gentle stream of nitrogen gas. Subsequently, the extract was reconstituted to 1 mℓ n-hexane. The GPC eluate was subjected to further clean-up by activated silica gel.

One portion (20%) of the GPC extract targeting PAHs was cleaned using activated silica gel packed in a glass column and eluted with 10 mℓ of n-hexane followed by 20 mℓ of dichloromethane. The remaining portion (80%) targeting PCBs and OCPs was cleaned with sulphuric acid–modified activated silica gel, prepared by mixing 33 mℓ of concentrated sulphuric acid (> 98%) with 50 g of freshly prepared activated silica gel. Thorough homogenisation of the mixture was ensured before column packing. Target analytes were eluted with 30 mℓ dichloromethane. After reduction to 1 mℓ using a gentle stream of nitrogen gas, terphenyl or PCB 121 internal standards were added to the sample, and ultimately analysed by GC-MS/MS for PAHs and PCBs/OCPs, respectively.

Instrumentation

The PAHs of interest were analysed using a 6890 GC system coupled with a 5971 mass selective detector (Agilent Technologies). Chromatographic separation of the components was done using a capillary column (30 m x 0.25 mm internal diameter, 0.25 µm film thickness) HP-5MS and helium as the carrier gas flowing at 1.5 mℓ·min^{-1}. Conditions of gas chromatography separation were as follows: injector temperature was set at 250°C, initial column temperature was set at 70°C and held for 0.5 min. This ramped at 25°C·min^{-1} to 150°C. It was then ramped at 30°C·min^{-1} to 200°C. This was further ramped at 8°C·min^{-1} to 280°C and held for 20 min. Detection of the separated PAHs was achieved using a MS/MS system operated in selected ion monitoring mode with the electron impact ionisation set at 70eV. The temperatures of the ion source, transfer line and the quadrupole were held at 230°C, 280°C and 150°C, respectively. Quantitation of the residues was accomplished using a 7-point standard calibration curve in the concentration range of 0 to 1 000 ng·ℓ$^{-1}$. GC-MS/MS was used for indicator PCBs and OCPs analysis. 6890N GC (Agilent, USA) equipped with a 60 m x 0.25 mm x 0.25 µm DB5-MS column (Agilent J&W, USA) coupled to Quattro MicroGC MS (Waters, Micromass, UK) operated in EI+ was used; at least 2 MRM transitions were recorded for each compound analysed. Injection was done in splitless mode at 280°C and 1 µℓ sample loaded. Helium was used as carrier gas at the flow of 1.5 mℓ·min^{-1}. The GC temperature programme was 80°C (1-min hold), then 15°C·min^{-1} to 180°C, and finally 5°C·min^{-1} to 300°C (5-min hold). Raw data were processed using TargetLynx software (Waters, Micromass, UK).

Quality control

Fabrication controls and field blanks were used to account for contamination of the SPMDs during device construction, and sampler deployment and retrieval from the site. Vapour-phase contamination during deployment of the SPMDs was factored in by the field blanks. These blanks were subjected to identical processing treatment as the deployed devices.

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TABLE 2
Mean concentrations of PAHs, OCPs and DDTs in SPMDs (ng SPMD^{-1}, n = 3)

Compound	Season			
	Winter	Spring	Summer	Autumn
PAHs				
Naphthalene	307 ± 11	149 ± 11	171 ± 4	286 ± 20
Acenaphthylene	158 ± 5	76 ± 6	132 ± 2	180 ± 7
Acenaphthene	37 ± 3	20 ± 2	25 ± 1	38 ± 3
Fluorene	76 ± 11	61 ± 7	49 ± 4	106 ± 7
Phenanthrene	164 ± 36	71 ± 9	75 ± 5	217 ± 13
Anthracene	875 ± 40	279 ± 5	56 ± 12	164 ± 3
Fluoranthene	147 ± 4	65 ± 3	119 ± 11	97 ± 7
Pyrene	105 ± 2	49 ± 3	88 ± 5	83 ± 8
Benz[a]anthracene	31 ± 1	16 ± 1	32 ± 2	33 ± 1
Chrysene	41 ± 1	22 ± 5	45 ± 6	44 ± 1
Benzo[b]fluoranthene	35 ± 4	26 ± 8	36 ± 1	38 ± 2
Benzo[k]fluoranthene	36 ± 2	ND	36 ± 2	38 ± 2
Benzo[a]pyrene	34 ± 6	32 ± 0	39 ± 7	43 ± 5
Indeno[1,2,3-cd]pyrene	37 ± 0	19 ± 1	38 ± 1	39 ± 1
Dibenz[a,h]anthracene	ND	ND	ND	ND
Benzo[ghi]perylene	35 ± 1	20 ± 2	41 ± 3	45 ± 2
ΣPAHs	**2 117 ± 57**	**905 ± 21**	**984 ±21**	**1 450 ± 29**
HCHs				
HCB 28	1.1 ± 0.2	0.9 ± 0.1	0.7 ± 0.0	0.6 ± 0.1
α-HCH	55.9 ±3.5	52.5 ± 5.1	32.3 ± 3.6	64.8 ± 5.5
β-HCH	154.3 ±7.8	153.4 ±0.4	70.9 ± 4.0	45.5 ± 2.9
Lindane	8.8 ± 0.9	8.1 ± 0.1	5.9 ± 0.8	9.8 ± 0.9
δ-HCH	3.2 ± 0.2	3.1 ± 0.2	1.4 ± 0.2	2.5 ± 0.4
e-HCH	9.9 ± 0.6	9.8 ± 0.6	4.5 ± 0.1	5.6 ± 0.7
ΣHCHs	**233.2 ± 8.6**	**227.7 ± 5.2**	**106.5 ± 5.4**	**128.7 ± 6.3**
DDTs				
o,p'-DDE	0.6 ± 0.1	0.8 ± 0.1	0.4 ± 0.0	0.3 ± 0.0
p,p'-DDE	5.3 ± 0.2	5.5 ± 0.4	3.6 ± 0.3	3.1 ± 0.2
o,p'-DDD	10.8 ± 1.1	13.6 ± 0.2	5.0 ± 0.4	4.2 ± 0.4
p,p'-DDD	31.1 ± 0.6	43.5 ± 0.8	15.7 ± 3.1	19.9 ± 2.7
o,p'-DDT	ND	ND	ND	ND
p,p'DDT	0.6 ± 0.1	0.7 ± 0.1	0.7 ± 0.1	0.7 ± 0.1
ΣDDTs	**48.5±1.3**	**64.1±0.9**	**25.3±3.1**	**28.2±2.7**
PCBs				
PCB 28	3.5 ± 0.50	3.1 ± 0.30	1.5 ± 0.10	2.1 ± 0.17
PCB 52	1.1 ± 0.06	1.0 ± 0.09	0.6 ± 0.00	0.5 ± 0.04
PCB 101	0.4 ± 0.06	0.4 ± 0.03	0.3 ± 0.07	0.4 ± 0.01
PCB 118	0.2 ± 0.02	0.2 ± 0.00	0.2 ± 0.01	0.2 ± 0.00
PCB 153	0.5 ± 0.03	0.5 ± 0.07	0.4 ± 0.02	0.7 ± 0.05
PCB 138	0.6 ± 0.05	0.3 ± 0.00	0.5 ± 0.05	0.5 ± 0.05
PCB 180	0.3 ± 0.02	0.3 ± 0.00	0.5 ± 0.02	0.4 ± 0.02
ΣPCBs	**6.5 ± 0.51**	**5.8 ± 0.32**	**3.9 ± 0.14**	**4.8 ± 0.19**

ND: not detected

RESULTS AND DISCUSSION

Occurrence of PAHs, PCBs and OCPs in the SPMDs

The absolute contaminant concentrations sequestered by SPMDs deployed at Hartbeespoort Dam during the 14-day deployment period in each of the four seasons of the year are presented in Table 2. Characteristic ions (m/z values) used in the analysis of polycyclic aromatic hydrocarbons in single ion monitoring (SIM) mode by GC/MS and characteristic MRM transitions (m/z values of parent and daughter ions) used in the analysis of PCBs and OCPs are given in the Appendix (Tables A1 and A2). Analyte concentrations were adjusted with respect to their recoveries obtained from recovery standards introduced prior to the dialytic process. The SPMD field blanks showed no quantifiable concentrations of the target

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contaminants. Determination of recoveries for all samples was carried out by spiking them with surrogate standards prior to extraction. Good recoveries were recorded that ranged from 55% to 123% for PAHs, 73% to 94% for PCBs and 72% to 104% for OCPs. The relative standard deviations between co-deployed triplicate samplers did not exceed 22% for PAHs, 24% for PCBs and 17% for OCPs. Limits of detection (LOD) and quantification (LOQs) for the method were 0.1 and 0.4 ng·ℓ$^{-1}$, respectively for PAHs. LODs for PCBs and OCPs were all less than 0.1 ng·ℓ$^{-1}$ whereas LOQs were 0.1 ng·ℓ$^{-1}$.

Estimation of dissolved water concentrations of analytes

Dissolved water concentrations of target analytes were calculated from amounts accumulated in SPMDs as follows: Amounts of analytes absorbed by the samplers follow a first-order approach to equilibrium. Aqueous concentrations were calculated from the amounts (N_s) absorbed by the SPMD, the in-situ sampling rate of the compounds R_s and their sampler-water partition coefficients K_{sw}:

$$C_w = \frac{N_s}{K_{sw}V_s[1 - \exp(-R_s t/(K_{sw}V_s))]} \quad (1)$$

where:

V_S is the volume of the SPMD and t is the sampler exposure time.

PRC dissipation also follows first-order kinetics. Sampling rates R_s were estimated using the non-linear least -squares method of Booij and Smedes (2010), considering the fraction f of individual PRCs (D_{10}-acenaphthene, D_{10}-fluorene, D_{10}-phenanthrene and D_{10}-pyrene) that remained in the SPMD after the 14-day exposure as a continuous function of their K_{sw}, with R_S as an adjustable parameter.

$$f = \exp\left(-\frac{R_S t}{K_{SW}V_S}\right) \quad (2)$$

where:

$f = N_{PRC}/N_{0,PRC}$; $N_{0,PRC}$ is the initial amount of the PRC at $t = 0$

N_{PRC} is amount of each PRC remaining after exposure

t is exposure period (14 days).

Assuming water boundary layer controlled uptake, R_s of individual target compounds in the higher hydrophobicity range was estimated by substituting Eq. (3), derived by Rusina et al. (2010), into Eq. (2).

$$R_S = FAM^{-0.47} \quad (3)$$

where: M is the molecular weight of the analyte, A is the surface area of SPMD (460 cm^2) and F is the regression coefficient that was optimised using the non-linear least squares method for estimating sampling rates. The necessary K_{sw} values were interpolated from the empirical equation (Huckins et al., 2006).

$$\log K_{sw} = -01618(\log K_{ow})^2 + 2.321 \log K_{ow} - 2.61 \quad (4)$$

The calculated free dissolved water concentrations of the PAHs, PCBs and OCPs are presented in Table 3.

Temporal trends of water-dissolved contaminants

Equation (3), which estimates a slight decrease in R_s with increasing molecular mass, was used to calculate compound-specific R_s values for all of the compounds studied. Depending on the water flow velocities, different R_s values were obtained in the various seasons, in agreement with the assumption of water boundary layer uptake. Mass transfer of analytes may also be affected by other factors such as temperature, biofouling and deposition of particulates on the surface of the SPMDs.

Estimated water soluble concentrations generally followed the trend: PAHs > OCPs > PCBs. PAHs are ubiquitous organic pollutants characterised by many natural and anthropogenic sources, unlike OCPs and PCBs (industrial products). Since the dam receives over 90% of its water from the Crocodile River, which originates in Johannesburg city, it is possible that a good portion of the pollutants sampled could be of industrial origin. PCB concentrations are on average 2 to 3 orders of magnitude lower than those of PAHs and OCPs because most of these manufactured products have long been banned and their use stopped, in line with the Stockholm Convention, and whatever was captured by the samplers is attributable to their environmental persistence due to slow degradation. The sum total of water-borne concentrations of the compounds ranged from 30.2 to 60.8 ng·ℓ$^{-1}$ (PAHs), 10.0 to 10.7 ng·ℓ$^{-1}$ (OCPs) and 38 to 150 pg·ℓ$^{-1}$ (PCBs). Generally, the seasonal trends for all of the compounds mirrored the amounts accumulated in the SPMDs. An observed predominance of smaller molecular weight PAHs was evident in all four seasons. This may be attributed to their higher solubility in water due to lower hydrophobicity and, hence, transportation from the point sources was probably more efficient.

PAHs

A remarkable seasonal variability in the amounts of sequestered PAHs was shown by the deployed SPMDs. Estimated total analyte concentrations ranged from 30.0 ng·ℓ$^{-1}$ (in summer) to a high of 60.8 ng·ℓ$^{-1}$ (in winter). These concentrations are comparable to those reported by Wang et al. (2009) (13.8–97.2 ng·ℓ$^{-1}$) at the Three Gorges River, China, and Vrana et al. (2014) (5–72 ng·ℓ$^{-1}$) in the Danube River, Slovakia/Austria. The trend of total concentrations of PAHs dissolved in water was as follows: winter > spring > autumn > summer. Individual PAH concentrations obtained in the various seasons also generally followed the same trend as the totals (Fig. 2). Smaller molecular weight PAHs constituted the highest percentage of the sequestered compounds.

The reported water-soluble concentrations of the heavy molecular weight PAHs in the current study were on average up to 2 orders of magnitude lower than the maximum contaminant limits (MCL) set by international regulatory bodies such as the United States Environmental Protection Agency (USEPA) (0.01 to 0.04 µg·ℓ$^{-1}$).

The elevated concentrations recorded during winter may be attributed to a number of factors. During the winter months, very little precipitation is recorded (average of about 4–9 mm for the study area) and, since the dam depends on river water for replenishment, its volume drastically drops. This in turn increases the percentage of the dam's water originating from treated wastewater, which can exceed 50% of the total volume (Harding et al., 2004). These wastewater treatment plants are located in the industrialised areas north of Johannesburg. In addition, average temperatures substantially drop during winter (to an average air temperature of 4–7°C as measured in the study area) which in turn discourages analyte losses via volatilisation. Atmospheric deposition of PAHs represents an

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TABLE 3
Estimated dissolved water concentrations, C_w, (ng·ℓ$^{-1}$) of PAHs, PCBs and OCPs from SPMDs deployed at Hartbeespoort Dam in different seasons of the year

Compound	Season			
	Winter	Spring	Summer	Autumn
PAHs				
Naphthalene	43.153	43.206	23.980	38.499
Acenaphthylene	3.862	3.897	3.214	4.354
Acenaphthene	1.115	1.173	0.759	1.099
Fluorene	1.176	1.858	0.716	1.646
Phenanthrene	1.283	1.316	0.386	1.808
Anthracene	7.321	2.200	0.310	1.519
Fluoranthene	0.709	1.340	0.223	0.639
Pyrene	0.698	0.994	0.170	0.561
Benz[a]anthracene	0.169	0.287	0.051	0.231
Chrysene	0.226	0.422	0.072	0.302
Benzo[b]fluoranthene	0.221	0.511	0.060	0.279
Benzo[k]fluoranthene	0.222	ND	0.060	0.282
Benzo[a]pyrene	0.199	0.294	0.065	0.233
Indeno[1,2,3-cd]pyrene	0.221	0.362	0.063	0.297
Dibenz[a,h]anthracene	ND	ND	ND	ND
Benzo[ghi]perylene	0.211	0.365	0.070	0.343
ΣPAHs	**60.768**	**58.225**	**30.199**	**52.082**
HCHs				
α-HCH	2.320	2.212	0.666	2.921
β-HCH	6.780	6.661	8.102	6.151
Lindane	0.445	0.389	0.189	0.542
δ-HCH	0.054	0.062	0.024	0.087
ε-HCH	0.442	0.386	0.187	0.260
ΣHCHs	**10.350**	**10.201**	**9.168**	**9.961**
DDTs				
o,p'-DDE	0.004	0.006	0.010	0.007
p,p-DDE	0.033	0.052	0.088	0.062
o,p'-DDD	0.065	0.104	0.176	0.124
p,p'-DDD	0.203	0.323	0.547	0.384
p,p'-DDT	ND	ND	ND	ND
p,p'-DDT	0.004	0.006	0.011	0.008
ΣDDTs	**0.309**	**0.491**	**0.832**	**0.585**
PCBs				
PCB 28	0.019	0.029	0.067	0.020
PCB 52	0.006	0.012	0.025	0.010
PCB101	0.003	0.005	0.014	0.007
PCB 118	0.001	0.001	0.003	ND
PCB 138	0.003	0.006	0.013	0.005
PCB 153	0.004	0.005	0.018	0.004
PCB 180	0.002	0.004	0.012	0.003
ΣPCBs	**0.038**	**0.062**	**0.150**	**0.049**

ND: not detected

important pathway for PAHs into the aquatic ecosystem. The increased concentrations in water in winter may correspond with elevated atmospheric concentrations during the same period due to enhanced combustion of coal for heating. The summer months experience high rainfall coupled with high temperatures. Resuspension of sediment-immobilised PAHs was expected to increase PAH concentrations in the water phase. Inputs from runoff and rivers originating from polluted areas upstream were also thought to be potential PAH sources. Although these factors may have been at play, it seems dilution effects (larger water volumes) as well as losses through volatilisation may have tempered the expected increase in contaminant concentrations. The autumn season is characterised by less precipitation and dropping temperatures. These conditions may have led to lower contaminant losses via volatilisation coupled with increased concentration due to decreased bulk water volumes.

The PCB concentrations obtained from the deployed

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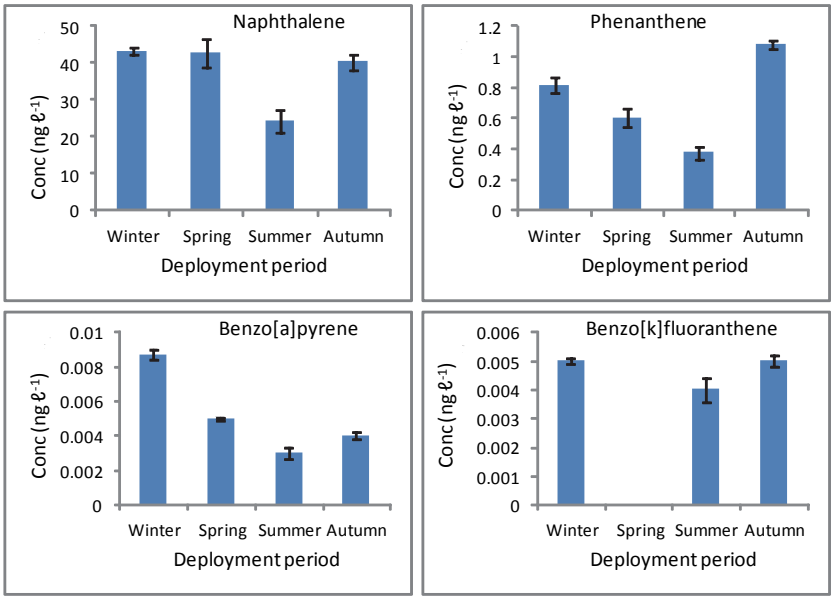

Figure 2
Temporal changes in water-dissolved concentrations of some individual PAHs at the site

SPMDs were generally lower, by about 2 to 3 orders of magnitude, than PAH and OCP concentrations. PCBs are organic contaminants of purely anthropogenic origin, in contrast to PAHs that have both natural and anthropogenic sources. In addition, most PCBs were banned some years back and the remnants captured by the samplers are as a result of the strong persistence of PCBs in the environment. Due to their strong hydrophobicity (shown by higher log K_{ow} values of up to several orders of magnitude), PCBs tend to partition away from the water phase and preferentially adsorb strongly onto particulate matter, colloids and sediments in water. Moreover, their emissions are likely to be much lower than those of PAHs because, unlike the western industrialised countries, South Africa may not have utilised PCBs heavily during its economic growth in the 1980s or later when usage of PCBs was banned (Ogata et al., 2009).

Estimated water concentrations of the sum total of PCBs are shown in Table 3. When ranked in increasing order, the water-dissolved analyte concentrations followed the trend: summer > spring > autumn > winter. Concentrations of the compounds ranged from a low of 0.038 ng·ℓ$^{-1}$ in winter to a high of 0.150 ng·ℓ$^{-1}$ in summer. These concentrations were comparable to those obtained by Vrana et al. (2014) in the Danube River (5 to 16 pg·ℓ$^{-1}$) and Allan and Ranneklev (2011) in the Alna River, Norway (0.7 to 85 pg·ℓ$^{-1}$). Clearly, PCB levels in summer were significantly higher than those recorded in all of the other seasons. This observation may be explained as follows: In the summer rainfall region of South Africa, within which the study area lies, the summer period usually experiences heavy rainfall (90–125 mm).

Most PCB congeners are highly hydrophobic compounds which preferentially adsorb strongly onto soil particles and sediments. Therefore, heavy rain events may disrupt these strong interactions thereby remobilising them into the water phase. This is partly supported by the fact that usage of these compounds has been banned for several years and therefore a majority of inputs could be coming from sediment samples. Surface runoff from urban centres (where these compounds are found in higher quantities) may also add to the pollutant load. A good portion of the water that eventually finds its way to the sample site can be traced to the industrial areas of Johannesburg (Fig. 1).

The estimated freely dissolved water concentrations of OCPs are given in Table 3. Seasonal ranking from lowest to highest followed the trend: summer, autumn, spring, winter. The sequestered amounts of OCPs that comprised hexachlorocyclohexanes (HCHs), and DDX (DDTs, DDDs and DDEs) were up to 2 orders of magnitude higher than PCBs but slightly less than those of PAHs. Among the analysed OCPs, HCHs contributed over 78% of the quantified amount and their free dissolved concentrations ranged from about 9.2 ng·ℓ$^{-1}$ in summer to 10.4 ng·ℓ$^{-1}$ in winter. Figure 3 presents the water dissolved concentrations of selected HCH isomers.

Particularly high levels of β-HCH were detected at the sampling site in all four seasons. This HCH isomer is characterised by a much lower vapour pressure, better solubility in water, and lower Henry's law constant than all of the other HCH isomers, which favour partitioning from air to water. Compared to the gamma- and alpha-HCHs, it is the most recalcitrant isomer (Stockholm Convention, 2007).

In a global monitoring study of persistent organic pollutants (POPs) in coastal waters, Ogata et al. (2009) reported high concentrations of HCHs in samples from South Africa. This was in contrast to levels obtained in other parts of the world (such as USA, Asia and Europe) which were lower. They attributed this observation to the application of lindane in South Africa, which contains γ-HCH as its main component. It is possible that technical-grade HCHs that also contain considerable amounts of β-HCH (5–12%) were applied. Because of its relative volatility, this globally-banned pesticide can easily find its way into water systems via atmospheric deposition.

In the soil-air interface, ratios of HCH isomers have been used to identify the historical pollution sources (Willett et al., 1998). β-/(α+γ)-HCH > 0.5 is an indicator of historical pollution while a ratio less than 0.5 indicates new introduction of HCHs. In the case of the current study, these ratios ranged from 1.8 in autumn to a high of 9.5 in summer. It is therefore proposed that in all four seasons, HCH input to the sampling site is predominantly historical in nature with minimal inputs from current application.

Since the overall seasonal trends of HCHs generally mirrored those of PAHs (with the exception of values obtained in spring), we conclude that the same factors may have affected

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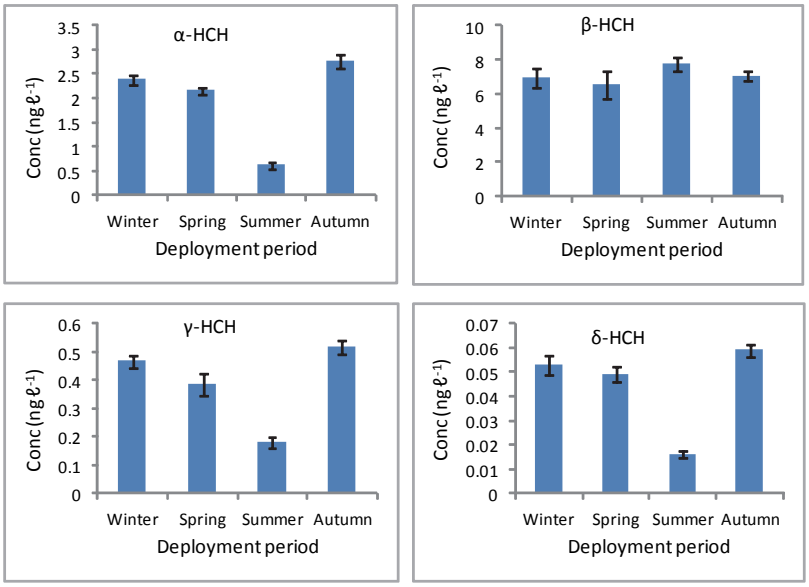

Figure 3
Water dissolved concentrations of individual HCHs as affected by seasonal change

them. However, the decrease in OCP concentrations from winter to spring was insignificant. This observation may be attributed to their comparatively lower volatility. Thus, losses through volatilisation resulting from increased temperatures during spring may not have been a major factor.

Interestingly, DDT and its metabolite residues showed seasonal patterns similar to those of PCBs, even though their water dissolved concentrations were generally higher. Estimated water concentrations of the DDT sum ranged from 0.31 ng·ℓ$^{-1}$ in winter to 0.83 ng·ℓ$^{-1}$ in summer, respectively. Volatilisation is a major route through which DDT and its metabolites are released into the atmosphere and, once there, these chemicals are cycled back to surface water through dry and wet deposition (Stockholm Convention, 2007). Findings from this study suggest that wet deposition of DDT and its metabolites may be playing an important role in re-introducing them to the sample site, as higher water concentrations coincide with high precipitation (summer). Moreover, considering the relatively high log K_{ow} values associated with DDX (5.8–6.79), remobilisation of the particle/sediment-bound fraction as a consequence of heavy rainfall may have been a possibility. Contributions from runoff originating from fields also cannot be ignored. Taken together, these factors may explain the seasonal trends of DDX.

Source identification of PAHs in the Hartbeespoort Dam

The principal sources of PAHs in the environment can be classified as either pyrogenic or petrogenic, with the pyrogenic inputs predominating in aquatic environments (Ekpo et al., 2012). Based on the SPMD-obtained PAH concentrations, identification of the probable sources was attempted. Reports by many authors on the apportionment of PAH sources in the environment using molecular ratios of certain PAHs are available in the literature (Baumard et al., 1998; Vrana et al., 2001; Zhang et al., 2004; Brandli et al., 2008). With respect to passive sampling, ratios of PAHs must be for compounds with near identical sampling rates to minimise bias arising from the mode of calculation of the rates for compounds with widely differing log K_{ow} (Allan and Ranekley, 2011). Furthermore, the same authors observed that unless PAHs are directly emitted to surface water, dissolved phase concentrations may not necessarily be representative of sources of contamination. From among the several available approaches, ratios of fluoranthene/(fluoranthene + pyrene) [Flt/(Flt + Pyr)] and anthracene/(anthracene + phenanthrene) [Ant/(Ant + Phe)] calculated from waterborne concentrations were applied in the identification of the possible sources of PAHs in the site.

Figure 4 shows the diagnostic ratios of PAH concentrations measured with SPMDs in Hartbeespoort Dam. An Flt/(Flt + Pyr) ratio > 0.5 indicates a pyrogenic source, as does an Ant/(Ant + Phe) ratio > 0.5. Ratios of indeno[1,2,3-cd]pyrene/(indeno[1,2,3-cd]pyrene + benzo[g,h,i]perylene) greater than 0.5 point to fossil fuel combustion or pyrogenic sources (Brandli et al., 2008) for the PAHs in the Hartbeespoort Dam. Thus, with the exception of concentrations obtained from SPMDs deployed in winter, all PAHs pointed to a pyrogenic origin. The winter-derived data showed a mixture of both pyrogenic and petroleum combustion sources. The spike in the petrogenic PAH fraction during winter may be attributed to the increased proportion of treated wastewater originating from Johannesburg. As Harding et al. (2004) reported, during winter, precipitation is almost nil and, consequently, more than 50% of the reservoir's inlet water is composed of treated wastewater. A steep increase in the Flt/(Flt + Pyr) ratio was observed from winter to spring before decreasing during summer. A further drop in the ratio, albeit gently, occurred between summer and autumn.

CONCLUSIONS

SPMDs are potentially effective tools for monitoring hydrophobic contaminants in aqueous systems such as those present in the Hartbeespoort Dam, South Africa. In addition to detecting concentrations of PAHs, PCBs and OCPs in the toxicologically most relevant dissolved phase, SPMDs also captured their seasonal variation in the water body. Generally, total contaminant concentrations in the dam increased in the order: summer, spring, autumn, winter. Concentrations of the PAH and HCH isomers decreased with increasing water temperature, which likely reflects seasonality of atmospheric deposition. The dissolved concentrations of PCB and DDT isomers are most likely related to desorption from suspended particles. Diagnostic ratios of PAHs measured in SPMDs were used to identify the possible sources of PAHs in the water. These ratios indicated

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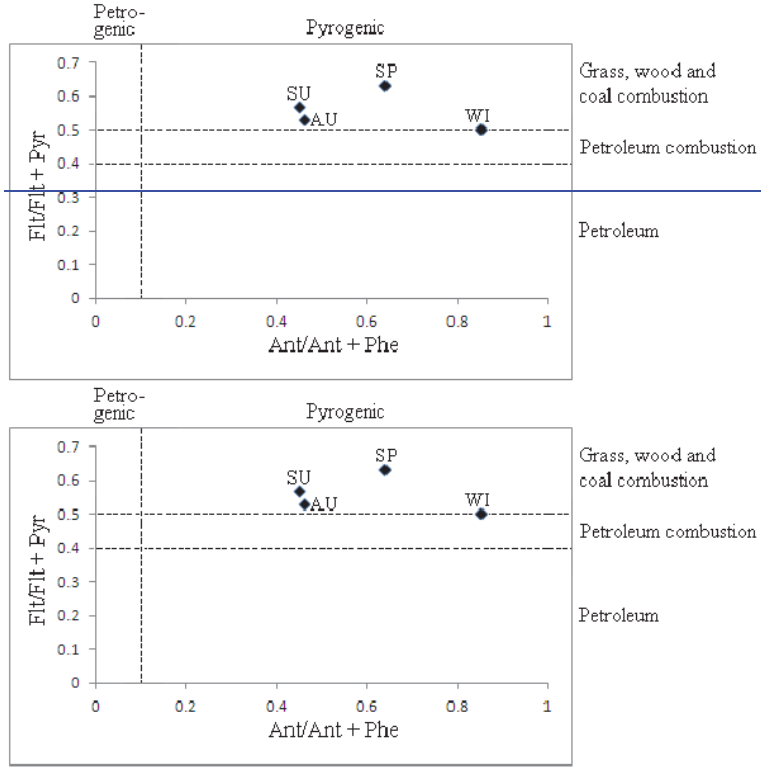

Figure 4
Diagnostic ratios of PAH concentrations measured with SPMDs in the Hartbeespoort Dam. WI: winter; SP: spring, SU: summer, AU: autumn, Flt: fluoranthene, Pyr: pyrene, Ant: anthracene, Phe: phenanthrene.

that the PAH concentrations in the dam during spring, summer and autumn were mainly of pyrogenic origin while the winter levels comprised both pyrogenic and petrogenic sources.

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APPENDIX

TABLE A1
Details of characteristic ions (m/z values) used in the analysis of polycyclic aromatic hydrocarbons in single ion monitoring (SIM) mode by GC/MS

Compound	Retention time (min)	[1]m/z 1	m/z 2	m/z 3
[2]Terphenyl	23.04	230	215	202
Naphthalene	8.37	128	129	126
Biphenyl	10.48	154	153	155
Acenaphthylene	11.49	152	153	150
Acenaphthene	11.91	154	153	155
Fluorene	13.3	166	167	164
Phenanthrene	16.42	178	179	176
Anthracene	16.61	178	179	176
Fluoranthene	21.13	202	203	200
Pyrene	22.09	202	203	200
Retene	23.46	219	234	205
Benzo[b]fluorene	23.9	216	215	217
Benzonaphthothiophene	26.39	234	235	232
Benzo[ghi]fluoranthene	26.58	226	227	224
Cyclopenta[cd]pyrene	27.45	226	227	224
Benzo[a]anthracene	27.49	228	229	226
Triphenylene	27.6	228	229	226
Chrysene	27.66	228	229	226
Benzo[b]fluoranthene	32.17	252	253	250
Benzo[j]fluoranthene	32.18	252	253	250
Benzo[k]fluoranthene	32.29	252	253	250
Benzo[e]pyrene	33.27	252	253	250
Bezno[a]pyrene	33.48	252	253	250
Perylene	33.8	252	253	250
Indeno[123cd]pyrene	38.39	276	277	274
Dibenzo[ah]anthracene	38.51	278	279	276
Dibenzo[ac]anthracene	38.52	278	279	276
Benzo[ghi]perylene	39.7	276	277	274
Anthanthrene	40.41	276	277	274
Coronene	50.13	300	301	298
[3]D_8-Naphthalene	8.37	136	137	134
[3]D_{10}-Phenanthrene	16.33	188	189	184
[3]D_{12}-Perylene	33.69	264	265	260

[1]The ion in the first column was used for quantification, the other two were used as qualifier ions to confirm compound identity
[2]Instrumental internal standard
[3]Recovery internal standard

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TABLE A2
Details of characteristic MRM transitions (m/z values of parent and daughter ion are given) used in the analysis of PCBs and OCPs by GC/MS/MS

Name	Retention time (min)	[1]MRM transition (Quantifcation)	MRM transition (Qualifier)
[2]PCB 121	20.24	325.9 > 255.9	327.9 > 255.9
[3]PCB 30	17.2	256 > 186	258 > 186
[3]PCB 185	27.28	393.8 > 323.9	395.8 > 325.9
PCB 28	17.13	256 > 186	258 > 186
PCB 52	18.15	289.9 > 220	291.9 > 220
PCB 101	21.05	325.9 > 255.9	327.9 > 255.9
PCB 118	23.27	325.9 > 255.9	327.9 > 255.9
PCB 153	23.95	359.8 > 289.9	361.8 > 289.9
PCB 138	24.91	359.8 > 289.9	361.8 > 289.9
PCB 180	27.22	393.8 > 323.9	395.8 > 325.9
PeCB	11.85	250 > 215	252 > 215
HCB	14.52	283.8 > 248.9	285.8 > 213.8
α-HCH	14.31	219 > 183	181 > 145
β-HCH	15.1	219 > 183	181 > 145
γ-HCH (Lindane)	15.29	219 > 183	181 > 145
δ-HCH	16.19	219 > 183	181 > 145
o,p'-DDE	20.89	246 > 176	318 > 248
p,p'-DDE	22.01	246 > 176	318 > 248
o,p'-DDD	22.27	235 > 165	237 > 165
p,p'-DDD	23.52	235 > 165	237 > 165
o,p'-DDT	23.59	235 > 165	237 > 165
p,p'DDT	24.84	235 > 165	237 > 165
ε-HCH	16.45	181 > 145	219 > 183

[1]The MRM transition in the first column was used for quantification, the other was used to confirm compound identity
[2]Instrumental internal standard
[3]Recovery internal standard

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