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PASSIVE SAMPLERS: DEVELOPMENT AND APPLICATION IN MONITORING ORGANIC MICROPOLLUTANTS IN SOUTH AFRICAN WATER BODIES AND WASTEWATER



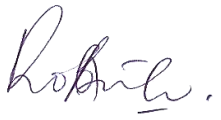
Robert Amdany

A Thesis submitted to the Faculty of Science, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the Degree of Doctor of Philosophy

July 2013

DECLARATION

I declare that this thesis is my own, unaided work. It is being submitted for the Degree of Doctor of Philosophy at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any other University



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30th day of **July**, **2013**

ABSTRACT

Annually, the global environment receives enormous amounts of persistent organic pollutants (POPs) that include polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), in addition to polycyclic aromatic hydrocarbons (PAHs). Their ubiquity has made them identifiable contaminants in almost every environmental compartment of the global system. In particular, aquatic systems have been adversely affected by these pollutants. Therefore, effective monitoring, both in ground and surface water, that can reliably assess their environmental impacts is required. Passive samplers have been proposed as suitable options to the traditional grab/spot/bottle sampling approach because they simultaneously sample, isolate and enrich target analytes. Moreover, apart from successfully detecting very low water dissolved analyte concentrations (trace and sub-trace levels), the devices can also provide time weighted average (TWA) concentrations that take into account episodic events. This is usually not practical with other sampling techniques.

The first two parts of this study were focused on the preparation and application of the semipermeable membrane device (SPMD) passive sampler for determining water-borne PAHs, PCBs and OCPs in selected water bodies situated in and around Johannesburg metropolis. Additionally, the same devices were used to monitor the temporal trends of the organic compounds in one sampling site over a one year period. Initially, SPMD preparation was done by enclosing triolein lipid that had been spiked with performance reference compounds (PRCs) in a clean layflat low density polyethene tube. Prior to actual field deployment, the samplers were placed in stainless steel protective cages. The devices were then deployed and left to passively sequester the contaminants in the water systems over a 14-day period. After retrieval and processing, analysis of the SPMD extracts for target analytes was achieved using gas chromatography combined with mass spectrometry (GC-MS/MS).

Water exposed SPMDs exhibited successful accumulation of the target compounds in all the sampling sites. Summed-up analyte amounts in individual samplers deployed in the various sites were in the range of 1223 to 4766 ng $SPMD^{-1}$ for PAHs, 6.5 to 76.1 ng $SPMD^{-1}$ for PCBs, and 4.5 to 921.6 ng $SPMD^{-1}$ for OCPs. Using the site specific sampling rates (R_s) obtained from the dissipation of PRCs, estimated water soluble analyte concentrations were determined from the accumulated quantities. Derived values indicated that the highest and lowest total PAH concentrations were estimated as 126.8 ng L^{-1} in Homestead Lake (HSL) and 33.5 ng L^{-1} in Centurion River (CR), respectively. On the other hand, freely dissolved total PCB concentrations varied between 20.9 pg L^{-1} at Airport River (AUP) and 120.9 pg L^{-1} at HSL. Total OCP concentrations ranged from 0.15 to 36.94 ng L^{-1} at AUP and Jukskei River 2 (JR 2), respectively. The major constituents of OCPs were hexachlorocyclohexanes (HCHs), and dichlorodiphenyltrichloroethane **(**DDT) with its degradation products. In most sites, more than 75% of the OCP concentrations were composed of HCH isomers. Irrespective of the sampling site, water-borne levels of all the target compounds showed a strong bias towards smaller molecular weight analytes. Such an observation was attributed to decreased water solubility resulting from increase in molar mass. Wet and dry atmospheric deposition, remobilisation of soil and sediment-bound analytes, leaching from landfills, accidental spills, illicit dumping, wastewater discharges and surface runoff from polluted urban areas were identified as some of the possible entry routes of the contaminants into the water systems.

Temporal trends of water-borne PAH, PCB, and OCP concentrations were investigated in a one year monitoring study at Ifafi (IFA) sampling site. Total PAH levels were 60.8, 58.2, 30.2 and 52.1 ng L^{-1} in winter, spring, summer and autumn, respectively. High PAH content in winter is usually due to increased sources as a consequence of the colder temperatures such as domestic wood combustion. Total PCB concentrations in water phase ranged between 38 and 150 pg L^{-1}, while those for OCPs were in the range of 10.0 to 10.7 ng L^{-1}. The findings clearly indicated detection of the highest PAH and HCH levels in winter, while

the summer campaign yielded the lowest concentrations. Low winter temperatures may have encouraged concurrent increases in atmospheric (dry) deposition and minimisation of analyte losses from water phase via volatilisation. However, concentrations of PCB, and DDT with its metabolites (DDX) were most elevated in summer but subdued in winter. Since these compounds are generally more hydrophobic than PAHs (as shown by their higher log K_{ow} values), increased water-borne summer concentrations may have been facilitated by heavy rainfall which caused desorption of the analytes sorbed to soils, sediments and water phase particulates. Surface runoff from contaminated areas may also have made a contribution to the overall analyte load in the sampling site in this season.

The third part of this work entailed the preparation and application of passive samplers that target pharmaceuticals and personal care products (PPCPs) in aquatic environments. As a consequence of their known and/or perceived health effects on animals and humans, this very diverse group of polar organic contaminants has in the recent past aroused intense attention among environmental scientists and the general public. PPCPs have active functional groups that elicit certain physiological responses in organisms and therefore, their possible impacts are an emerging issue of environmental concern. Currently, the Polar Organic Chemical Integrated Sampler (POCIS) is touted as one of the best sample preparation techniques for the polar organics. Unlike the exhaustive solid phase extraction (SPE) method, POCIS samples only the freely dissolved portion of the analytes and provide their TWA concentrations. In this study, POCIS was prepared, calibrated and applied in the field to determine two non-steroidal anti-inflammatory drugs, namely naproxen and ibuprofen, and one personal care product, triclosan. The samplers were initially calibrated in the laboratory with the aim of obtaining sampling rates (R_s) for each target compound. Thereafter, the devices were exposed to the raw influent and treated effluent of two wastewater treatment plants (WWTPs) for a period of 14 days. POCIS-extracted compounds were then analysed using high performance liquid chromatography (HPLC) systems combined with ultra violet (UV) and fluorescence (FLD) detectors. Laboratory calibration of POCIS yielded R_s values for the three PPCPs that were

between 0.087 and 0.383 L d^{-1} in quiescent conditions, and 0.125 and 0.936 L d^{-1} in stirred conditions. Sample agitation increases analyte mass transfer and, hence, higher R_s. From the accumulated amounts in field-deployed POCIS devices, estimated freely dissolved concentrations of PPCPs in wastewater influent ranged from 55.0 to 78.4 μg L^{-1} and 52.3 to 127.7 μg L^{-1} in Goudkoppies and Northern WWTPs, respectively. Average concentrations of individual PPCPs in the effluents ranged from 10.7 to 13.5 μg L^{-1} in Goudkoppies WWTP, and 20.4 to 24.6 μg L^{-1} in Northern WWTP. Analyte removal efficiencies were in the range 68 to 86% in Goudkoppies WWTP, and 61 to 82% in Northern WWTPs. SPE-extracted grab samples yielded significantly higher analyte concentrations (up to two-fold) in comparison to POCIS-derived estimates. This discrepancy was attributed to SPE's ability to extract both, the truly dissolved, and particle sorbed fractions of the contaminants.

Part four of this thesis covers the development of a hollow fibre based sample preparation method and subsequent analysis of extracts by liquid chromatography combined with UV and FLD detection systems. The hollow fibre membrane was made of silicone rubber. By using a water-based liquid membrane, this technique is a slight deviation from the traditional 3 phase supported liquid membrane (SLM) systems that uses an organic solvent as the membrane. During the method development, it was found that the large sample volumes extracted, long extraction periods, and sample stirring compromised the stability of the organic membrane. In order to achieve the best extraction conditions, optimisation of several parameters prior to field application was performed. The developed method was eventually used in the extraction and clean-up of naproxen, ibuprofen and triclosan in wastewater (pH 4).

After evaluating the various parameters that influence analyte extraction by the hollow fibre system, and choosing donor and acceptor phase pHs of 4.0 and 11.0, respectively, high enrichment factors of up to 369 were achieved in spiked reagent water. This made it possible to get a sensitive method with relatively low limits of detection, but, from affordable equipment. Although analyte recoveries in

wastewater samples using the developed method were comparatively lower (51 - 73%) than SPE values (all greater than 62%), the developed system exhibited excellent selectivity as shown by the clean chromatograms obtained even in the presence of complex sample matrix. Estimated concentrations of PPCPs in the influent and effluent wastewater of Goudkoppies WWTP using this method varied between 1.1 and 18.4 μg L^{-1} and 0.4 and 2.7 μg L^{-1}, respectively. Wastewater samples from Northern WWTP gave values that ranged from 2.3 to 22.5 μg L^{-1} in the influent and 0.8 to 6.1 μg L^{-1} in the effluent. It was noted that Northern WWTP exhibited higher analyte concentrations than Goudkoppies WWTP, possibly because it serves a larger human population. The hollow fibre system was tested as a passive sampler by deploying in the same sampling sites for 14 days. After the exposure period, the sequestered analyte amounts were used to estimate their TWA concentrations in the sites over the exposure period. On average, the effluents from both WWTPs had analyte concentrations that were in the range of 0.1 to 0.8 μg L^{-1}, whereas levels of between 0.7 and 1.9 μg L^{-1} were obtained in the influent. The variance in concentrations between grab samples and the passive sampling estimates was attributed to losses from ionisation of the analytes at ambient pH of wastewater (pH 8.2), decrease in acceptor phase buffering capacity over time and biofilm infestation of the membrane assisted passive sampler (MAPS).

In the final part of this work, the influence of temperature on PPCP extraction by the developed hollow fibre system with a stagnant acceptor phase was investigated. Determination of the mass transfer parameters such as diffusion coefficient and flux at 298K, 303K and 313 K was undertaken. The diffusion coefficient and flux was found to increase with increased temperature. It was also evident that at higher temperatures, mass transfer was influenced by the degree of trapping in the acceptor phase. However, diffusion from the bulk donor phase through the aqueous membrane controlled the transport of analytes at lower temperatures. Therefore, the influence of temperature on mass transfer in the hollow fibre extraction method is more pronounced in donor-controlled and/or membrane-controlled systems.

To my Family:

Irene, Jeptoo and Sumukwo

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LIST OF ABBREVIATIONS

ARV	Antiretrovial
ATSDR	Agency for Toxic Substances and Disease Registry
BCF	Bioconcentration factor
DAD	Diode array detector
DDE	Dichlorodiphenyldichloro-ethylene
DDT	Dichlorodiphenyltrichloroethane
ESI	Electrospray ionisation
EU	European Union
FLD	Fluorescence detector
GS-MS	Gas chromatography-mass spectrometry
GS-MS/MS	Gas chromatography-mass spectrometry/mass spetrometry
HCH	Hexachlorocyclohexane
HF-SLM	Hollow fibre supported liquid membrane
HLB	Hydrophilic lipophilic balance
HPLC	High performance liquid chromatography
HSDB	Harzadous Substances Data Bank
IARC	International Agency for Research on Cancer
LC	Liquid chromatography
LC-MS	Liquid chromatography-mass spectrometry
LC-MS/MS	Liquid chromatography-mass spectrometry/ mass spectrometry
LOD	Limit of detection
LOQ	Limit of quantification
MAPS	Membrane assisted passive sampler
NSAIDs	Non-steroidal anti-inflammatory drugs
OCPs	Organochlorine pesticides
PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PCDDs	Polychlorinated dibenzo-para-dioxins
PCDFs	Polychlorinated dibenzofurans

PES	Polyether sulfone
POCIS	Polar organic chemical integrated sampler
POPs	Persistent Organic Pollutants
PPCPs	Pharmaceuticals and personal care products
PRCs	Performance reference compounds
PSDs	Passive sampling devices
RSD	Relative standard deviation
SPE	Solid phase extraction
SPMDs	Semipermeable membrane devices
TWA	Time weighted average
UNEP	United Nations Environment Programme
UNIDO	United Nations Industrial Development Organisation
USEPA	United States Environmental Protection Agency
UV	Ultra violet
WHO	World Health Organisaion
WRC	Water Research Commission of South Africa
WWTP	Waste water treatment plant

Chapter 1:

Introduction

1.0 INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs), as well as persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) and organochlorine compounds (OCPs) are of particular interest because of their potential toxicity, carcinogenicity, possible mutagenicity as well as tendency to bioaccumulate. Their ubiquitous nature makes them readily available in the atmospheric, terrestrial and aquatic environmental sectors. In the aquatic environment, they are present both as truly dissolved and particle bound. The bioavailable fraction, which corresponds to the dissolved fraction, is of primary interest for risk assessment (Sabaliunas and Sodergren, 1997). As by-products of incomplete combustion of organic compounds, pyrosynthesis or pyrolysis of hydrocarbons, PAHs are the most available and are released to the environment through natural and anthropogenic activities (Levinson et al., 2008). PAHs may also reach water systems through oil spills and direct industrial effluent discharges. On the other hand, PCBs and OCPs are POPs of exclusive industrial origin.

Due to their characteristically high hydrophobicity and very low solubility in water, these compounds easily sorb to finely dispersed soil colloids and particulates in water phase. Thus, their truly dissolved concentrations are often several orders of magnitude lower than particulate levels. As such, water phase concentrations are generally too low (ng L^{-1} to pg L^{-1} range) and insufficient for direct reliable quantitative chemical analysis. Consequently, proper analysis of PAHs, PCBs and OCPs in natural water is not easy and many sampling problems are encountered.

In an attempt to mitigate the effects of POPs, the chemical industry has gradually shifted emphasis towards the development of less persistent, hydrophilic organic compounds, believed to pose less environmental risks due to their low bioconcentration abilities. However, evidence is growing that the large fluxes of these seemingly more environmentally friendlier compounds, that include pesticides, pharmaceuticals, personal care products, industrial and domestic use

chemicals, and their degradation products end up in the aquatic systems and may be responsible for incidences of acute toxicity and sub-lethal chronic abnormalities reported in aquatic organisms (Flaherty and Dodson, 2005; Boxall et al., 2004; Brooks et al., 2003). Incidences of subdued or even impaired reproduction, endocrine disruption effects, neurotoxicity and behavioural alteration of organisms attributable to these compounds have been reported (Greenlee et al., 2005; Welshons et al., 2003). In particular, the pharmaceutical and personal care product (PPCP) class pose enormous dangers to aquatic organisms. This group of polar organics have active functional groups designed to elicit diverse pharmacological responses in the target organism but very little is known about their effects on non-target aquatic life forms.

The major entry route of PPCPs into the aquatic environment is via treated effluent discharged from wastewater treatment plants (WWTPs). Other contributors include surface runoff, leaking septic tanks and sewage lagoons, direct environmental disposal of unused drugs and landfill leachates (Alvarez et al., 2010). The fate of these contaminants during wastewater treatment is largely unknown as the current WWTPs were not specifically designed to degrade them. Indeed, some findings suggest that many of these chemicals survive the treatment process and are even returned to their biologically active forms through de-conjugation (Braga et al., 2005; Miao et al., 2004; Gonzalez-Barreiro et al., 2003; Ternes, 1998).

The importance of sampling in any analytical procedure cannot be gainsaid as this step greatly influences the quality of the outcome. Chances of remediating errors committed at this stage later on during the analytical process are extremely remote. The traditional approach of grab sampling usually associated with analyte determination in water is riddled with many pitfalls, especially when losses encountered during sample pre-treatment steps are considered.

A viable alternative to grab sampling is to use passive samplers. These are man-made devices designed to mimic the potential uptake and possible

bioaccumulation of organic compounds by aquatic, terrestrial, and marine organisms (Alvarez, 2010). Passive samplers 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. By providing time-weighted average (TWA) values that take into account fluctuations in pollutant concentrations, the devices are better suited for long term monitoring of contaminants in an environmental compartment (Kot et al., 2000).

Among the passive sampler devices (PSDs), the semipermeable membrane devices (SPMDs), and the polar organic chemical integrated sampler (POCIS) have been widely applied to screen for and even estimate the concentrations of hydrophobic contaminants and polar organics, respectively, in the water phase (Morin et al., 2012; Alvarez et al., 2010; Allan et al., 2009; Verweij et al., 2004). SPMDs are robust, integrative passive samplers composed of a triolein receiving phase for contaminant accumulation enclosed in a low density polyethene membrane (LDPE). By simulating the passive diffusion and partitioning steps of bioconcentration, SPMD provides quantitative estimates of hydrophobic organic contaminant in the ambient exposure medium. The 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., 2001a). Through incorporation of permeability reference compounds (PRCs) during SPMD preparation, differences in environmental exposure conditions between deployment sites, times and different monitoring programs can be adjusted for by studying the dissipation rates of these compounds (Huckins et al., 2002; Booij et al., 1998).

The POCIS is a relatively young passive sampling tool suited for sampling hydrophilic organic micropollutants in aquatic systems (Morin et al., 2012). This device is composed of a solid sorbent receiving phase enclosed in between two

microporous polyethersulphone (PES) diffusion-limiting membranes that are firmly held in place using two compression rings made of steel or plastic (Alvarez et al., 2010). Even though several other passive sampling devices have been tested for this group of contaminants, POCIS is reported to be the most effective (Alvarez et al., 2005; Jones-Lepp et al., 2004; Petty et al., 2002). The sampler's suitability encompass a wide array of hydrophilic organics as well as a few hydrophobic organics with log K_{ow} values of between 3.0 and 4.0.

Although South Africa is a signatory of the Stockholm Convention and also having a relatively strong industrial presence, information on pollution by POPs and PPCPs remain 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 such countries may not give a very reliable prediction of the South African situation. Nevertheless, several studies by Nieuwoudt and co-workers, Röllin and co-workers, Das and co-workers, and Okonkwo and co-workers (Nieuwoudt et al. 2011; Röllin et al., 2009; Das et al., 2008; Okonkwo et al., 2008), among others, exist in the literature, but they are few and far apart. Save for a recent study by Degger et al. (2011) on the use of SPMDs to determine some POPs in certain South African marine environments, very little other information on using passive samplers to target such compounds is available in the literature. Adoption of this sampling approach may yield more comprehensive and reliable findings, especially the bioavailable concentrations in aquatic systems. This fraction is critical for environmental risk assessment.

Very little information on PPCPs, especially, ibuprofen, naproxen and triclosan in South African wastewater is available in the literature. Worse still, the use of any passive sampling technique that targets the bioavailable portion of polar organic contaminants in such systems has so far not been reported. Adoption of such technologies proven to have worked in other parts of the world will be a boost to assessing the extent of environmental pollution associated with these compounds.

Chapter 2:

Literature review

2.0 LITERATURE REVIEW

2.1 Persistent Organic Pollutants (POPs)

2.1.1 Introduction

Persistent Organic Pollutants (POPs) are organic compounds of natural or anthropogenic origin characterised by a particular combination of physical and chemical properties that impart in them exceptionally strong environmental persistence as a consequence of their resistance to photolytic, chemical and biological degradation (Aneck-Hahn et al., 2007; Wong et al., 2005; Buccini, 2003). They are largely hazardous compounds defined by strong hydrophobicity, low water solubility and typically lipophilic. Because of these inherent properties, POPs tend to bioaccumulate in the fatty tissues of living organisms once they enter the food chain. POPs are semi-volatile compounds and as such, environmental agents such as wind and water can transport them across international boundaries far from their point sources. As a result of this long-range translocation, POPs produced or used in one part of the world can have serious environmental consequences in other regions where they have never been used or even produced. Hence, these organic contaminants have been identified in every environmental compartment (ATSDR, 2009) as well as in all climatic and geographical zones of the global system.

PAHs and POPs (such as PCBs and OCPs), are either chemicals deliberately produced by industry for a wide variety of applications (e.g. pesticides and coolants) or accidental by-products of various activities that include industrial and combustion processes (Eljarrat and Barceló, 2002), as shown in Figure 2.1. POPs often comprise a wide range of compounds that include, but not limited to, polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), dioxins, furans, polybrominated diphenyl ethers (PBDE and certain phthalates.

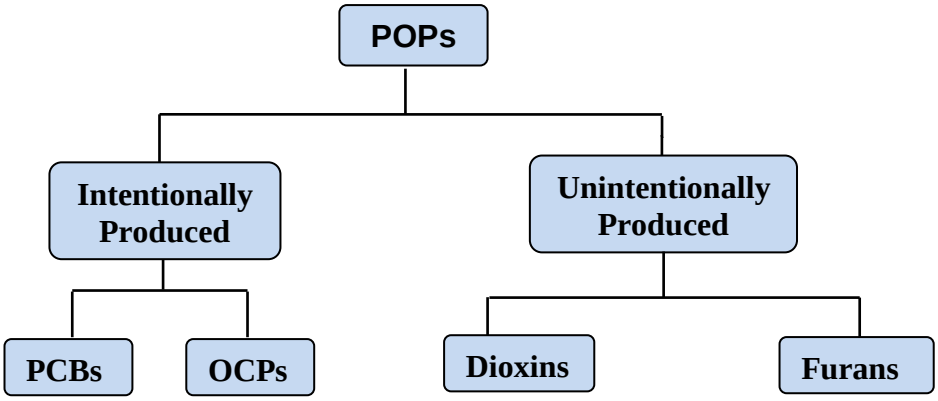


Figure 2.1: Classification of persistent organic pollutants (POPs) (Sharawi et al., 2010)

Chlorinated derivatives usually exhibit greater stability to physical, chemical and biological degradation and thus, more persistent in the environment. Moreover, increased chlorination in a compound elevates its tendency to bioaccumulate, and subsequently, biomagnify in organisms. PCBs and OCPs are present in aquatic systems worldwide because of their wide-spread usage, long-range transport, and persistence (Ogata et al., 2009). Some key POPs or POPs precursors are shown in Table 2.1.

Human exposure to POPs can occur through many avenues such as food, environment, and occupational accidents. Such exposures, whether acute or chronic, may result in serious health implications that could lead to illnesses or even fatalities. Several investigations have been carried out to assess the environmental risks associated with POPs. Many findings have linked POPs to potential health problems such as oestrogenic effects, endocrine disruption capabilities, impairment of immune systems, generation of functional and physiological effects on reproduction capabilities, reduced survival and growth of offspring, and potential carcinogenicity (Beard, 2006; Bhatia et al., 2005; Wahlstrom et al., 2003; Turusov et al., 2002; Snedeker, 2001; UNIDO, 2000).

The physico-chemical characteristics and their application practices principally influence the distribution patterns of individual POPs in any given environment.

Table 2.1: Some key POPs or POPs precursors and information relevant for deposition and release from deposition

Compound	Water solubility*	Vapour pressure*	Log K_{ow}**	Types of wastes
PCBs	Low: 0.0009 to 0.058mg L^{-1}	6.5E-2 to 7.7E-5 Pa	6.29 - 8.7	Condensers, transformers, demolition wastes, shredder residues
HCH isomers	Moderate 0.2 to 10 mg L^{-1}	12E-3 to 2.1E-5 Pa	3.5 - 3.7	Lindane/HCH production wastes, pesticides
PCDDs/PCDFs	Very low: 7.9 to 317 ng L^{-1}	2.17E-5 to 9.8E-8 Pa	6.64 - 7.02	Production wastes organochlorines (e.g. chlorophenols, triclosan, PVC), PCP treated wood, combustion residues
HCBz (PeCBz)	Low HCB: 0.004 to 0.006 mg L^{-1}	2.3E-4 Pa	5.5 - 6.1	Production wastes (e.g. EDC/PVC, tetrachloromethane, trichloromethane etc.), combustion residues
HCBD	Moderate: 4 mg L^{-1}	20 Pa	4.9	Production waste (e.g. EDC/PVC, tetrachloromethane, trichloromethane, etc.)
PBDEs	Low: 0.020 to 0.030 mg L^{-1}	3E-3 to 5E-6 Pa	4.8 - 10	Electrical and electronic wastes, polyurethane in furniture, etc., auto shredder residues
PFOS, PFOA and precursors	High PFOA: 3.4 to 9.5 g L^{-1} PFOS: 570 mg L^{-1}	Low to high depending on pH PFOA: 4.19 Pa PFOs: 3.31E-4	N/A	PFC and Teflon production waste, firefighting foam, production PFC-coated textiles, papers, and furniture (and other products

* Measured at 20 to 25^{0}C; ** Octanol/water partition coefficient; PCBs, polychlorinated biphenyls; HCH, hexachlorocyclohexane; PCDDs/PCDFs, Polychlorinated dibenzo-p-dioxins and furans; HCB, Hexachlorobenzene; PBDEs, polybrominated diphenyl ethers; PFOS, perfluorooctanesulphonic acid (Weber et al., 2011)

Thus, a thorough understanding of the pollutants' transport mechanism with respect to their global distribution is critical, especially where regulatory efforts and possible redress actions in heavily affected areas are to be undertaken.

To evaluate the effectiveness of the regulations and remediation, monitoring of POPs is essential. Because of the threats posed by the trans-boundary movement of POPs, monitoring of these contaminants at a global scale has increasingly become an urgent issue. Under the auspices of the United Nations Environmental Programme (UNEP), an international convention on POPs was signed in Stockholm, Sweden, by a number of world countries (UNEP, 2001). Many more countries later on ratified the Stockholm convention and membership currently stands at over 160 nations. The main aim of the convention is to protect human health and the environment from POPs by reducing or eliminating their usage, discharge and emission. The convention's focus area can be narrowed down to the discontinuation of production and use of POPs that are intentionally manufactured, unintentionally manufactured, released from anthropogenic sources, and destruction of available stocks and wastes. The initial set of 12 chemicals identified as priority POPs were nine pesticide classes (aldrin, chlordane, dieldrin, endrin, heptachlor, hexachlorobenzene, toxaphene, mirex, DDT, dichlorodiphenyltrichloroethane, one industrial chemical class, polychlorinated biphenyls (PCBs), and polychlorinated dibenzodioxins/furans PCDD/Fs) that are associated with various industrial/combustion emissions (Harner et al, 2006).

Whereas the original emphasis of the Stockholm Convention was on chlorinated compounds, brominated and fluorinated POPs, that include, polybrominated diphenylethers (PBDEs) and polybrominated biphenyls (PBB), were later on added to the list of priority pollutants in May 2009 (Weber et al., 2011). Brominated compounds have found extensive application in flame retarding formulations especially in furniture, electronics, textiles, upholstery, insulation foam etc. (Stockholm Convention, 2009).

2.1.2 Environmental fate

In order to understand how and why POPs have become a global problem, it is

necessary to comprehend the importance of certain factors known to influence their fate and transport. Simple physical and chemical characteristics of the substances can be used to predict their distribution among environmental compartments and between water, soil, sediments, air and organisms (Meylan et al, 1993; Mackay et al., 1992). Taken together, data and models have given an insight into understanding the environmental fate and transport of a large group of POPs (Ritter et al., 1995)

2.1.2.1 Physicochemical properties and environmental partitioning

The physical and chemical characteristics of a POP strongly influences its transport pathways and, hence, distribution in the environment. The physical properties of greatest importance are water solubility, vapour pressure (P), Henry's law constant (H), octanol-water partition coefficient (K_{ow}), and the organic carbon-water partition coefficient (K_{oc}) (Ritter et al., 1995). Using these physical parameters, and in conjunction with several models, environmental distribution of POPs can be predicted (McLeod et al., 2010; Smaranda and Gavrilescu, 2008; Mackay et al., 1993, 1992).

2.1.2.2 Persistence

How long a POP can persist in the environment is a critical characteristic since such compounds are prone to long-distance translocation, far beyond the immediate area of application or generation. A number of processes such as photolysis, abiotic oxidation, hydrolysis and biotransformation can significantly reduce the persistence of the contaminants in the environment. The relative importance of these processes depends on the rates at which they occur under natural environmental conditions which, in turn, depend on the chemical structure and properties of the substance and its distribution in the various compartments of the environment (Ritter et al., 1995).

Although environmental factors are not major determinants in the degradation and transformation of POPs, decreased potency has been witnessed in polar regions even for those factors that might otherwise indicate some effectiveness. This is particularly important as studies have shown that the continued use and release of POPs in other parts of the globe results in their accumulation in the polar areas (Meyer and Wania, 2007; Halsall et al., 2001; Ritter et al., 1995). This part of the globe experiences very low temperatures and limited sunlight incidences throughout the year. The result is drastically reduced biological activity and photolysis of POPs, hence, greater persistence in such regions.

Environmental parameters such as pH, temperature, ionic strength, metal ion catalysts and presence of sediments may modify how fast POPs are hydrolysed in the environment. However, since a good percentage of these compounds are halogenated, and especially, chlorinated, hydrolysis becomes less pronounced due to the strength of the C-Cl bond. Photodegradation as a means of elimination is also relatively insignificant because of their stability. Despite all these observations, photodegradation on particulate surfaces is still highly variable and dependent on the surface type, the wavelength and intensity of light (SETAC, 1996).

2.1.2.3 Transport

Environmental factors have been shown to have a strong influence on some of the physical properties. For instance, temperature strongly affects vapour pressure, water solubility, and, therefore, Henry's law constant (Ritter et al., 1995). Indeed, Hornbuckle et al., (1994) and McConnel et al., (1993) in a study of PCBs and HCB in the Great Lakes found out that the direction and magnitude of the air-water gas exchange changes seasonally with temperature. Due to the elevated temperatures, greater volatilisation occurs in summer as a result of warming of the surface water and thus, the net exchange direction for substances in the open ocean also reflects differences in surface water temperature and atmospheric concentration (Ritter et al., 1995). For example, net movement of POPs in the

warm waters of the Bay of Bengal in the Indian ocean is from the ocean to the atmosphere (Iwata et al., 1993; Jantunen and biddleman, 1995) while that in cooler polar regions is the opposite (Biddleman et al., 1995).

2.1.2.4 Deposition

Many POPs are present as gases even at low temperatures and are absorbed from the gas phase by water, snow, soil and plant surfaces (Braune et al., 2005). Deposition of such compounds in areas away from their sources may be influenced by temperature. Figure 2.2 presents a summary of the processes involved during the transport and deposition of POPs.

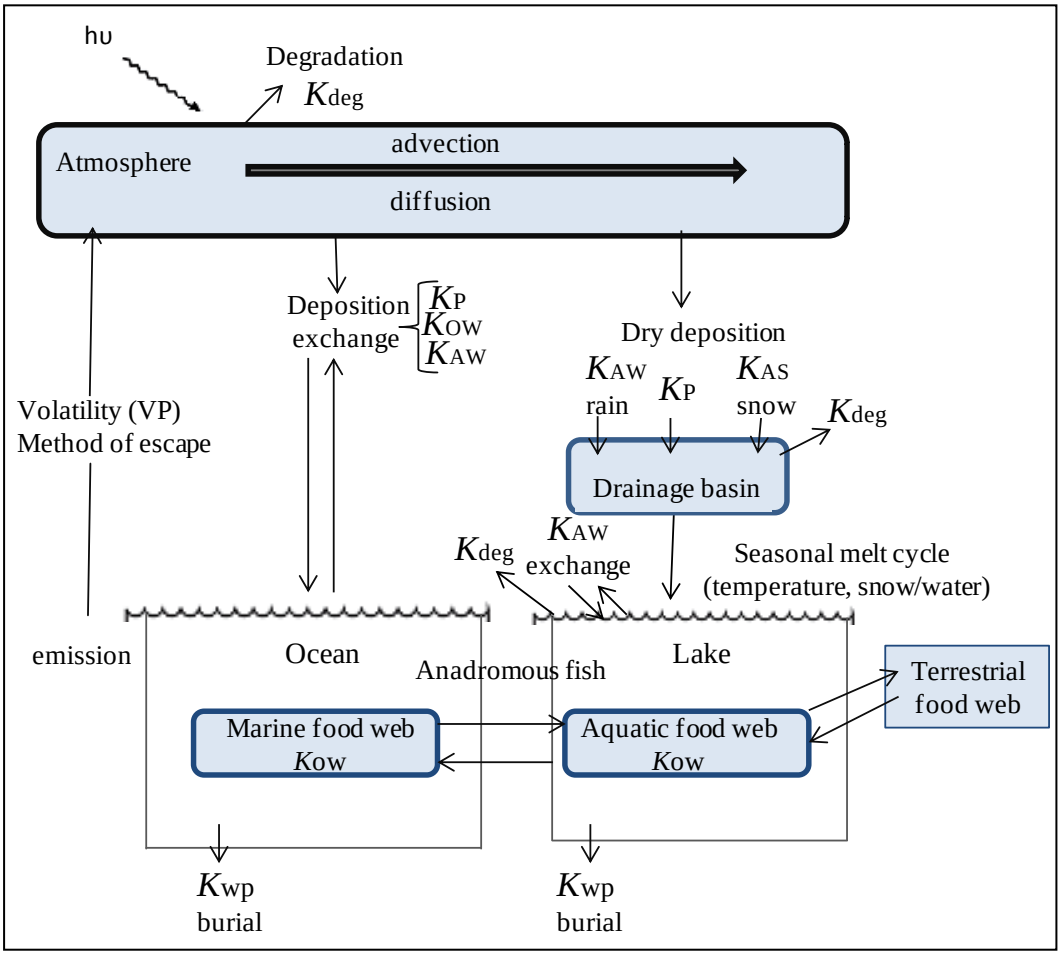


Figure 2.2: A schematic diagram showing processes involved during transport and deposition of POPs: K_{AW} - air/water, K_p - particle/air, K_{OA} - octanol/air, K_{ow} - octanol/water, K_{AS} - air/snow, K_{wp} - water/particle partition coefficients; K_{deg} - degradation coefficient (Weber et al., 2011).

The distribution of PCBs, OCPs, PCDDs and PCDFs is inversely related to vapour pressure and thus, temperature (Ritter et al., 1995). A decrease in temperature encourages more partitioning of the contaminants from the vapour phase to atmospheric particulate matter. This increases the likelihood of their removal and transport to the earth's surface through rain and snow (Falconer and Bidleman, 1994).

2.1.3 Polycyclic Aromatic Hydrocarbons (PAHs)

2.1.3.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) also referred to as polynuclear aromatic hydrocarbons or polyaromatic hydrocarbons comprise a large and diverse group of organic compounds characterised by at least two fused benzene rings. As hydrocarbons, these molecules are composed of carbon and hydrogen atoms only. Depending on the number of aromatic rings, the compounds can be classified either as low or high molecular weight PAHs with the former defined by having less than four aromatic rings and the latter having more than four rings. Several hundred individual PAHs are documented, and they generally occur as complex mixtures rather than single compounds (Lee, 2010).

PAHs are found in all environmental compartments (Boehm, 2006; Stout et al., 2004). Large molecular weight PAHs are recalcitrant molecules that can persist in the environment due to their hydrophobicity and low water solubility (Bamforth and Singleton, 2005). PAH concentrations in the environment vary widely, depending on the proximity of the contaminated site to the production source, the level of industrial development, and the mode(s) of transport (Kanaly and Harayama, 2000).

Environmental concerns of PAHs have necessitated their inclusion in lists of priority pollutants by several regulatory agencies such as the US EPA, European Union EPA, and Environment Canada. US EPA has identified 16 unsubstituted

PAHs as priority pollutants, some of which are considered possible or probable human carcinogens (Shailaja and D'Silva, 2003). Their distribution in the environment and potential risks to human health has been the focus of much attention (Manoli and Samara, 1999). The 16 US EPA priority PAHs along with their structures are given in Figure 2.3.

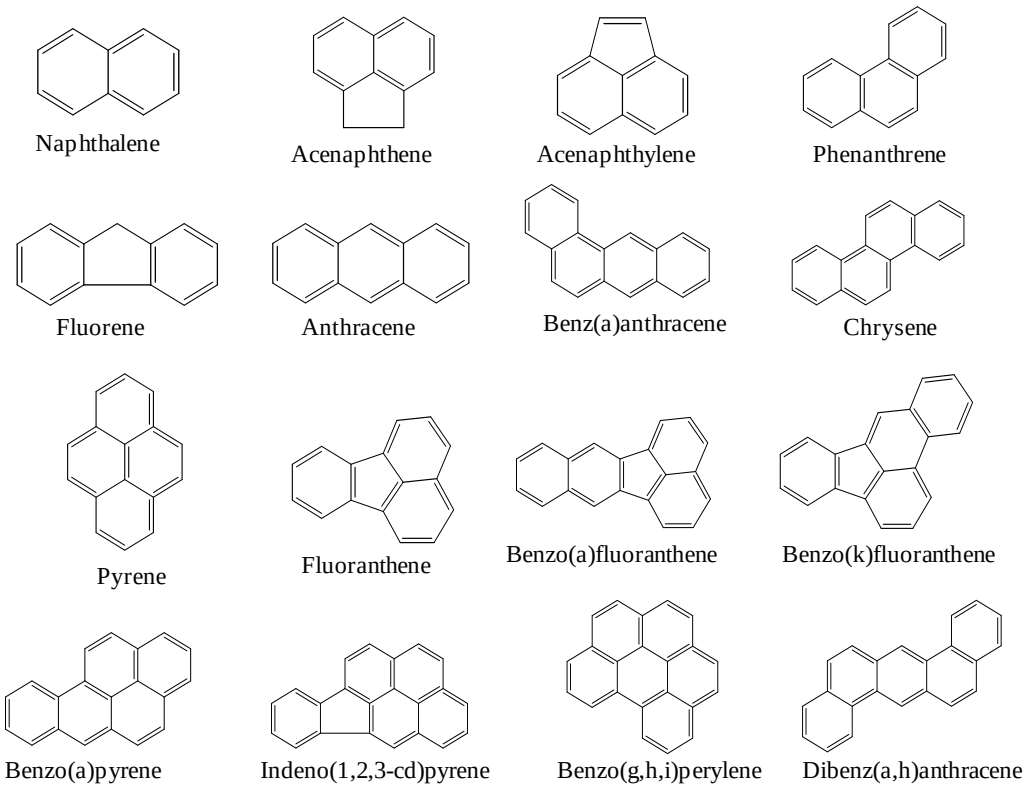


Figure 2.3: Structures of the 16 priority PAHs according to US EPA

2.1.3.2 Physical and chemical properties of PAHs

The structure and physical properties of PAHs can greatly impact their volatility, solubility, sorption, and decomposition behaviours (Schwarzenbach et al., 2003). Physical characteristics such as melting point, boiling point, vapour pressure, log K_{ow}, and solubility in polar and non-polar solvents (Table 2.2) are to a large extent influenced by their conjugated π-electron systems, which in turn, depends on the number of aromatic rings and the molecular mass (Environment Australia, 1999). PAHs are solids with low volatility at room temperature (ATSDR, 2009).

Table 2.2: Physical and chemical properties of PAHs[a]

Compound	No. of rings	Mw	Solubility Mg L^{-1}	M.P (^{0}C)	B.P (^{0}C)	Specific gravity	Log K_{ow}	Log K_{oc}	V.P. (Pa)	Henry's law constant Atm-m^3 mol^{-1}
Acenaphthylene	3	152	1.93	92-93	265 -275	0.8988 at $16^0C/2^0C$	4.07[k]	1.40[k]	0.029 at 20^0C[k]	1.45×10^{-3}
Acenaphthene	3	154	3.93	95	96.2	1.0242 at $90^0C/14^0C$	3.98[k]	3.66[k]	4.47×10^{-3} [m]	7.91×10^{-5}
Fluorene	3	166	1.68-1.98	116-117	295	1.203 at $0^0C/4^0C$	4.18[k]	3.86[k]	3.2×10^{-4}	1.0×10^{-4}
Phenanthrene	3	178	1.20	100	340	No data	4.45[k]	4.15[k]	6.8×10^{-4}	2.56×10^{-5}
Fluoranthene	3	202	0.20-0.26	11	375	1.252 at $0^0C/4^0C$	4.90[k]	4.58[k]	5.0×10^{-6}	6.5×10^{-6}
Anthracene	3	178	0.076	218[b]	342[b]	1.23 at $25^0C/4^0C$[e]	4.45[k]	4.15[k]	1.7×10^{-5} at 25^0C[k]	1.77×10^{-5}
Pyrene	4	202	0.077	156	393	1.271 at 23^0C	4.88[k]	4.58[k]	2.5×10^{-6} at 25^0C	1.14×10^{-5}
B[a]A	4	228	0.010p	158-159c	400[i]	No data	5.61[k]	5.30[k]	2.2×10^{-8} at 20^0C[k]	1.0×10^{-6}
Chrysene	4	228	2.8×10^{-3}	255-256[b]	448[b]	1.274 at 20^0C	5.16[k]	5.30[k]	6.3×10^{-7}	1.05×10^{-6}
B[a]P	5	252	2.3×10^{-3}	179 -179.3[f]	495[f]	No data	6.06[k]	6.74[k]	5.6×10^{-9} [k]	4.9×10^{-7} [k]
B[a]F	5	252	0.0012[q]	168.3[b]	No data	No data	6.04[k]	5.74[k]	5.0×10^{-7} at 20-25^0C[r]	1.22×10^{-5}[k]
B[b]F	5	252	0.0012	168.3	No data	No data	6.04[k]	5.74[k]	5.0×10^{-7}	1.22×10^{-5}
B[k]F	5	252	7.6×10^{-4} at 25^0C	215.7	480	No data	6.06[k]	5.74[k]	9.59×10^{-11}	3.87×10^{-5}
B[ghi]P	6	276	2.6×10^{-4} at 25^0C	273	550	No data	6.50[k]	6.20[k]	1.03×10^{-10} [k]	1.44×10^{-7}

[a]All information obtained from HSDB 1994, except where noted; [b]IARC, 1993; [c]Eller, 1984; [e]Weast, 1983; [f]Weast, 1989; [i]Sax and Lewis, 1989; [k]Mabey et al., 1982; [m]EPA, 1987; [r]Nirmalakhandan and Speece, 1988; B[a]A, Benz[a]anthracen; B[a]F, Benzo[a]fluoranthene; B[b]F, Benzo[b]fluoranthene; B[ghi]P, Benzo[ghi]perylene.

With the exception of some lighter members that volatilise at ambient temperatures, they are relatively non-volatile. In fact, PAHs with 4 or more rings show insignificant volatilisational loss under all environmental conditions (Moore and Ramamoorthy, 1984). Most PAHs with low vapour pressure (10^{-5} to10^{-13} kPa at 25^{0}C) in the air are adsorbed on particles (WHO, 2010) and hence transported over long distances.

PAHs typically have low vapour pressures and are most frequently found in air attached to particulate matter. However, some PAHs can evaporate and be found in the air in vapour phase (WHO, 2000). Environmental reports have indicated that more than 80% of PAHs with greater than five rings are associated with atmospheric particles with an aerodynamic diameter of less than 2.5 μm (EU working group on PAHs, 2001).

The distribution of atmospheric PAHs between gas and particulate phase is mostly determined by the vapour pressure of the compound (Lima et al., 2005). PAHs with 3 to 4 rings (phenanthrene, fluoranthene, and pyrene) are generally present in the atmosphere in the gas phase. Equal concentrations in the gas and particle phases are found for chrysene and benzo[a]anthracene while PAHs with 5 or more rings are mostly in the particle phase (Fraser et al., 1998; Yamasaki et al., 1982). The measured vapour pressures of PAHs are in agreement with these observations. Partitioning between the gas and particle phases is also a function of the number of particles available in the atmosphere. For example, since small quantities of particulate matter are produced during combustion of kerosene, PAHs emitted by this process tend to partition preferentially to the gas phase (Oanh et al., 2002) as contrasted with wood burning which generate abundant quantities of particles such that even small compounds (e.g. fluoranthene) can partition to the particle phase (Schauer et al., 2001).

The water solubility of PAHs range from slightly soluble (naphthalene) to very insoluble (dibenz[a,h]anthracene) (Lima et al., 2005). Typically, solubility is inversely proportional to the molar mass of the molecule because hydrophobicity

increases with increasing molecular weight. Other factors that affect water solubility of these hydrocarbons include structural orientation, water temperature, and alkyl substitution of the aromatic ring. A rise in water temperature has a similar effect as an increase in ring alkyl substitution, as both tend to enhance the compound's solubility (Garrett et al., 1998). Conversely, molecules with linear conformations are less soluble than angular or perifused molecules because intermolecular interactions are more pronounced in the former than the latter. When dissolved in water, PAHs get sorbed to particulate matter and eventually settle out of the water column onto the bottom sediments. Thus, water-phase PAH concentrations are usually very low relative to the concentrations in the bottom sediments (Moore and Ramamoorthy, 1984). Because most PAHs are chemically inert, they tend to persist in the environment for relatively long periods. However, when exposed to strong ultraviolet energy such as those originating from solar radiation, they undergo photochemical decomposition. Atmospheric PAHs that commonly adhere to airborne particulate matter may also react with ozone, hydroxyl radicals, nitrogen oxides, sulphur oxides, nitric acid, and sulphuric acid which then alter their environmental fate or conditions (Lee, 2010). PAHs may also be degraded by certain microorganisms in the soil (ATSDR, 1994)

Identification of individual PAHs is made possible because these compounds are characterised by very distinct ultra violet (UV) absorbance spectra and each isomer has a different UV absorbance spectrum. Additionally, most PAHs have fluorescence properties which enable them to emit characteristic wavelengths of light when they are excited (Buha, 2011).

2.1.3.3 Sources of PAHs

PAHs are formed when complex organic substances are exposed to high temperatures or pressures, and particularly, their incomplete combustion. They are by-products of both natural and anthropogenic processes. A small number of PAHs are produced for commercial use, for example, naphthalene, fluorene, anthracene, phenanthrene, fluoranthene, and pyrene (Franck and Stadelhofer,

1987). They are mainly used as constituents in the production of plastics, dyes, pesticides, and some drugs (Manoli and Samara, 1999). However, most PAHs are not products of deliberate industrial synthesis and hence, have no known economic importance. Forest fires are the single most important natural source of PAHs. Other pyrogenic non-anthropogenic sources of PAHs include volcanic eruptions, and degradation of biological materials (Ravindra et al., 2008). These sources do not significantly contribute to the overall PAH emission (Wild and Jones, 1995; Bakowski and Bodzek, 1988).

Anthropogenic sources are numerous and result in emissions of PAHs into all environmental compartments. Industrial and human activities such as processing of coal and crude oil, combustion of natural gas, garbage incineration, vehicular exhausts, cooking processes and tobacco smoke, to name but a few, are major contributors of PAHs. Such sources can be categorised into two broad groups: combustion of materials for energy supply (e.g. coal, oil, gas, and wood), and combustion for waste eradication (waste incineration) (Wild and Jones, 1995; Bakowski and Bodzek, 1988; Ramdahl et al., 1983). Industrial and residential heating, power generation, and mobile sources (vehicles, trains, airplanes and sea traffic) fall into the first group of sources whereas the second category mainly covers incineration of municipal and industrial wastes (Maliszewska-Kordybach, 1999). Other multifarious sources of PAHs include unregulated agricultural burning, smoke from crematoria, cigarette smoking, recreational fires, and volatilisation from soils.

2.1.3.4 Exposure

PAHs are strongly lipid-soluble organic compounds, as indicated by their high log K_{ow} values. Their entry routes into animal and human bodies primarily occur through dermal exposure, inhalation and absorption in the gastrointestinal tract.

Both animal and human studies have demonstrated that PAHs can be absorbed through the skin (Tenth report on carcinogens, 2003). Although dermal absorption

is not a major exposure pathway, these compounds are reported to rapidly penetrate the skin and the process is enhanced by the presence of oils on the skin.

Exposure to PAHs via inhalation is attributed to their being present in ambient and indoor air (Chetiyanukornkul, et al., 2006). People living near hazardous waste sites can also be exposed by breathing air containing PAHs. In the South African set-up, domestic fire combustion and vehicular emissions are important sources of PAHs and may result in potential exposure. However, it is not known how rapidly human lungs absorb PAHs (ATSDR, 1995). Once inhaled and deposited in the alveoli, a large fraction of the bioavailable PAHs is absorbed, mostly unaltered, into the blood stream via the alveolar type I cells (Gerde et al., 2001).

Uptake of PAHs through the gastrointestinal tract is billed as one of the major pathways. Animal studies have shown that between a third and a half of all PAHs found in the body were absorbed through the gastrointestinal tract (WHO, 2000). Two factors can significantly improve their absorption through this tract: presence of the contaminant as solutes in various dietary lipids, and existence of bile salts in the intestinal tract (Buha, 2011).

Irrespective of the entry route, once absorbed, distribution of PAHs occurs fast across the entire body, such that detectable concentrations can be obtained from virtually all body organs. Because of their lipophilic nature, PAHs tend to concentrate most in the liver, and the fat-rich tissues of the body. A good portion of absorbed PAHs is quickly metabolised by the liver and excreted through faecal matter and urine (ATSDR, 1995a). As a consequence, bioconcentration of PAHs in humans is not very pronounced.

2.1.3.5 Health effects

The adverse health effects of PAHs to humans, animals, as well as a variety of flora and fauna species is widely documented (Yu et al., 2011, Joner et al., 2001).

Acute health effects

Acute health effects of PAH exposure to animals and humans are dependent on the exposure period, route, concentrations, and how noxious the compound is. Age and the individual's health status may also play a vital role. Generally, acute toxicity of PAHs in human health is not well established. However, occupational exposures to high levels of pollutant mixtures containing PAHs have resulted in symptoms such as eye irritation, nausea, vomiting, diarrhoea and confusion (Buha, 2011). The difficulty lies in identifying the individual PAH(s) that causes the effects. Studies have also indicated that anthracene, benzo(a)pyrene and naphthalene are direct skin irritants while anthracene and benzo(a)pyrene are reported to cause an allergic skin response in animals and humans (IPCS, 1998).

Chronic health effects

PAHs and their metabolites may biochemically interfere with the cell functioning resulting in gene mutations, developmental defects, tumors, and even cancer. The major health and ecological concerns of PAHs are their carcinogenic potential (Baird et al., 2005). Animal studies have revealed PAHs' potential to cause cancer but that ability is dependent on the characteristics of the individual compound. Laboratory studies on animals subjected to long exposure periods have reported development of various cancer types such as lung, stomach, and skin cancers. A limited number of individual PAHs are reported to be confirmed human carcinogens while a few others are suspected carcinogens (IARC, 1987; USEPA, 1994).

Many individual PAHs have been tested for tumorigenicity and it was observed that PAHs with bay regions were likely to be potent carcinogens, and those with fjord regions or a sterically hindered bay region were even more potent (Figure 2.4) (Baird et al., 2005).

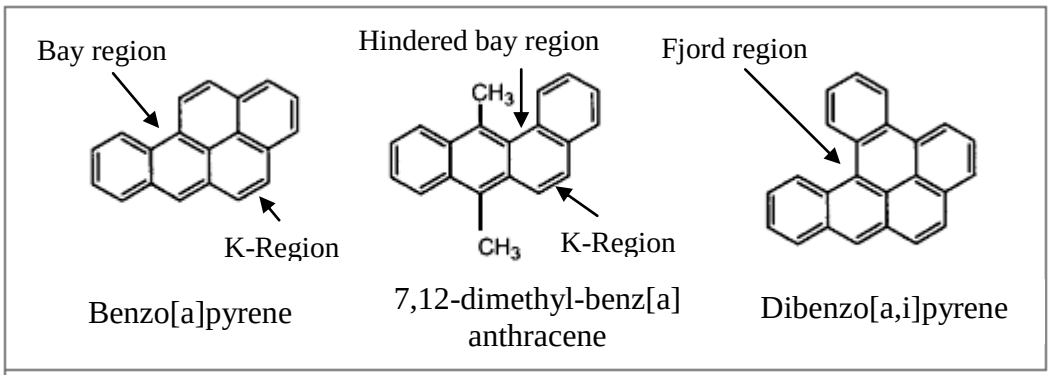


Figure 2.4: Structural features of PAHs that contribute to toxicity (Baird et al., 2005)

Table 2.3: PAHs identified as possible or potential human carcinogens by US EPA, IARC and Environment Canada

Polycyclic Aromatic Hydrocarbon	USEPA	IARC	Environment Canada
Naphthalene	√	-	-
Benzo(a)Pyrene	√	√	√
Benz(a)anthracene	√	√	-
Benzo(b)fluoranthene	√	√	√
Benzo(j)fluoranthene	√	√	√
Benzo(k)fluoranthene	√	√	√
Chrysene	√	-	-
Cyclopenta(c,d)Pyrene	√	-	-
Dibenz(a,h)anthracene	√	√	-
Dibenz(a,e)fluoranthene	√	-	-
Dibenzo(a,e)Pyrene	√	√	-
Dibenzo(a,h)Pyrene		√	-
Dibenzo(a,i)Pyrene	√	√	-
Dibenzo(a,l)Pyrene	-	√	-
Indeno(1,2,3-cd)Pyrene	-	√	√
Dibenz(a,h)acridine	-	√	-
Dibenz(a,j)acridine	-	√	-
5 methylchrysene	-	√	-
Dibenz(a,c)anthracene	√	√	√

(ATSDR, 2009; Environment Canada, 1999; IARC, 1993)

The USEPA has classified 14 out of 25 PAHs investigated as probable human carcinogens and the remaining 11 PAHs were not classifiable as possible human carcinogens due to inadequate human and animal evidence (National Library of Medicine, 2003). Table 2.3 summarises those PAHs identified by USEPA, IARC and Environment Canada as possible or potential human carcinogens.

Benzo[a]pyrene is recognised as a priority pollutant by the US EPA (Renner, 1999) as this compound is known to be one of the most potent carcinogen of all known PAHs (Baird et al., 2005; Juhasz and Naidu, 2000). Other common members of this group include benzo[a]anthracene, benzo[b]fluoranthene, benzo [k]fluoranthene, chrysene, dibenz[a]anthracene, and indeno[1,2,3-c,d]pyrene (Buha, 2011). Of peculiar importance is the inclusion of naphthalene as a possible human carcinogen by the USEPA, based on limited evidence of carcinogenicity in animals (National Library of Medicine, 2003). This is especially worrisome considering the widespread availability of this compound coupled with its higher solubility in water.

Some epidemiological and mortality studies have positively correlated an increase in cancer incidents in humans with exposure to PAH mixtures. Dermal exposure to coal tar and shale oils containing PAHs have been associated with increased incidences of skin tumours in humans (Tenth report on carcinogens, 2003).

Some PAHs are reported to show possible embryotoxic effects in animals although the significance in humans has not been exhaustively determined. Nonetheless, some studies have alluded to an association between prenatal exposures to PAH pollution and adverse birth defects that include premature delivery, low birth weight, heart malformations, and lower intelligence quotients (IQ) (Center for Children's Environmental Health, 2010).

Studies on rodents have also shown that PAHs may also be capable of affecting the skin and suppressing the immune system. How these compounds induce immunotoxicity is still not well understood, although it is postulated that

immunosuppression may be involved in the same mechanisms by which PAH induce cancer. These effects have however, not been reported in humans (ATSDR, 1995a)

2.1.3.6 Environmental fate

The environmental fate of PAHs is primarily dictated by their physicochemical properties, although natural processes, concentration of oxidizing pollutants, temperature, light intensity, and type of sorbent are also important factors (Matsuzawa et al., 2001; Kamens et al., 1988).

Atmosphere

PAH emissions of pyrogenic origin are released into the atmosphere either in the gas or particulate phases and their deposition is strongly dependent on the partitioning between these compartments (Lima et al., 2005). Atmospheric partitioning of PAHs is influenced by the compound's properties such as vapor pressure, ambient temperature, concentration, and amount and type of fine particles present in the atmosphere (Yamasaki et al., 1982). Since PAHs are hydrophobic compounds that readily get adsorbed onto particulates, the type of sorbent can also significantly influence the fate of these compounds in the atmosphere. Wet and dry depositions are the major removal mechanisms of PAHs from the atmosphere. Wet deposition constitutes precipitation through rain or snow. Typically, PAHs present in the gas phase dissolve within clouds and into raindrops (Offenberg and Baker, 2002), while PAHs bound to particles are washed out from the atmosphere by precipitation.

Dry deposition results from the direct fallout of PAHs adsorbed to atmospheric particles. The mechanism is largely dependent on the size of these particles (Windsor and Hites, 1979) and this mode greatly influences the transportation patterns of the contaminants. For example, smaller PAH-bearing particles can be transported for over 1300 km before settling to the surface, while the larger ones

settle much closer to the source, say, less than 13 km (Windsor and Hites, 1979). Particulate PAHs tend to be distributed across the particle size spectrum in relation to their molecular weights, with lower molecular weight species typically associated with larger particles in ambient air (Bae et al., 2002; Kaupp and McLachlan, 2000; Offenberg and Baker, 1999). Allen et al., (1996) reported that five-ring PAHs predominantly adsorbed onto particles in the 0.1 to 2 μm size range, while 3 and 4-ring members were mostly associated with larger particles measuring between 0.5 to 6 μm. It has also been observed that volatile PAH compounds usually affiliated with particulate matter, exhibit higher scavenging ratios (Offenberg and Baker, 2002) than their less volatile counterparts. This reinforces the observation that dry deposition is a major removal mechanism of PAHs from the atmosphere (Golomb et al., 1997; Offenberg and Baker, 2002). A schematic diagram of the fate of PAHs in the atmosphere is given in Figure 2.5.

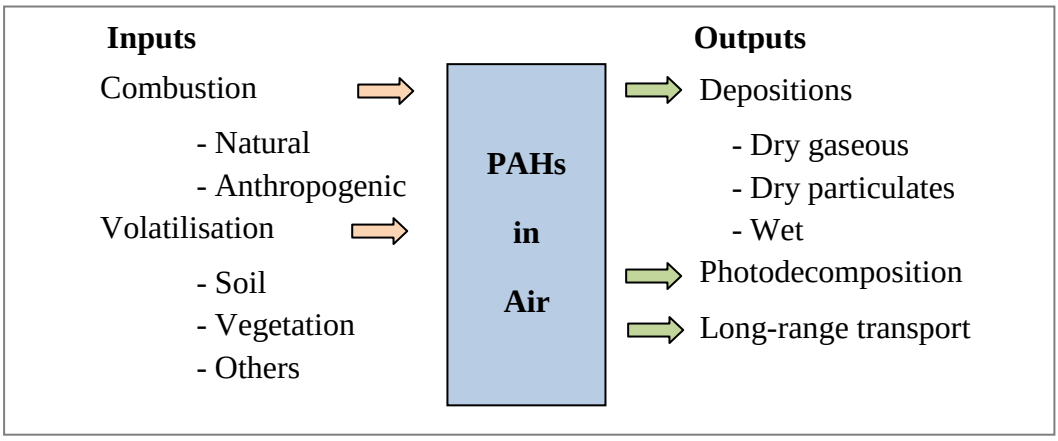


Figure 2.5: Schematic diagram of PAH fate in the atmosphere

Water phase

PAHs are strongly hydrophobic compounds defined by low aqueous solubility. In the water phase, PAHs will tend to adsorb onto settling particles significantly reducing their water-soluble fraction. Although this is the overall scenario, there exist significant differences in the solubility of individual members that can have an impact on their environmental distribution. For instance, in sediment trap studies, Lipiatou et al., (1993) reported that while the profile of benzofluoranthenes did not vary significantly with depth, that of phenanthrene showed a marked

decrease in flux. The authors attributed this finding to the higher aqueous solubility of phenanthrene which enabled its partitioning in the water phase unlike the more hydrophobic benzofluoranthenes. Such partitioning, as witnessed for phenanthrene, can lead to faster degradation of the compound in the water column. Conversely, the strong adsorption of PAHs onto particles can reduce their bioavailability, slowing their biodegradation rates and preserving them in the sediments (McGroddy et al., 1996) for longer periods.

Soil and sediment

Soil-borne PAHs are mainly lost through microbial-driven transformation reactions as compared to other degradation processes viz hydrolysis, oxidation, and photolysis (Sims and Overcash, 1983). However, PAHs adsorbed to surface soils may also be affected by volatilisation and photolysis processes because of their exposure to the effecting agents. Low-molecular-weight PAHs (such as naphthalene, phenanthrene, and anthracene) are more likely to undergo microbial degradation than their higher-molecular-weight counterparts (Budzinski et al., 1998; Cerniglia and Heitkamp, 1989). Typically, a negative correlation is observed between the number of fused rings making up a PAH and its susceptibility to microbial degradation. It has also been witnessed that alkyl-substituted PAHs degrade more slowly than their unsubstituted parent compounds.

A previously held assumption that biodegradation had no effect on PAHs deposited in anoxic sediments has been found to be false (Rothermich et al., 2002; Cerniglia and Heitkamp, 1989). It is now known that under denitrifying and sulphate reducing conditions, PAHs deposited under such conditions can equally undergo microbial degeneration. As expected, the more soluble, lower-molecular-weight PAHs degrade faster than the less soluble, higher molecular weight compounds (MacRae and Hall, 1998). Furthermore, even in cases involving PAHs with identical molecular weights, biodegradation is biased towards the more water-soluble species. A case in point is phenanthrene and anthracene. Though

both PAHs have the same molecular weights, anthracene's degradation is relatively slower than for phenanthrene. It has also been observed that the extent of contamination due to the presence of other pollutants has a direct bearing on the rate of microbial degradation. Bossert and Bartha (1986) reported reduced biodegradation of PAHs in a soil containing a chemical toxic to microorganisms. The presence of such contaminants in waste sites may hamper the effectiveness of degrading microorganisms.

In addition to environmental factors, physico-chemical properties of PAHs also determine how fast they are biodegraded in the soil (Wilson and Jones, 1993). Such environmental factors include temperature, pH, oxygen concentration, PAH concentration and contamination history of soil, soil type, moisture, nutrients, and other substances that may act as substrate metabolites (Sims and Overcash, 1983). These factors can in turn, affect the size and composition of microbial populations. For example, in low pH soils, fungi are dominant over bacteria, and thereby control the biogradation activity in such environments (ATSDR, 1995a).

2.1.4 Polychlorinated biphenyls (PCBs)

2.1.4.1 Introduction

These compounds constitute an important class of persistent organic contaminants of industrial origin. Since their discovery as environmental pollutants in 1966, polychlorinated biphenyls (PCBs) have been detected in all parts of the world and in all environmental compartments such as water, air, sediments, bird tissue, and fish tissue (Sharawi et al., 2010) and in human breast milk (She et al., 2007; Kunisue et al., 2006). Their intrinsic properties, such as strong environmental persistence, resistance to metabolism in organisms and tendency to accumulate in lipids have contributed to their ubiquity in environmental media and have induced concern about their hazardous effects. PCBs are a class of chemical compounds in which 2 to 10 chlorine atoms are attached to the biphenyl molecule. The general chemical structure of chlorinated biphenyl is shown in Figure 2.6.

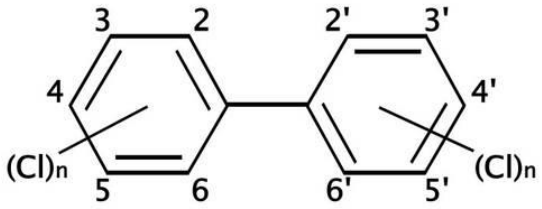


Figure 2.6: General structure of polychlorinated biphenyls (PCBs)

2.1.4.2 Sources of PCBs

PCBs are exclusively manufactured chemicals that found wide application in industrial processes from the 1930s until late 1980s. No natural sources of these compounds are known to exist. Approximately 1.3 to 2 million tonnes of PCBs were manufactured over that period, half of which were produced by Monsanto chemical company (USA), with the other 38% from Germany, the USSR, France and the UK (Breivik et al., 2007). It is estimated that over 30% of this total amount has so far found its way into the environment. With variations depending on the country, a small percentage has been treated or destroyed, between 12.9% and 16.5% are still in use in PCB transformers and capacitors, and most of the remainder have been sent to landfills where they may eventually leach, volatilise or otherwise escape into the environment (Breivik et al., 2007).

Although their production was effectively ceased in 1977, huge quantities of these contaminants are still found in the environment as wastes or even stockpiles that are yet to be disposed. PCBs can be released into the general environment via a number of avenues that include poorly maintained toxic waste sites, illegal or improper dumping of PCB wastes (e.g. transformer fluids), through leaks or fugitive emissions from electrical transformers containing PCBs, and by disposal of PCB-containing consumer products in municipal landfills. Currently, PCBs found in the ambient environment can largely be attributed to environmental cycling of what was previously released. These contaminants are also often found both in the effluent and in the sludge of municipal wastewater.

2.1.4.3 Uses of PCBs

PCBs were extensively used in many industrial applications. Commercial PCB mixtures were widely used as dielectric fluids in capacitors and transformers, heat transfer fluids, hydraulic fluids, lubricating oils, and as additives in paints, carbonless copy ("NCR") paper, adhesives and sealants. Prior to 1977, these compounds were used as heat exchanger fluids in aluminium, copper, iron and steel manufacturing processes (Korytar et al., 2002) in addition to their utilisation as plasticisers in natural and synthetic rubber products. By far, most of the PCBs were used in capacitors and transformers as their commercial utility was based largely on their chemical stability, low flammability and excellent electrical insulating properties (Johnson et al., 2006; Erickson 1997, 2001).

2.1.4.4 PCB congeners

209 different PCB congeners are known, most of which are compounds characterised by enhanced resistance to degradation (Panic et al., 2006; Villa et al., 2003; Korytar et al., 2002). A PCB congener is any single, unique well-defined chemical compound in the PCB category and its name normally specifies the total number of chlorine substituents and the position of each chlorine atom.

Technical preparations of PCBs are mixtures of individual chlorobiphenyls, chlorinated at various positions and to various degrees (Brunström and Andersson, 1988). Those PCBs chlorinated at the para-position, and at least one of the meta-positions of each ring, but lacking the ortho chlorines, are considered to be the most toxic (Safe, 1984; Silkworth and Grabstein, 1982). These PCBs can adopt a coplanar conformation which is structurally similar to 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and thus capable of binding to the soluble aryl hydrocarbon (Ah)-receptor signal transduction pathway, albeit less avidly than TCDD (Andersson and Brunstrom, 1988). Structure-toxicity studies suggest that the co-planar PCBs and their mono-ortho analogs are Ah-receptor agonists and contribute significantly to the toxicity of the PCB mixtures (USEPA, 2012).

2.1.4.5 PCB homologs

Further classification of PCB congeners can be done based on the number of chlorine substituents on the rings, which can range from one to ten. Homologs are subcategories of PCB congeners having equal numbers of chlorine substituents (USEPA, 2012) and as such, all PCB congeners defined by a similar number of chlorine atoms are placed in the same homolog group. For example, all dichlorobiphenyls are PCB congeners that have two chlorine substituents. They belong to the same homolog group although their molecular arrangements need not be identical. Table 2.4 presents the homolog groups of PCB congeners.

Table 2.4: PCB homologs

CASRN	IUPAC Name
27323-18-8	Monochlorobiphenyl
25512-42-9	Dichlorobiphenyl
25323-68-6	Trichlorobiphenyl
26914-33-0	Tetrachlorobiphenyl
25429-29-2	Pentachlorobiphenyl
26601-64-9	Hexachlorobiphenyl
28655-71-2	Heptachlorobiphenyl
55722-26-4	Octachlorobiphenyl
53742-07-7	Nonachlorobiphenyl

CASRN: Chemical Abstracts Service (CAS) Registry Number; IUPAC Name: The names presented in the table are the IUPAC names; Type: The type of the PCB entity: Congener, Homolog, Mixture, Category (USEPA, 2003)

2.1.4.6 Physical and chemical properties of PCBs

PCB congener mixtures are viscous liquids with a clear to pale yellow colour, whereas individual PCB congeners are usually white crystalline solids. The more chlorinated the compounds, the deeper the colour of the resulting liquid. Thus, variation in the physical characteristics among PCB mixtures is to a large extent, determined by the chlorine content in the compounds. Table 2.5 shows some of

the physical properties of PCBs. Specific gravity, boiling point, and viscosity increase as the chlorine content increases in individual congeners, whereas water solubility and vapour pressure decrease (USEPA, 2012). Aqueous solubilities of these compounds are in the range of 5.5×10^{-6} g g^{-1} to 1.2 g g^{-1} (Mackay, 1991). In view of these very low concentrations, approaches to sample collection, handling, preservation and other analytical operations require careful thought in order to minimise sample losses. Log K_{ow} values range from about 4.3 to 8.26 implying that one can anticipate partition ratios than range from 10,000 to over 100 million.

Due to their strong hydrophobicity, PCBs tend to favour a non-polar phase and will partition away from water to particulates and sediments. Sorption is particularly boosted by availability of high total organic carbon content, strong aluminium and iron presence and smaller particle sizes (Cortes et al., 1991). Because of their large sizes and low solubility, kinetics of sorption is slow, and the distribution constants for PCBs are found to be proportional to the soil organic carbon content (Paya-Perez et al., 1991). Co-planar PCBs have been reported to sorb more strongly to the soil than non-planar congeners with the same degree of chlorination (Cortes et al., 1991; Paya-Perez et al., 1991). Toxic co-planar, non- and monoorthochlorobiphenyls have a lower vapour pressure than other isomers and as such, preferentially partition to the particulate phase and thus get selectively deposited (Falconer and Bidleman, 1994). The stability of PCB compounds is remarkable and decomposition through chemical, thermal, and biochemical processes is not readily feasible. Furthermore, thermal degradation of these compounds presents the risk of generating extremely toxic dibenzodioxins and dibenzofurans through partial oxidation. Ironically, the very properties that made PCBs valuable products in several industrial applications are the same properties that negatively affect the environment, courtesy of their long-term persistence and, particularly, the highly substituted congeners.

Table 2.5: Some physical properties of PCB homologs

Homolog	Melting point (^{0}C)	Boiling point (^{0}C)	Vapour pressure (Pa) at 25^{0}C	Water solubility at 25^{0}C (g m^{-3})	Log K_{ow}	Approximate bioconcentration factor in fish	Approximate evaporation at 25^{0}C (g m^{-2}h^{-1})
Biphenyl	71	256	4.9	9.3	4.3	1000	0.92
Monochlorobiphenyl	25 to 77.9	285	1.1	4.0	4.7	2500	0.25
Dichlorobiphenyl	24.4 to 149	312	0.24	1.6	5.1	6300	0.065
Trichlorobiphenyl	28 to 87	337	0.054	0.65	5.5	1.6×10^4	0.017
Tetrachlorobiphenyl	47 to 180	360	0.012	0.26	5.9	4.0×10^4	4.2×10^{-2}
Pentachlorobiphenyl	76.5 to 124	381	2.6×10^{-3}	0.099	6.3	1.0×10^5	1.0×10^{-3}
Hexachlorobiphenyl	77 to 150	400	5.8×10^{-4}	0.038	6.7	2.5×10^5	2.5×10^{-4}
Heptachlorobiphenyl	122.4 to 149	417	1.3×10^{-4}	0.014	7.1	6.3×10^5	6.2×10^{-5}
Octachlorobiphenyl	159 to 162	432	2.8×10^{-5}	5.5×10^{-3}	7.5	1.6×10^6	1.5×10^{-5}
Nonachlorobiphenyl	182.8 to 206	445	6.3×10^{-6}	2.0×10^{-3}	7.9	4.0×10^6	3.5×10^{-6}
Decachlorobiphenyl	305.9	456	1.4×10^{-6}	7.6×10^{-4}	8.3	1.0×10^7	8.5×10^{-7}

(ATSDR, 2000)

2.1.4.7 Biological fate of PCBs

PCBs have been associated with several health concerns, both in animals and man. Laboratory investigations and environmental impact studies in the wild have implicated POPs in endocrine disruption, reproductive and immune dysfunction, neurobehavioral disorder and carcinogenicity (Katsoyiannis and Samara, 2005). Human studies have tended to corroborate animal investigations in the view that PCBs have shown both carcinogenic and non-carcinogenic potential. The different health effects of PCBs may be interrelated, as alterations in one system may have significant implications for the other systems of the body (US EPA, 2012). Some of the potential health risks are discussed below.

Reproductive and developmental effects

A wide array of test animals has been used to investigate effects of PCB exposure on their reproduction. For example, in rhesus monkeys, exposure to PCBs was associated with alterations in the menstrual cycle, decreases in fertility, increases in spontaneous abortion, and a reduced number of conceptions and birth weight (ATSDR, 2000). Effects were observed long after the dosing with PCBs occurred (Arnold et al. 1995; Barsotti and Miller, 1984). Recent studies on human populations exposed to PCBs indicate that children born to women who worked with PCBs in factories showed decreased birth weight and a significant decrease in gestational age with increasing exposures (USEPA, 2012). Apart from disturbances in reproductive processes, consumption of PCB-contaminated fish has also been linked to neurobehavioral and developmental deficits in newborns and older children. Since similar effects have been observed in several animal species exposed to the compounds, such findings should be of interest to man as the same reproductive effects may be expected.

Carcinogenicity

There is concrete evidence that PCBs cause cancer in animals and epidemiologic studies have raised concerns about their potential carcinogenicity. Mayes et al.

(1998) reported that four commercial PCB mixtures fed to mice induced liver tumours and that several of these tumours were hepatocholangiomas, a rare biliary tract tumour seldom seen in control rats. In studies of occupationally exposed workers, increases in the incidence of malignant melanoma and cancers of the liver, gall bladder, biliary tract, and brain have been reported (ATSDR, 2000). However, such epidemiologic findings have not been conclusive with respect to human effects. Therefore, since animal studies have provided compelling evidence that PCBs cause cancer and studies on humans have raised further concerns regarding the potential carcinogenicity of PCBs, when taken together, the data strongly suggest that PCBs are probable human carcinogens (USEPA, 2012).

Endocrine Effects

PCBs have been identified as possible environmental endocrine disruptors through modulating effects on thyroid hormone levels in animals and humans (ATSDR, 2000). PCBs may alter thyroid-mediated processes or even interfere with the female sex hormone balance. Indeed, it has been shown that PCBs decrease thyroid hormone levels in rodents, and that these actions have resulted in developmental deficits in the animals (USEPA, 2012). Oestrogen hormone plays a critical role in promoting the development and maintenance of the female reproductive system and it is feared that some PCB congeners might impede these functions. Depending on the spatial orientation of their chlorine constituents, some congeners exhibit weak estrogenic activity, whereas others act as antiestrogens (ATSDR 2000).

Immune Effects

A vibrant immune system is vital in warding off infections. Anything that compromises it can precipitate serious health concerns in both humans and animals. Among animal studies that have been done to investigate effects of PCB exposure on the immune system, findings from rhesus monkeys are the most

relevant because their immune systems are very closely related to those of humans. Studies in monkeys and other animals have revealed a number of serious effects on the immune system following exposures to PCBs, including a significant decrease in size of the thymus gland (critical to the immune system) in infant monkeys, reductions in the response of the immune system following a challenge with sheep red blood cells (a standard laboratory immunity test), and decreased resistance to Epstein-Barr virus and other infections in PCB-exposed animals (USEPA, 2012).

Many human studies linked to PCB exposure, have also yielded interesting findings. For instance, Svensson et al. (1994) observed a significant negative correlation between the percentage of white blood cells and weekly fish consumption in a group of men who regularly ate fish sourced from the Baltic Sea, a site that had experienced extensive PCB contamination. Immune system effects have also been observed in Inuit infants who were believed to receive elevated levels of PCBs and dioxins from their mother's breast milk (Dewailly et al. 1993).

Other Effects

PCB exposure has been associated with an array of other health effects in both animals and humans. They included cardiovascular, musculoskeletal, liver toxicity, hypertension, dermatological and ocular effects (ATSDR, 2000). Indeed, a study of people living near a Monsanto plant that used to manufacture PCBs showed a serum concentrations of PCBs, especially those congeners with multiple ortho- chlorines, were strongly associated with both systolic and diastolic blood pressure (Goncharov et al., 2010). However, the existing data are still insufficient to infer possible cardiovascular toxicity of PCBs in humans (ATSDR 2000).

2.1.5 Organochlorine pesticides (OCPs)

The United States EPA defines a pesticide as any substance or mixture of

substances intended for preventing, destroying, repelling, or mitigating any pest or meant for use as a plant regulator, defoliant or desiccant. Pests include insects, mice and other animals, unwanted plants, fungi, or microorganisms like bacteria and viruses (USEPA, 2001). Although pesticides, in their rudimentary forms, have been in use for a long time, the advent of synthetic organic chemicals in early to mid twentieth century revolutionalised this industry. With advances in technology, a rapid increase in the number and variety of these chemicals has been witnessed in recent times.

Pesticides are classified into three main groups namely insecticides, herbicides and fungicides, characterised by very different physico-chemical properties, large differences in polarity, volatility and environmental persistence (Sharawi et al., 2010). Insecticides can further be grouped according to their chemical families viz organochlorines, organophosphates and carbamates. A lot of interest has been dedicated to organochlorine compounds because of their known or perceived environmental impacts. Typically, organochlorines constitute a collection of compounds that contain carbon, hydrogen, and chlorine atoms. Chemically stable, strongly lipophilic and considerably toxic, the compounds have slow degradation rates and tend to bioaccumulate in lipid-rich tissues (Tiemann, 2008). Thus, in spite of their early promise, this group of insecticides are now much less used because of their environmental pollution concerns (Strompl and Thiele, 1997)

Nine of the organochlorine pesticides as well as polychlorinated dibenzo-*p*-dioxins, furans, and biphenyls are the subject of the Stockholm Convention (Barr and Needham, 2002). Apart from calling for an immediate ban on the production, import, export, and use of most of these POPs, the treaty recommends clear disposal guidelines (UNEP, 2001). Indeed, a large number of organochlorine pesticides have been universally banned in line with the Stockholm convention. Pesticide residues find their way into the environment by means of volatilisation, runoff, infiltration, transport along food chain etc. (Sharawi et al., 2010)

Many studies have shown the health impacts of organochlorine exposure in animals (Maranghi et al., 2007; Sweeney, 2002; Snedeker, 2001). These compounds are documented animal toxicants (Siang et al., 2007; Dewailly 1993) and their individual toxicities are dependent on a number of factors such as molecular size, volatility, and effects on the central nervous system (CNS). In general, they cause either CNS depression or stimulation, depending upon the agent and dose (Berkowitz, 1996). Toxicity in humans is largely due to stimulation of the CNS (Fenster et al., 2006). In addition to their toxicity, organochlorine pesticides possess estrogenic properties that may lead to disruption of the reproductive system in animals (Tiemann, 2008; Borgeest et al., 2002). Maranghi et al., (2007), reported an increased uterine estrogen receptor expression in female mice exposed to lindane pesticide. The carcinogenicity of organochlorines and their metabolites in experimental animals is also widely reported (Ahlborg et al., 1995). The predominant tumor types in rodents exposed to these compounds are carcinomas and adenomas of the liver (Dich et al., 1997). It is also speculated that exposure to organochlorine pesticides for elongated periods may lead to impairment of other vital body organs like kidney, thyroid and bladder in animals.

Organochlorine pesticides find their way into animal and human systems mainly through inhalation, oral ingestion and dermal absorption. Since these compounds are strongly lipophilic, they are readily stored in high lipid content body tissues such as the liver, brain and adipose fat layer. As such, the chronic health effects of organochlorines may, to a large extent, be attributed to their lipophilic tendencies.

2.1.5.1 Hexachlorocyclohexanes (HCHs)

Introduction

Hexachlorocyclohexane (HCH) is an industrially manufactured organochlorine compound that exists in eight isomeric forms, each named according to the position of the hydrogen atoms in the structure of the molecule (ATSDR, 1995b).

The isomers differ in their axial-equatorial (a-e) substitution pattern around the ring and are denoted using the Greek letters α, β, γ, δ, ε, η, and θ (Willet et al., 1998). Figure 2.7 presents the structures of the eight HCH isomers.

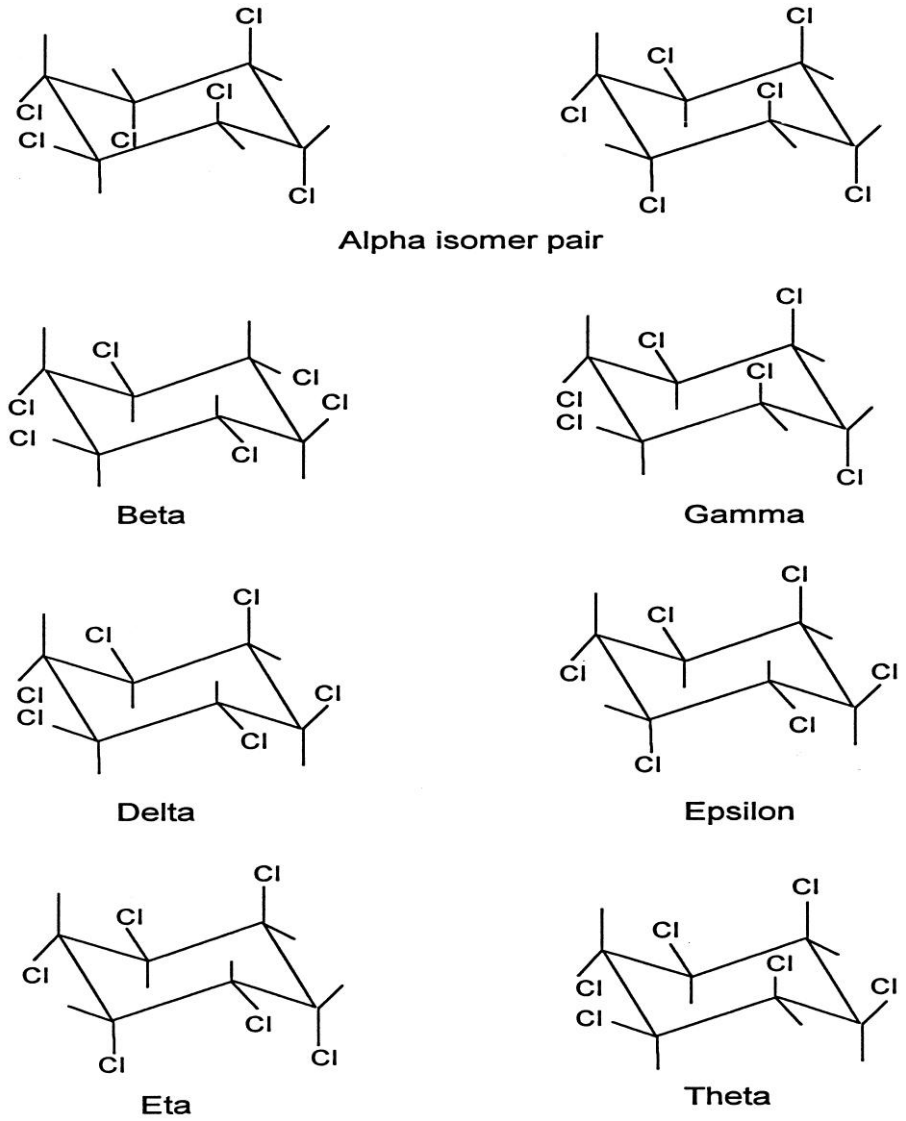


Figure 2.7: Structures of HCH isomers, including the two α-enantiomers. The axial and equatorial positions of the chlorine atoms are as follows: α: aaaaee, β: eeeeee; γ: aaaeee, δ: aeeeee, ε: aeeaee, η: aaeaee, and θ: aeaeee a - axial, e - equatorial (Willet et al., 1998)

Among the isomers, γ-HCH, also called lindane, has the highest insecticidal potency and is therefore widely used. Due to its past use, lindane has been

detected in all environmental compartments and levels in air, water, soil, sediment, aquatic and terrestrial organisms and food have been measured worldwide. Technical mixtures of all isomers have also been widely used as commercial pesticides (Willet et al., 1998). Technical-grade HCH is a mixture of at least five isomers with approximately 60 - 70% α-HCH, 5 - 12% β-HCH, 10 - 15% γ-HCH, 6 - 10% δ-HCH, and 3 - 4% ε-HCH (Li and Macdonald, 2005; ATSDR, 1995b). Usually technical-grade HCH mixture is produced through chlorinating benzene via free-radical substitution reaction. Lindane is then obtained by treating the product with methanol or acetic acid followed by fractional recrystalisation to increase the yield of γ-HCH isomer to about 99% (Willet et al., 1998).

As observed in other organochlorine compounds, HCHs are defined by strong lipid solubility, persistence in the environment, and susceptibility to long-distance transportation by environmental agents such as wind, air currents, water and biota. These contaminants also readily undergo bioaccumulation in the food chain and subsequently rapid bioconcentration in microorganisms, invertebrates, fish, birds and mammals (Stockholm Convention, 2007).

When compared to other OCPs, HCHs are significantly more prevalent in all environmental compartments. This observation may be attributed to their higher solubility in water and volatility. To mitigate their impacts on the environment, HCHs, (and specifically lindane), have been banned in over 50 countries and their use severely restricted in many others.

Applications

The only identifiable use of HCH-containing products is based on the insecticidal activity of the γ-isomer (lindane) (Extoxnet, 1996). Lindane is applied in the treatment of wood and wooden structures, grains, and livestock (HSDB, 2009; ATSDR, 1995b). It is also used as an insecticide on fruits and vegetable crops, rice paddies, baits and seed treatment for rodent control (Willet et al., 1998). Very

small quantities are used as prescription medication for the management of scabies and head lice in humans (ATSDR, 1995b).

Physical and chemical properties

Mixtures of HCH isomers are brownish to white crystalline powders with a penetrating, musty odour (IARC, 1974). Physical and chemical properties of individual isomers differ slightly from one other, as illustrated in Table 2.6. These differences are brought about by the spatial orientation of the chlorine atoms in the molecule. For instance, the α-isomer is practically insoluble in water but soluble in chloroform and benzene, whereas, the β-isomer is very slightly soluble in water and slightly soluble in chloroform and benzene (NTP, 2011).

Table 2.6: Selected physical properties of HCH isomers

Property	α-HCH	β-HCH	γ-HCH	δ-HCH
Molecular weight	290.8	290.8	290.8	290.8
Specific gravity	1.87	1.89	1.85	NA
Melting point (^{0}C)	158	209	112.5	141.5
Boiling point (^{0}C)	288	60 at 0.50 mm Hg	323.4 at 760 mm Hg	60 at 0.36 mm Hg
Log K_{ow}	3.8	3.78	3.72	4.14
Water solubility	0.002 g L^{-1} [a]	0.0002 g L^{-1} [b]	0.0073 g L^{-1} [a]	0.0314 g L^{-1} [a]
Vapour pressure	4.5 x 10^{-5} mm Hg[a]	3.6 x 10^{-7} mm Hg[b]	4.2 x 10^{-5} mm Hg[b]	3.5 x 10^{-5} mm Hg[a]
BCF in human fat[c]	20 ± 8	527 ± 140	19 ± 9	8.5

Source: HSDB, 2009; NA = not available; [a]At 25^{0}C; [b]At 20^{0}C; [c]Bioconcentration factor

Additionally, β-HCH has a much lower vapour pressure, higher melting point and higher bioconcentration factor in human fat as compared to the α-isomer (Willet et al., 1998). A closer look at the structure of β-HCH (Figure 2.7) reveals that all its chlorine atoms are in the equatorial position.

It is hypothesized that such a spatial orientation of the chlorines bestows the structure the greatest physical, chemical and metabolic stability and this could explain the isomer's recalcitrance in the environment. Conversely, the γ-isomer has three chlorines in axial positions creating two ways that HCl can be eliminated by anti-periplanar dehydrohalogenation, generating pentachlorocyclo hex-1-ene (PCCH) metabolites (Müller, 1995). This is reflected in its lower stability to degradation agents.

Exposure

Potentially, human exposure to HCHs occurs through oral ingestion, skin contact, and/or inhalation of ambient air (HSDB, 2009; Chanon, 2003) with the intake of HCH-contaminated foodstuffs being the major route. Fat-rich food items are especially prone to HCH contamination because of the elevated lipophilicity of the contaminants. Dermal exposure occurs when shampoos and lotions containing lindane are used for the treatment of lice and scabies (FDA, 2009). Indeed, some studies have reported high average blood concentrations of lindane of up to 0.028 $\mu g\ mL^{-1}$ in children tested after scabies treatment with one of these products (ATSDR, 1995b). Several HCH isomers have also been reported in human tissues such as adipose fat, breast milk, and blood (NTP, 2011).

Health effects

Several animal studies have shown that HCHs have neurotoxic effects, mainly targeting the central nervous system (CNS). Exposure to high amounts of HCHs in mammals has been reported to cause hyperexcitability syndrome, convulsions, and seizures that may eventually lead to death (ATSDR, 1995b). As GABA

antagonists, HCHs are thought to inhibit calcium ion influx, which leads to an accumulation of calcium ions at neuronal endplates, thereby causing sustained release of excitatory neurotransmitters (Eskenazi et al., 2004).

α- and γ-HCHs are reportedly, the most toxic HCH isomers. In humans, effects from acute exposure at high concentrations to lindane may range from mild skin irritation to dizziness, headaches, diarrhoea, nausea, vomiting, convulsions and even death (CEC, 2005). Other responses observed in humans following acute or chronic α-HCH inhalation include respiratory, cardiovascular, haematological, hepatic and endocrine effects (Dewailly et al., 1993). The same authors noted that in many of the investigations, the young, malnourished, and those with frequent application were at increased risk of toxicity. Investigations on HCHs have also indicated that some isomers may have genotoxic effects. Specifically, α-HCH has shown some genotoxic potential, but the evidence is so far not conclusive (US EPA, 2006).

Animal studies have also indicated the potentiality of HCHs to disrupt endocrine systems (Li et al., 2002) in addition to causing immunosuppressive effects. Indeed, in one study, it was observed that exposure to lindane during gestation with a single dose of 30 mg kg^{-1} of body weight at day 15 of pregnancy induced altered libido and reduced testosterone concentration in male offspring rats (USEPA, 2006).

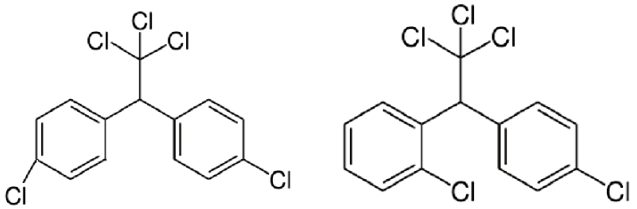
Furthermore, animal studies have shown potential carcinogenicity as tumours in mice and rats were reported after sub-chronic and/or chronic exposure of these compounds (USEPA, 2006). The IARC has therefore, classified all HCH isomers as possible carcinogens to humans while the EPA has determined that there is suggestive evidence that lindane is carcinogenic, although, so far, no sufficient evidence to assess its human carcinogenic potential exists (ATSDR, 1995b).

2.1.5.2 DDT and its metabolites

Introduction

1,1,1-trichloro-2,2-bis(chlorodiphenyl)ethane **(**DDT), a persistent organochlorine compound, is an industrially manufactured chemical with no known natural sources (WHO, 1979). It was first extensively used during the Second World War for control of vectors responsible for typhus and malaria (Hayes, 1991). Prior to the insidious environmental effects of DDT were realised, global consumption of this pesticide was extensive and indiscriminate. Its choice as a pesticide was especially attractive because it was an effective, inexpensive broad spectrum pesticide (Sharawi et al., 2010). By drastically decreasing threats caused by insect-borne diseases, and simultaneously boosting agricultural production by minimising costs associated with pests, this pesticide won universal acclaim as a wonder compound.

Part of the success of DDT can be attributed to its persistence in the environment that made frequent applications unnecessary (Beard, 2006). However, its enhanced chemical stability, strong lipophilic properties and resistance to biological degradation meant slower removal from the environment, as well as ability to concentrate in organisms. Technical-grade DDT constitutes a mixture of up to 14 compounds with the active ingredient, p,p'-DDT, accounting for between 65 - 80%. Other major components include o,p'-DDT (15 - 21%), p,p'-DDD (4%), and 1-(p-chlorophenyl)-2,2,2-trichloroethanol (1.5%) (Metcalf, 1995). Figure 2.8 shows structures of the two DDT isomers.



A B

Figure 2.8: Chemical structures of DDTs. (A) p,p'-DDT and (B) o,p'-DDT

DDT is a recalcitrant environmental contaminant, currently banned in many countries. The ban initially started with the industrialised countries in the northern hemisphere in the early 1970s. Later on, many third world countries followed suit between 1980 and 1990. Although agricultural application of DDT is universally prohibited, selective use of the pesticide for vector control is still allowed (Snedeker, 2001). In this context, despite South Africa outlawing the application of DDT for crop protection, it still sought for an exemption to use the insecticide for control of malaria-causing mosquitoes in some parts of the country (Aneck-Hahn et al., 2007). The probable effects of these activities have been reported. Several studies have found significantly high DDT and DDE concentrations in breast milk obtained from lactating women residing in areas covered in the malaria control programme (Okonkwo et al., 2008; Bouwman et al., 2006; Bouwman et al., 1992) and impaired semen quality in young men living in such areas (Aneck-Hahn et al., 2007).

Application of DDT

DDT is an effective insecticide defined by long residual persistence, low acute mammalian toxicity, and low cost (Metcalf, 1995). It was, (and still is in some regions) widely used in the control of mosquitoes, black flies and other disease-carrying vectors.

In agriculture, DDT was widely used to control crop insects such as the pink boll worm on cotton, codling moth on deciduous fruit, corn stalk borer, gypsy moth, spruce budworm e.t.c. (ATSDR, 2002). Inside the homes, DDT was used as a moth killer and repellent. It was also used in the control of lice in humans. The massive application of DDT in all these areas is reflected in the quantities produced and used. For instance, the U.S. agricultural sector alone consumed about 12.2 million kilograms of DDT in 1966 and 6.3 million kilograms in 1971 (Gianessi and Puffer, 1992). Production of DDT reached its peak during the early 1960s at about 81 million kg yr^{-1} (Woodwell et al., 1971).

As mentioned previously, in malaria prone regions of the world, that include the tropics and Southern Africa, DDT is sprayed onto the interior surfaces of homes to decrease the incidence and spread of the disease by controlling mosquitoes (Attaran et al., 2000; Roberts et al., 1997). By working both as a mosquito toxin and as a contact irritant and repellent, this compound thus limits the survival of the mosquitoes and decreases the chances of an individual being bitten within the sprayed homes (ATSDR, 2002). p,p'-DDD also found limited application as an insecticide while o,p'-DDD has been used medically to treat cancer of the adrenal gland (PDR, 1999). DDE has however, never been commercially utilised in any known way.

DDT degradation

DDT is not a naturally occurring compound, and its presence in the environment is as a consequence of anthropogenic input. 1,1-dichloro-2,2-bis(p-chlorophenyl)-ethylene (DDE) and 1,1-dichloro-2,2-bis(p-chlorophenyl)ethane (DDD) are the principal degradation products of DDT. Technical-grade DDT may also contain DDE and DDD as contaminants in small percentages.

In the environment, DDT can undergo transformation by losing chlorine and/or hydrogen atoms to yield DDE and DDD (Klecka et al., 2000). DDD is formed from DDT through reductive dechlorination, either microbially mediated (Wedemeyer, 1966) or as the result of chemical reactions (Baxter 1990; Glass 1972) some of which are mediated by biomolecules. Three approaches can lead to the conversion of DDT to DDE: sunlight initiated photochemical degradation (Maugh, 1973), bacterial-aided dehydrochlorination (Pfaender & Alexander, 1972), and biodegradation by higher animal species (Kurihara et al., 1998). As witnessed in PCBs, the strong chemical resistance (and persistence) of DDTs can be ascribed to the presence of chlorine substituents on the molecules.

Physical and chemical properties of DDT and its degradation products

Technical-grade DDT is an amorphous powder that melts in the range 80 to 94^{0}C (Metcalf, 1995). All the three isomers of DDT are white crystalline solids with tasteless and almost odourless properties. The physical and chemical properties of o,p'- and p,p'-DDT, DDD and DDE are listed in table 2.7. These compounds are highly lipid soluble, as reflected by their high log K_{ow} values (Howard and Meylan, 1997) with low water solubility. Table 2.7 presents some of the physical and chemical properties of DDT and its metabolites.

Environmental fate

The persistence of DDT and its degradation products in the environment is well documented (Turusov et al., 2002; Vieira et al., 2001; Hitch and Day, 1992). This persistence, combined with high partition coefficients (log K_{ow} between 5.87 and 6.91) provides the necessary conditions for DDT to bioconcentrate in organisms (Ritter et al., 1995). However, entry of DDT and its metabolites into animal and human bodies is mediated through a number of avenues, as elaborated in the following paragraphs. Prior to its banning, large quantities of DDT were released into all environments during production, transportation and application. Thus, the current situation is a possible reflection of the legacy of their discharge.

Inter-media translocation of DDT and its metabolites may be effected through adsorption, solubilisation, remobilisation, bioaccumulation, and volatilisation, whereas intra-media transportation may be achieved through diffusion, wind, and currents.

Volatilisation is the major route through which DDT and its metabolites in the soil and water-phase are released into the atmosphere. Additional sources (though, minor) of atmospheric DDT may arise from its current usage, especially spraying practices in vector control programmes.

Table 2.7: Physical and chemical properties of o,p'- and p,p'-DDT, DDE and DDD[a]

Property	o,p'-DDT	p,p'-DDT	o,p'-DDE	p,p'-DDE	o,p'-DDD	p,p'-DDD
Molecular weight	354.49[b]	354.49[b]	318.03[b]	318.03[b]	320.05[b]	320.05[b]
Melting point (^{0}C)	74.2[e]	109[b]	No data	89[b]	76 to 78[b]	109 to 110[b]
Boiling point (^{0}C)	No data	Decomposes	No data	336[b]	No data	350[b]
Density	0.98 – 0.99 g cm^{-3}	0.98 – 0.99 g cm^{-3}	No data	No data	No data	1.385 g cm^{-3}
Solubility: Water	0.085 mg L^{-1} at 25^{0}C[b]	0.025 mg L^{-1} at 25^{0}C[b]	0.14 mg L^{-1} at 25^{0}C[b]	0.12 mg L^{-1} at 25^{0}C[b]	0.1 mg L^{-1} at 25^{0}C[b]	0.09 mg L^{-1} at 25^{0}C[b]
Organic solvents	No data[g]	Slightly soluble in ethanol, very soluble in acetone, ethyl ether[f]	No data[g]	Lipids and most organic solvents	Soluble in ethanol, isooctane , carbon tetrachloride[j]	No data[g]
Log Kow	6.79[h]	6.91[b]	6.00[b]	6.51[b]	5.87[b]	6.02[b]
Log Koc	5.35[j]	5.18[h]	5.19[j]	4.70[i]	5.19[j]	5.18[j]
Vapour pressure	1.1 x 10^{-7} at 20^{0}C torr[b]	1.60 x 10^{-7} at 20^{0}C torr[b]	6.2 x 10^{-5} at 25^{0}C torr[b]	6.00 x 10^{-6} at 25^{0}C torr[b]	1.94 x 10^{-5} at 30^{0}C torr[b]	1.35 x 10^{-6} at 25^{0}C torr[b]
Henry's law constant	5.9 x 10^{-7} atm-m^3 mol^{-1} [b]	8.3 x 10^{-6} atm-m^3 mol^{-1} [b]	1.8 x 10^{-3} atm-m^3 mol^{-1} [b]	2.1 x 10^{-5} atm-m^3 mol^{-1} [b]	8.17 x 10^{-5} atm-m^3 mol^{-1} [b]	4.0 x 10^{-6} atm-m^3 mol^{-1} [b]
Appearance	White crystalline powder	Colourless crystals, white powder	No data	White crystalline solid	No data	Colourless crystals, white powder
Physical state	Solid[d]	Solid[d]	No data	Crystalline solid	Solid	Solid

[a]All information obtained HSDB, 1999a, 1999b, 1999c, 1999d unless otherwise noted; [b]Howard and Meylan, 1997; [d]NIOSH, 2002; [e]Sax, 1979; [f]Lide, 1998; [g]Chemical expected to be soluble in most organic compounds; [h]Swann et al., 1981; [i]Sabljic, 1984; [j]Meylan et al., 1992 (ASTDR, 2002)

Once in the atmosphere, the chemicals are cycled back to land and surface water through dry and wet deposition (ATSDR, 2002). As these processes are repeated over and over, the contaminants are pushed further into the cold arctic and antarctic regions, where they get sorbed to polar ice, and accumulate in resident animals. While in the atmosphere, about one half of DDT gets adsorbed to particulate matter and the other half exists in vapour phase (Bidleman, 1988). However, this scenario is not replicated for DDE and DDD, where only a small percentage gets adsorbed onto atmospheric particles. Interaction between photochemically produced hydroxyl radicals with vapour-phase DDT and its metabolites may also occur in the atmosphere.

In the aquatic environment, the dominant fate processes of DDT and its metabolites are volatilisation and adsorption to biota, suspended particulate matter, and sediments (ATSDR, 2002). The tendency of DDT and its metabolites to volatilise from water can be predicted by their respective Henry's law constants (Howard and Meylan, 1997). These compounds may also undergo photolytic degradation when exposed to sunlight. Another sink for DDTs in the aquatic ecosystem is through bioaccumulation in the fatty tissues of organisms that take them up through the food web (Crinnion, 2009; Travis and Arms, 1988). In a study of a fresh water lake, DDT was found to accumulate to higher concentrations in fattier fish occupying high trophic levels than in leaner species occupying lower trophic levels (Kidd et al., 2001).

Once in the soil, these compounds get strongly adsorbed on or close to the surface layers and minimal leaching into the lower soil layers and ground water is witnessed (ATSDR, 2002). Regardless of the strong interaction, loss of these compounds through volatilisation is still possible, especially where the adsorption has occurred in moist soils. DDT and its metabolites can also undergo photodegradation and biodegradation on the soil surface with the soil conditions primarily determining the biodegradation products. Under aerobic conditions, DDT is transformed to DDE, whereas, DDD is yielded under anaerobic conditions. Among other factors, the persistence of DDT in a given soil

environment is known to be influenced by climatic conditions. For instance, dissipation is much greater in tropical than in temperate regions and in such tropical regions, most of the DDT is lost within a year of introduction (ATSDR, 2002). Indeed, in a study of sprayed forest soils in Maine, U.S.A., the half-life of the disappearance of DDT residues was noted to be 20 - 30 years (Diamond and Owen, 1996). The long residence time of the contaminant in the soil could be attributed to the temperate climatic conditions experienced in the region.

Health effects

Although there are no documented acute effects of environmental concentrations of DDT or its metabolites on human health, it may be difficult to ignore the possibility of chronic effects. The first adverse impacts of DDT were associated with thinning of eggshells in birds, leading to reproductive disorders (Beard, 2006). Recent in vitro studies have shown that DDT has weak estrogenic activity, while DDE is a powerful androgen receptor (Tiemann, 2008; Sonnenschein and Soto, 1998; Chen et al., 1997; Kelce et al., 1995). A trend showing decreasing semen quality in the male population exposed to DDT has also been reported (Aneck-Hahn et al., 2007; Skakkebaek, 1993; Carlsen et al., 1992). From these findings, it is possible that environmental exposure to DDT and its metabolites may encourage endocrine disruption activities in humans (Beard, 2006). Negative effects on fetal growth and development have been linked to exposure to DDT and its metabolites. For instance, some studies have associated maternal serum and umbilical cord blood levels of p,p′-DDT and/or p,p′-DDE, with preterm birth (Freire et al., 2011: Longnecker et al., 2001), decreased birth weight (Pathak et al., 2010; Weisskopf et al., 2005), and/or intrauterine growth retardation (Siddiqui et al., 2003; Longnecker et al., 2001).

Studies on rodents under laboratory conditions have indicated that exposure to DDT may cause cancerous tumours in the liver, lungs, adrenal glands or lymphatic tissues (ATSDR, 2002). Similar or related findings were not observed in higher animals such as dogs and monkeys. Initially, it was hypothesised that

since DDT congeners and metabolites exhibit oestrogenic and anti-androgenic characteristics, they might act as tumour promoters in hormonally sensitive cancers (Beard, 2006). In humans, a number of cohort and case studies carried out in 1990s and more recently have suggested an association between breast cancer and DDT (Wolff and Toniolo, 1995; Falck et al., 1992) as well as increased mortality from pancreatic cancer in DDT-exposed subjects (Beard et al., 2003). Additionally, in an agricultural health study cohort, Alavanja et al. (2003) reported increased rates of prostate cancer in male applicators using DDT. More recently, Cohn et al., (2007) reported that exposure to p,p′-DDT early in life may increase breast cancer risk, and many U.S. women heavily exposed to DDT in childhood died before age 50. In spite of all these findings, the majority of well controlled studies have so far not corroborated the positive correlation (Calle et al., 2002; Snedeker et al., 2001; Weiderpass et al., 2000). Thus, no concrete evidence has yet been established between environmental exposure to DDT, DDE and DDD and cancer in humans.

2.1.6 Polychlorinated dibenzo-p-dioxins and furans

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo-p-furans (PCDFs) are two structurally similar groups of planar tricyclic compounds (Figure 2.9) that exhibit comparable toxicities and properties (Sharawi et al., 2010; Ritter et al., 1995).

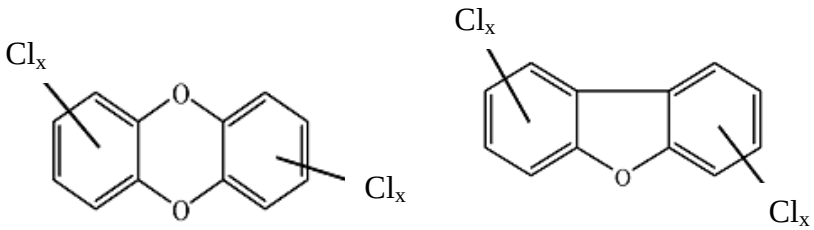


Figure 2.9: General molecular structures of PCDDs and PCDFs

PCDDs and PCDFs are two groups of persistent, semi-volatile and toxicologically significant trace organic contaminants (Lohman and Jones, 1998). Of major concern is their toxicity after entering the environment from various sources, usually, at ultra-trace levels (Ahlborg et al., 1992). Besides their toxicities, the

pathway air deposition-water systems-food chain transfer-wildlife/human exposures in aquatic systems are of key importance for these bioaccumulating chemicals (Lohman and Jones, 1998).

In the recent times, a growing trend of including certain sub-groups of PCBs into this class of compounds has been witnessed, because such PCBs also posses dioxin-like properties (Sharawi et al., 2010).

2.1.6.1 Physico-chemical properties of PCDD/Fs

There exist 75 possible positional isomers of PCDDs and 135 for PCDFs, whose chlorine atom substituents may range from one to eight. With a wide variation in their physico-chemical properties between homolog groups and congeners (Table 2.8), the chemical properties of individual isomers has not been well elucidated due to difficulties in their determination and thereby, complicating an explanation of their properties which vary with the number of chlorine substituents (Lohman and Jones, 1998; Mackay et al., 1991).

These compounds are generally highly insoluble in water, lipophilic and very persistent (Ritter et al., 1995). In the aquatic environment, their high octanol-water coefficients (K_{ow}) facilitate strong partitioning to soils and sediments, instead of the water phase. Their octanol-air partition coefficients (K_{oa}) vary over several orders of magnitude from the mono-CDD/Fs ($K_{oa} \approx 7$ to 8) to the octa-CDD/F ($K_{oa} \approx 11$ to 12), and this range of values is important in influencing the gas-particle partitioning of these semi-volatile organic compounds in the atmosphere under ambient conditions (Lohman and Jones, 1998).

Table 2.8: Some physical and chemical properties of PCDDs and PCDFs

Dioxins

Congener group	Mw (g mol^{-1})	V.P. (Pa x 10^{-3})	*S* (mg L^{-1})	Log K_{ow}
M_1CDD	218.5	73-75	295-417	4.75-5.00
D_2CDD	253.0	2.47-9.24	3.75-16.7	5.60-5.75
T_3CDD	287.5	1.07	8.41	6.35
T_4CDD	322.0	0.00284-0.272	0.0193-0.55	6.60-7.10
P_5CDD	356.4	0.00423	0.118	7.40
H_6CDD	391.0	0.00145	0.00442	7.80
H_7CDD	425.2	0.000177	0.0024	8.00
O_8CDD	460.0	0.000953	0.000074	8.20

Furans

Congener group	Mw (g mol^{-1})	V.P. (Pa x 10^{-3})	*S* (mg L^{-1})	Log K_{ow}
D_2CDF	237.1	14.6	14.5	5.44
D_3CDF	306.0	0.199	0.419	6.1
P_5CDF	340.42	0.0172	0.236	6.5
H_6CDF	374.87	0.0031-0.0036	0.0177-0.0088	7.0
H_7CDF	409.31	0.000054-0.000057	0.00135	7.4
O_8CDF	443.8	0.000101	0.00116	8.0

Mw: molecular weight, V.P: vapour pressure, *S*: water solubility, K_{ow}: octanol-water partition coefficients (Mackay et al., 1992)

2.1.6.2 Sources of PCDDs and PCDFs

When compared to natural sources, PCDDs and PCDFs attributed to anthropogenic origins account for the greatest contribution to the environment. This has been the case since 1930s, when environmental levels of these compounds witnessed a steady rise coinciding with the large-scale production and use of chlorinated chemicals (Zielinska and Samy, 2006; Fortin and Caldbick, 1997). Dioxins and furans are not intentionally produced, and as such, they have no commercial applications. As by products or chemical impurities in a range of

manufactured organochlorine products (Pereira, 2004; Ballschmiter and Bacher, 1996; Hagenmaier et al., 1990), these compounds easily end up in the environment. Emissions of PCDD/Fs to the atmosphere and their subsequent atmospheric transport and behaviour have resulted in their widespread dispersal through the environment (Lohman and Jones, 1998).

Anthropogenic sources of PCDDs and PCDFs can be classified into chemical processes, combustion processes and secondary sources (Pereira, 2004; Alcock et al., 1998). Chemical processes associated with the release of these contaminants include production of pesticides and other chlorinated substances, and in the manufacture of PCBs. Combustion processes encompass human activities such as, incineration of municipal waste, hazardous chemical waste, hospital waste, coal and peat, landfill gas combustion, crematoria, and cement manufacture (Fiedler, 1993). Diffuse sources of dioxins and furans include car exhausts, cigarette smoke, sewage sludge, biocompost, and wood burning (Ballschmiter and Bacher, 1996; Hagenmaier et al., 1990).

2.1.6.3 Health effects of PCDD/Fs

From among the 75 possible dioxin and 135 possible furan congeners, 17 of them have shown significant potential toxicity, and bioacummulative ability (Pereira, 2004; Ritter, et al., 1995). Even within this group of congeners, significant differences in toxicities and bioconcentration factors are still evident, as shown by a variance of up to three orders of magnitude.

Among the PCDDs, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) has been extensively investigated and reported to be the most toxic congener (Pereira, 2004). Apart from this congener being acutely toxic, such that its potency is only exceeded by natural toxins like Botulin A and Diphtherietoxin, it is also a strong tumour promoter (Mahnke, 1997). Figure 2.10 shows the basic structures of chlorinated dibenzo-p-dioxin and dibenzo-p-furan.

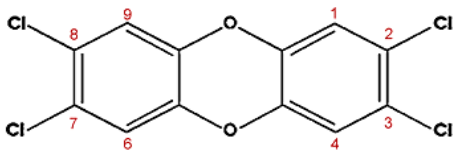
PCDD/F uptake and partitioning is largely controlled by how lipophilic the individual compound is. The rate at which the contaminant is eliminated and consequently, accumulated in the body is determined by metabolic processes.

In order to facilitate a comparison of mixtures, International Toxicity Equivalency Factors have been assigned to individual dioxins and furans based on relative toxicity to TCDD (Ritter et al., 1995). For example, if 2,3,7,8-TCDF is about 10% as toxic as TCDD, its toxic equivalent value of assigned as 0.1.

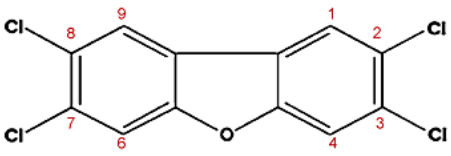
2.1.6.4 Environmental fate

PCDD and PCDF show close resemblance in their behavioural and distribution patterns in the environment. The atmosphere is the key transport mechanism through which these compounds are translocated from their source points to other areas.

Once in the atmosphere, they readily adsorb to particulate matter, thus aiding in their transportation to other environmental compartments (Pereira et al., 2004). Wet and dry depositions are the main mechanisms through which atmospheric PCDD/Fs get deposited onto surface water, soil surfaces and plants. Their ability to be transported for long distances coupled with their persistence make them truly ubiquitous.



2,3,7,8-tetrachlorodibenzo-p-dioxin



2,3,7,8-tetrachlorodibenzo-p-furan

Figure 2.10: Basic structures of 2,3,7,8-tetrachlorodibenzo-p-dioxin and 2,3,7,8-tetrachlorodibenzo-p-furan

They preferentially reside in the surface layers of the soil, usually bound to the

organic matter. PCDD/F exposure to plants occurs mainly through wet and dry deposition, and they mostly affect the upper parts of the plants (Hulster and Marchner, 1993). The transfer of PCDD/Fs to animals, and consequently biomagnification along the trophic chains, apparently occurs by ingestion (Ritter et al., 1995). After entering the food chain through any of the exposure routes, PCDD/Fs tend to bioaccumulate, courtesy of their strong lipophilic characteristics.

2.2 Pharmaceuticals and personal care products (PPCPs)

2.2.1 Introduction

Traditionally, much attention has been focussed on POPs and their environmental impacts. However, the ever increasing production and worldwide consumption of pharmaceuticals and personal care products (PPCPs) has added a new dimension to the scope of pollution related to organic compounds. This relatively new class of so-called “emerging” organic contaminants has posed new environmental challenges among scientists, especially, in the last few years (Zhang et al, 2009). Of particular concern is the adverse ecological consequences attributed to such compounds occasioned by their toxicity and ability to bioconcentrate in organisms.

Although the presence of these contaminants in surface water and wastewater effluents was reported as early as in the 1970s (Garrison et al, 1976), very little attention was accorded to them until later on when the link between ethynylestradiol, a synthetic birth-control compound, and its effects on fish populations was established (Zhang et al., 2009; Kim et al., 2007; Desbrow et al., 1998; Jokbling et al., 1998). Subsequent studies on PPCP compounds and their degradation products have revealed a worldwide presence in various environmental matrices that include surface water, wastewater, sediments and sludge (Fatta et al., 2007).

2.2.2 Pharmaceuticals

Among the various compounds considered as emerging pollutants, pharmaceuticals at trace and ultra-trace levels are of particular concern because of their ubiquity in the aquatic environment and their health effects (Fatta et al., 2007). Depending on their hydrophilic properties, these compounds can be found in water systems as truly dissolved or particle bound. Pharmaceuticals are predominantly polar organic compounds with certain active groups and designed to combat certain ailments in the intended organism. Even though, the effects of most of these compounds on non-target aquatic organisms still remain unclear, some findings, for instance, have shown that continual sub-lethal levels of antibiotic residues in aquatic environments have led to emergence of antibiotic-resistant strains of bacteria (Kummerer et al., 2004). Certain pharmaceuticals are also known to cause disruptions of endocrine functions.

2.2.2.1 Sources

The presence of PPCPs in the environmental systems depends on several factors that include the quantity of drugs manufactured, the dosage frequency and the amount and excretion frequency. Principal sources of pharmaceutical contaminants in the environment are domestic and hospital discharges, veterinary applications, and industrial waste streams (Söderström et al., 2009; Nikolaou et al., 2007). Most of these discharges find their way into wastewater treatment plants (WWTPs) where they get degraded and thereafter, released into the natural water systems.

Since conventional wastewater treatment processes are not specifically designed to degrade this class of compounds, their removal efficiency is limited (Braga et al., 2005; Carballa et al., 2004) and a significant portion exit the treatment plants unaltered. In addition, their metabolites can also be potentially harmful to organisms. Pharmaceuticals in veterinary applications may also end up being dispersed in agricultural fields where they can eventually enter the aquatic environment through rain events (Santos et al., 2005) or underground waterways.

Disposal of unused drugs in landfills which may subsequently leach into ground water and other waterways may yet present as other diffuse sources of these contaminants.

2.2.2.2 Classes of pharmaceuticals

Some of the most widely used pharmaceuticals and frequently detected in WWTP effluent are non-steroidal anti-inflammatory drugs (NSAIDs), antibiotics, lipid regulators, tranquilizers, antiepileptics, contraceptives, beta-blockers, and x-ray contrast media (Zhang et al., 2009; Santos et al., 2005; Petrovic et al., 2005; Ternes et al., 2004). Table 2.9 lists classes of pharmaceuticals with examples of a few individual members.

Removal of pharmaceuticals in WWTPs, just as other chemical substances, depends on their ability to be retained onto solid particles and on their biodegradability. Because of their tendency to strongly adsorb onto particulate matter, lipophilic pharmaceuticals are easily removed from the wastewater through physico-chemical interactions, but, their hydrophilic counterparts (which apparently constitute a greater percentage) tend to be retained in the aqueous phase and therefore potentially more harzadous.

Non-steroidal anti-inflammatory drugs (NSAIDs)

This group of pharmaceuticals is among the most prescribed globally and thus frequently found in both surface water and treated wastewater effluent (Miège et al., 2009). The most commonly detected NSAIDs in water systems include acetaminophen, diclofenac, ibuprofen and naproxen (Benotti et al., 2009). NSAIDs comprise a group of polar organic compounds that contain carboxylic moieties and one or two phenolic hydroxyl groups (Comerton et al., 2009). At acidic pH, no ionic functional groups are present because the hydroxyl and carboxyl moieties are protonated (Ternes, 2001; Farre et al., 2008).

Table 2.9: Major classes of pharmaceutical compounds and examples in each group

Compound	Therapeutic class	Mw	Molecular formula	Log K_{ow}	pKa	$t_{1/2}$ (h) in H_2O
Erythromycin	Antibiotics	734	$C_{37}H_{67}NO_{13}$	3.06	8.80	1.5
Azythromycin		749	$C_{38}H_{72}N_2O_{12}$	4.02	8.74	68
Sulfamethoxazole		253	$C_{14}H_{11}N_3O_3S$	0.89	6.00	10
Trimethropim		290	$C_{14}H_{18}N_4O_3$	0.91	7.12	8-10
Ofloxacin		361	$C_{18}H_{20}FN_3O_4$	n/a	n/a	9
Atenolol	β-Blockers	266	$C_{14}H_{22}N_2O_3$	0.16	9.60	6-7
Sotalol		272	$C_{12}H_{20}N_2O_3S$	0.24	n/a	12
Metoprolol		267	$C_{15}H_{25}NO_3$	1.88	9.68	3-7
Propranolol		260	$C_{16}H_{21}NO_2$	1.2-3.48	9.50	4-5
Tamoxifen	Anticancer	372	$C_{26}H_{29}NO$	n/a	n/a	120-168
Ketoprofen	NSAIDs	254	$C_{16}H_{14}O_3$	3.12	4.45	2-2.5
Diclofenac		296	$C_{14}H_{10}Cl_2NO_2$	4.51	4.14	1-2
Indomethacine		258	$C_{19}H_{16}ClNO_2$	4.27	4.5	4.5
Meclofenamic acid		241	$C_{15}H_{15}NO_2$	5.12	4.2	1-4.5
Meberverine	gastrointestinal	429	$C_{25}H_{35}O_5$	n/a	n/a	2.5
Acetaminophen	Lipid regulators/ cholestrol-lowering statin drugs	151	$C_8H_9NO_2$	0.46	9.38	1-4
Mevastatin		391	$C_{25}H_{38}O_5$	3.95	n/a	-
Pravastatin		446	$C_{23}H_{36}O_7$	3.1	n/a	77
Bezafibrate		362	$C_{19}H_{20}ClNO_4$	4.25	n/a	1-2
Gemfibrozil		250	$C_{15}H_{22}O_3$	4.77	n/a	1.5
Clofibric acid		214	$C_{10}H_{11}O_3Cl$	n/a	n/a	18-22
Carbamazepine	Psychiatric drugs		$C_{15}H_{12}NO$	2.47	7.00	25-65
Fluoxetine			$C_{17}H_{16}F_3NO$	3.82	8.7	24-144
Paroxetine			$C_{19}H_{20}FNO_3$	3.95	n/a	3-65
Ranitidine	receptor antagonists	314	$C_{13}H_{22}N_4O_3S$	0.27	n/a	2-3
Monensin	Growth promoters	1056	C36H61NaO11	2.75-3.89	6.65	692
Lansoprazole	Antiulcer	369	$C_{16}H_{14}F_3N_3O_2S$	2.58	8.73	1-1.5
Thioridazine	Antidepressant	371	$C_{21}H_{26}N_2S_2$	n/a	n/a	7-20

Mw: Molecular weight, K_{ow}: Octanol-water partition coefficient; $t_{1/2,}$ half life; NSAIDs: Non-steroidal anti-inflammatory drugs (Fatta et al., 2007)

However, at high pH levels, they tend to get ionised. Because of their relatively high hydrophilicity, NSAIDs prefer to partition to the aqueous phase rather than adsorbing onto particulate matter. In the current work, two NSAIDs namely naproxen and ibuprofen were studied.

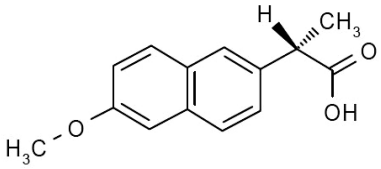
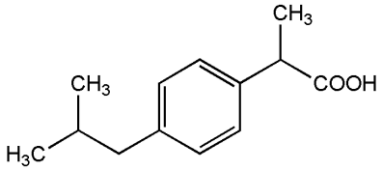
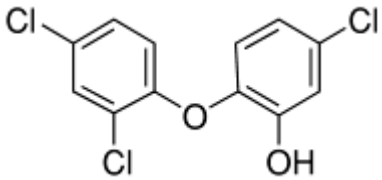
Naproxen and ibuprofen

Naproxen and ibuprofen (Table 2.10) are commonly used non-steroidal, anti-inflammatory drugs having analgesic and antipyretic properties. Naproxen is normally used to relieve moderate to severe aches and pains. Most of its therapeutic activity is probably mediated through prostaglandin synthesis inhibition (Kaynak and Sahin, 2008). In addition, they are clinically applied to manage rheumatoid arthritis and other painful musculoskeletal disorders. The presence of these compounds with their metabolites in the aquatic systems has been widely reported (Gentili, 2007). They are acidic compounds that are polar in nature and usually characterised by the presence of carboxylic moieties. At low pH (acidic), the carboxylic and hydroxyl moieties are protonated and thus no ionic functional groups are present. However, at basic conditions, de-protonation of these functional groups occurs resulting in the formation of ionic compounds. Because most of these compounds are widely used over-the-counter drugs, their subsequent detection in treated wastewater and surface water has been reported.

Antibiotics and antimicrobials

This class of organic compounds are widely applied in human and veterinary medicine to prevent and/or treat microbial infections (Comerton et al., 2009), and their production is evidently extensive. They comprise a broad spectrum of organic compounds characterised by the presence of acidic and basic functional groups in their structures, non volatility, and existence in their ionised form at neutral pH ranges (Diaz-Cruz and Barceló, 2005).

Table 2.10: Some physical and chemical properties of naproxen, ibuprofen and triclosan

Compound	Structure	Mw	MF	pKa	Log K_{ow}	Water solubility (mg L^{-1})	Sample pH (ideal)	Acceptor pH (ideal)
Naproxen		230.26	$C_{14}H_{14}O_2$	4.15[a]	3.18[b]	15.9[d]	2.15	7.45
Ibuprofen		206.3	$C_{13}H_{17}O_2$	4.91[a]	3.97[b]	21[d]	2.91	8.21
Triclosan		289.5	$C_{12}H_7O_2Cl$	7.90[c]	4.8[c]	4.62[d]	5.90	11.20

Mw: Molecular weight, MF: Molecular formula, K_{ow}: Octanol-water partition coefficient, pKa: Acid dissociation constant,
[a]Lindqvist et al., 2005, [b]Zorita et al., 2009, [c]USEPA, 2008, [d]Sagrista, 2013.

Commonly applied sub-groups of antibiotic/antimicrobial compounds include sulphonamides, tetracyclines, penicillins, and quinolines. Individual antibiotic/antimicrobial compounds such as sulfamethoxazole, sulfamethazine, trimethoprin and erythromycin have been frequently detected in water systems worldwide and thus have been used by most researchers as target analytes (Benotti et al., 2009). For instance, sulfamethoxazole, a common sulphonamide, has been detected at median concentration levels of 0.114 µg L^{-1} in river water and as high as 7.35 µg L^{-1} in hospital effluent (Lin et al., 2009).

Steroids and hormones

Steroids and hormones constitute an important part of the priority list of pharmaceutical compounds which are prescribed regularly and have been frequently identified in the aquatic environment. Intense interest in this class of compounds arises due to their potential endocrine disrupting properties (Comerton et al., 2009; Metcalfe et al., 2001). They are generally characterised by moderate to high hydrophobicity and contain phenolic and sometimes aliphatic hydroxyl groups (Comerton et al., 2009). Several studies have reported the presence of estrone, 17-β-estradiol, 17-α-ethinylestradiol, progesterone and testosterone in source water systems with minimal amounts detected in drinking water (WRC, 2013). Due to the similarity in the physico-chemical properties of both natural (e.g. 17β-estradiol) and synthetic (e.g. 17-α-ethinylestradiol) oestrogens, their simultaneous analysis is possible (Gabet et al., 2007; Ternes, 2001).

β-blockers and β_2-sympathomimetics

Although these compounds are generally characterised by low persistence in the aquatic environment, their significance is amplified by the large quantities consumed. Examples from this class of compounds include metoprolol, antenolol, sotalol, bisoprolol and salbutamol. They have been detected at concentration levels as high as 2290 ng L^{-1}, 400 ng L^{-1}, 260 ng L^{-1} and 50 ng L^{-1} for atenolol,

sotalol, metoprolol and propranolol respectively in water systems (Alder et al., 2010). Betablockers and β_2-sympathomimetics medicinal classes have a basic character and contain a secondary aminoethanol structure as well as several hydroxyl groups (Comerton et al., 2009). As a consequence of the large number of functional groups in their structures, they exhibit extremely high polarities (Parvlovic, 2007; Radjenovic et al., 2007; Ternes, 2001).

Iodinated X-ray contrast media

This category of pharmaceuticals is extensively used in medical facilities owing to their crucial roles in imaging of organs or blood vessels during diagnostic tests. They contain iodine atoms, which absorb X-rays making them critical aids in X-ray imaging. They also exhibit high polarities and strong resistances to microbial as well as other environmental degradation (Schultz, 2008; Perez and Barcelo, 2007). Examples of compounds used in X-ray contrast media include diatrizoate, iopamidol and iopromide (WRC, 2013).

Lipid regulators

These are cholesterol-lowering drugs which function as lipid regulators and usually applied in humans. Among this group of pharmaceuticals, gemfibrozil has aroused intense attention most probably due to its suspected carcinogenicity and potential terratogenicity (WRC, 2013). Some parts of the world has witnessed prescription of significantly high doses of this drug (Lin et al., 2009) which in turn led to significant environmental pollution and their subsequent detection in aquatic systems. Atorvastatin and simvastatin are the other members of lipid regulators that are widely consumed. For instance, atorvastatin has been reported as the most prescribed pharmaceutical in the US (Benotti et al., 2009).

Antiretroviral drugs

A significant increase in the production and consumption of antiretroviral (ARV) drugs has been observed in recent times coinciding with the sharp rise in human immunodeficiency virus (HIV) infections in people. ARV drugs have been used as part of the standard care of HIV-infected individuals in many countries (WRC, 2013). In addition to the treatment of HIV, ARVs have also been administered against a broad spectrum of viral infections such as swine influenza virus, herpes, and hepatitis (Singer et al., 2007; De Clercq, 2002; Snoeck and De Clercq, 2002). An increasing rate of ARV use has been witnessed in developing countries, and especially, sub-saharan Africa, where HIV infection rates have alarmingly shot up in the past 20 or so years (UNAIDS, 2000).

After ingestion, and as in the case of other pharmaceutical compounds, ARVs are not completely metabolized in humans and some of it exits the body through faecal matter and/or urine (Prasse et al., 2010). These compounds may eventually enter the aquatic systems through WWTP discharges due to incomplete degradation. Examples of commonly used ARVs include acyclovir, abacavir, lamivudine, nevirapine oseltamivir, penciclovir, ribavirin, stavudine, and zidovudine

2.2.3 Personal care products (PCPs)

Personal care products (PCPs) consists of a broad range of synthetic organic chemicals that include disinfectants, pesticides, fungicides, preservatives, antioxidants and musk compounds used as fragrances in many consumer products (Morley et al., 2005). They are added to products such as soaps, lotions, sunscreens, toothpastes and many cosmetics. Specific examples of commonly used PCPs include fragrances such as nitro- and polycyclic musks, sunscreens and UV blockers such as oxybenzone, insect repellents such as N,N-diethyl-meta-toluamide (DEET), antioxidants and preservatives such as phenols and parabens (Pietrogrande and Busaglia, 2007). Although they are not major product

ingredients, their common addition in consumer products makes them widely available in the water environment. The broad range of PCPs in use today poses potentially complex and not very well understood environmental concerns (Ternes et al., 2004). Although some of these chemicals are successfully removed during wastewater treatment, the fate of many others remains unclear. Among the many PCPs, this study focussed on triclosan.

2.2.3.1 Triclosan

Triclosan, 5-chloro-2-(2,4-dichlorophenoxy)phenol (Table 2.9), is one of the most widely used PCP. This polychlorinated phenyl urea pesticide has been applied as an antibacterial additive in personal care products for several decades (Halden and Paul, 2004). It is a personal care compound added as a preservative and/or an antiseptic agent to various consumer products that include toothpaste, toilet soap, deodorants, shampoo, skin creams, baby toys, sportswear and footwear products (Brausch et al, 2011; Coogan et al., 2007). Although toxicity of triclosan in mammals has not been reported, this broad spectrum bactericide is known to be acutely toxic to aquatic organisms (Lu et al., 2009). Indeed, ecotoxicological studies have shown that triclosan reduces survival rates of fish in addition to being toxic to bacteria and algae even at the low parts per million levels (De Lorenzo et al., 2008; Orvos et al., 2002; Adolfson et al, 2000). As a consequence of its toxicity, a number of regulatory agencies have instituted restrictions on the usage of triclosan in personal care products (EECC; Ministry of Health, China, 2007).

Triclosan is a white crystalline powder with a faint odour and melting point of 56.5^0C. Its octanol-water partition coefficient at 25^0C is 4.8 whereas at the same temperature, it has a low vapour pressure and bulk density are of 5.2×10^{-6} mm Hg and 1.55×10^3 kg m^{-3} respectively (USEPA, 2008). Triclosan is soluble in water at 0.012 g L^{-1} and readily soluble in alkaline solutions and in many organic solvents and is a relatively stable, lipophilic compound (Sagrista, 2013). The environmental occurrence of triclosan has been reported and the compound has been detected in wastewater, surface water, and sediments (Kumar et al., 2010;

Van Stee et al., 1999; Okamura and Nishikawa, 1996). In fish, the presence of its degradation product, methyl triclosan, has been reported (Miyazaki et al., 1984). Triclosan is a chlorinated phenoxyphenol with a pKa of 8.1 (Pillonel, 1999). The pH of surface waters that usually range between pH 7 and pH 9 has a big influence on its speciation and hence, its fate and behaviour (Singer et al., 2002). The relatively high hydrophobicity (log K_{ow} 4.8) of its protonated form (Pillonel, 1999) may lead to considerable sorption to particles in water column or in sediments. However, elimination of triclosan from surface water may be possible because its dissociated form such as methyl triclosan absorbs sunlight and is thus photodegradable (Pillonel, 1999). On the other hand, triclosan is quite stable against hydrolysis (Irgasan, 1999).

2.3 Sampling and sample preparation of organic contaminants in water

2.3.1 Introduction

Sampling is a critical step in any environmental study as it greatly influences the quality of the outcome. Errors committed at this step are quite difficult to correct later on and as such, sampling is as vital as the other subsequent steps. It is therefore imperative to adopt sound sampling strategies in any analytical process. In most cases, before the actual exercise is carried out, a protocol is written down in form of a sampling plan (Chimuka, 2001) to ensure that a truly representative sample of the sampling site is chosen. By adopting the correct sampling procedure, the possibility of identifying and correcting potential sources of interferences, such as, sample contamination, losses attributed to physical, chemical or biological action and other extraneous factors is possible. Overall, the outcome of a well-planned sampling process ensures that the objectives of the study are well met. Unfortunately, there is no single procedure for sampling and how to go about it is as varied as the situations themselves (Chimuka, 2001). In

this section, attention is paid to sampling of organic compounds in aqueous systems: natural waters and wastewater, using passive sampling techniques.

2.3.2 Traditional water sampling techniques

Traditional water monitoring programmes consist of collecting water/wastewater samples (also called grab, bottle or spot samples) at specific points of time, performing sample enrichment in the laboratory (liquid-liquid extraction, solid-phase extraction etc.) and sample clean-up to remove potential interferences. This is usually followed by instrumental analysis, either by gas chromatography (GC), or liquid chromatography (LC). Several detection systems can be used that include Ultra violet (UV), Fluorescence (FLD) and mass spectrometry (MS).

Although grab sampling is arguably still the most widely used and validated environmental sampling technique, this traditionally accepted sampling methodology has many shortcomings. For instance, water samples represent residue composition at the moment of sampling and thus episodic events such as spills or storm water runoff are often missed as contaminants can dissipate prior to the next sampling interval (Rubio and Perez-Bendito, 2009; Vrana et al., 2005). Repetitive sampling to accommodate analyte fluctuations and/or transient occurrence or installing automatic sampling systems that can take numerous water samples over a given period of time can be physically, logistically and financially difficult especially in remote areas (Alvarez et al., 2005; Ternes et al., 2002). Without sufficient repetitive sampling, it is impossible to formulate estimates of the time weighted average (TWA) concentrations of the contaminants of interest. Determination of TWA concentrations is a fundamental part of an ecological risk assessment process for chemical stressors (Huckins et al., 1993). Furthermore, concentrations of dissolved contaminants are not accurately measured because large volumes of water are required for quantifying and assessing trace organic contaminants.

2.3.3 Active sampling

In monitoring organic contaminants in aquatic environments, sample preparation methods that include liquid-liquid extraction (Dean, 1998), solid phase extraction (Poole and Wilson, 2000) and solid phase microextraction (Beltran et al, 2000; Arthur and Pawliszyn, 1990) are still immensely popular. Because they have been in use for many years, these sampling techniques are well developed and are known to provide very good accuracy and precision (Chimuka and Cukrowska, 2006).

In active sampling, environmental factors that affect passive samplers are easily controlled because extraction is performed in the laboratory. When compared to other recently developed sampling approaches such as passive sampling, quality assurance procedures in active sampling are well known. In spite of all these, sample preparation is generally known to consume 60% of the environmental monitoring process and most errors are introduced during this step (Nyoni, 2010). Use of these methods for monitoring contaminants at the low ng L^{-1} to μg L^{-1} levels in water may be challenging (Lu et al., 2002). Such difficulties are often encountered when collecting and extracting large volumes of water needed for trace contaminant analysis. They include sampling and handling induced changes in some water quality parameters and loss of analyte during filtration, volatilization and sorption.

2.3.4 Biomonitoring

Certain aquatic living organisms are known to provide reliable information on the truly dissolved bioavailable fraction of organic contaminants in the water environment. Persistent organic pollutants such as PCBs, OCPs and PAHs are strongly lipophilic and although such contaminants may be present at very low concentrations in water, they slowly move across animal membranes (e.g. fish gills) and concentrate in the fat tissues of such aquatic organisms (Gorecki and Namiesnik, 2002; Kot et al., 2000). Information on the equilibrium concentration

of the water-borne contaminants can be obtained from analysis of the lipid or tissue extracts of the organisms. A number of biomonitoring organisms have been reported and compared with passive samplers with good correlation observed in most cases (Chimuka and Cukrowska, 2006). Aquatic organisms can only qualify for this role if they reflect the pollutant levels at a certain location and their variation over a period of time.

Biomonitors too have some limitations in their application. For example, organisms may not survive in certain environmental conditions and age, size, sex, and physical condition might affect the uptake rates of compounds (Vrana et al., 2005). The organisms should also be abundant and less mobile in the environment so as to achieve reliable long-term monitoring. Moreover, extraction procedures of analytes from the tissues of animals prior to instrumental analysis are tedious and complex (Vrana et al., 2005).

2.3.5 Passive sampling

As highlighted earlier, passive samplers offer an attractive alternative to traditional sampling methods. Passive sampling constitutes any sampling technique based on the free flow of analyte molecules from the sampled medium (e.g. water) to a collecting medium as a result of a difference in chemical potentials of the analyte between the two media (Rubio and Perez-Benedito, 2009; Paschke et al., 2005; Vrana et al., 2005; Gorecki and Namiesnik, 2002). The net flow of analyte molecules from one medium to the other continues until equilibrium is established in the system or until the sampling session is terminated. Thus, the quantity of the collected analyte by the sampler is dependent on both its concentration in sampled medium and the exposure time (Gorecki and Namiesnik, 2002). The ratio of analyte distribution between the two media involved or the experimental calibration of the device can then be used to determine the analyte's concentration. Therefore, use of integrative passive samplers can enable estimation of TWA concentrations of pollutants of interest and permits sequestration of residues from episodic events commonly not detected

with grab sampling. In addition, this technique can allow the concentration of ultra-trace, yet, toxicologically relevant contaminant mixtures to be determined over extended periods of time (Yu et al., 2006).

A passive sampler is designed to mimic the parts of animals that cause bioconcentration. It contains a sorption medium where contaminants can pass through with highly purified oil, solvent or solid sorbent in which the contaminants dissolve into or adsorb onto. The device is left in the water for a few days to several weeks, during which it sequesters hydrophobic or hydrophilic water-borne contaminants depending on the sampler design. At the end of the period, the sampler is removed and then analysed for the contaminants.

Passive methods may generally be classified as either based on adsorption or absorption (Kot et al., 2000). Adsorptive methods involve the physical or chemical retention of the contaminants by surfaces of adsorbent as influenced by surface binding and/or surface area. Absorptive methods involve not only the surface phenomena, but also analyte permeation in the interceding material, hence providing the possibility of compound discrimination due to the membrane's physicochemical characteristics (Kot et al., 2000). The membrane used as the diffusion barrier in permeation passive sampling is the most critical component of the sampler. Mass transfer of pollutants through the membrane is influenced to a great extent by the nature of the membrane material.

Permeation process proceeds in three stages: adsorption of the analyte at the outer surface of the membrane followed by dissolution and diffusion of the dissolved analyte through the membrane and finally, desorption of analyte from the inner surface of the membrane**.** The slowest step, and hence, the rate determining step is the diffusion of analytes dissolved in the membrane material. Other parameters such as water temperature, fluctuation of analyte concentrations and turbulence can affect passive sampling. The last two or so decades has witnessed an exponential growth in the application of passive sampling (Vrana et al., 2005). Several types of these devices have been designed for monitoring pollutants in the

aquatic systems by accumulating both hydrophobic and hydrophilic organic micropollutants and allowing detection at even the ng L^{-1} levels. Three types of passive samplers are discussed in the following section.

2.3.5.1 Factors affecting performance of passive samplers

Water sampling rates (Rs) of specific analytes by PSDs depend on a complex set of interacting environmental variables including temperature, water flow, sorption of the compounds to dissolved organic carbon, biofouling, photodegradation and the geometry of the mounting cages (Stuer-Lauridsen, 2005; Vrana et al., 2005; Booij et al., 1998).

Turbulence

Transfer through the water boundary layer (WBL) is generally the rate-limiting step for the uptake of organic compounds, and therefore, the sampling rates (R_s) for these compounds depend on the hydrodynamic conditions at the exposure site (Booij et al., 2007). Actual field conditions in which passive samplers are deployed are usually different from laboratory conditions. One of the most difficult environmental factors to control is turbulence of the environmental media. Turbulence affects especially compounds with log K_{ow} values > 4.5 (Huckins et al., 2006, 2002) because their uptake by SPMDs is heavily influenced by external WBL (Augulyte and Bergqvist, 2007). Increased water turbulence causes thinning of WBL leading to enhanced uptake rates of the compounds by the sampler. The effects of turbulence can be minimised by mounting the sampler in a protective cage which will reduce the flow velocities of the water close to the sampler's surface. However, of critical significance is the use of *in situ* calibration techniques based on the dissipation of performance reference compounds (PRCs) added to the sampler prior to deployment (Verweij et al., 2004; Booij et al., 2002).

Biofouling

The growth of bacterial mats, periphyton and even microfauna (biofouling)

can have a major impact on analyte uptake rates (Mason et al., 2005). By randomly forming on the membrane surface, the biofilm layer increases the overall mass transfer resistance of the compounds by decreasing or even blocking pores in the diffusion limiting membrane. A study by Richardson et al. (2002) on the uptake of OCPs and PAHs by SPMDs revealed that biofouling of the membranes reduced amounts of absorbed contaminants by about 30 - 40% when compared to unfouled controls (Booij et al., 2007). A viable solution to this problem is to incorporate PRCs in the samplers before exposing them in the field (Verweij et al., 2004; Booij et al., 2002; Booij and van Drooge, 2001).

Temperature

The sampling rates of compounds in an environmental media generally increase with an increase in temperature. Michel et al. (2009) observed an increase in the mass transfer of triazole compounds in a supported liquid membrane with an increase in temperature. The effects of temperature on sampling rates have been also been observed in SPMDs (Yusa et al., 2005) and in membrane enclosed sorptive coating (MESCO) sampler (Vrana et al., 2001). Knowing the prevailing temperatures during field deployment of samplers is important in addition to evaluating the influence of temperature on each analyte of interest in the laboratory. However, use of *in situ* calibration methods by incorporating PRCs in the samplers before deployment still remain the best bet in mitigating temperature effects.

2.3.6 Passive sampling devices (PSDs)

2.3.6.1 The semipermeable membrane devices (SPMDs)

Among the permeation samplers, the semi-permeable membrane devices (SPMDs) (Figure 2.11) have attained the most widespread application and have proved very effective in their capacity to accumulate lipophilic contaminants. SPMDs are versatile and rugged in that they can be used to monitor contaminants

both in air and aquatic environments (Seethapathy et al., 2008; Greenwood et al., 2007; Kot-Wasik et al., 2007). An SPMD for water sampling consists of a lay-flat low density polyethene (LDPE) tubing enclosing a thin film of a high molecular weight lipid, typically high purity synthetic triolein (Alvarez, 2010; Vrana et al., 2005; Kot et al., 2000).

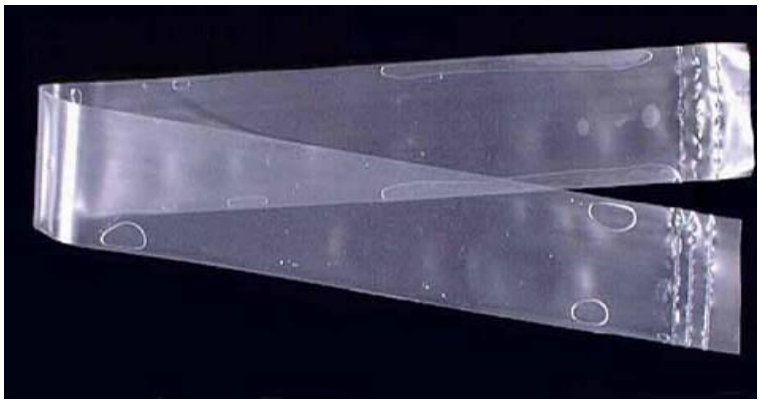


Figure 2.11: Semipermeable membrane device (SPMD) (Alvarez et al., 2004)

LDPE is a non-porous material with no fixed pores, only transient cavities with typical size of 1 nm (Vrana et al., 2005). In an aquatic environment, SPMDs passively accumulates hydrophobic organic compounds by mimicking biological membranes in its ability to allow selective diffusion of organic compounds. Hydrophobic organic compounds such as PAHs, PCBs and OCPs with partition coefficients (log K_{ow}) in the range of 3.0 to 6.0 are suitable for extraction by this technique (Vrana et al., 2005; Huckins et al., 1993).

Uptake of contaminants from the environment is strongly dependent on the compound's physical and chemical properties such as molecular weight and water solubility. In addition, environmental conditions that include temperature, flow rate and biofouling influence this uptake. In general, for a given non-ionic organic compound, an SPMD will effectively sample depending on the compound's hydrophobicity (as quantified by its log K_{ow}). Any hydrophobic compound with log K_{ow} > 3 and a cross-sectional diameter less than 10 Å (1 nm) can be significantly sampled by SMPDs in water (Alvarez, 2010).

SPMDs have many advantages as compared to grab sampling. They include ease of deployment, standardized character, possibility of using long sampling times without approaching equilibrium and accurate representation of the freely dissolved fraction of the analyte in water (Vrana et al., 2005; Kot et al., 2000). However, its main shortcoming is the lengthy and complicated sample preparation procedure required to recover the accumulated pollutants from the receiving phase. The method is also not very environmentally friendly as large amounts of solvents are used in the process. Moreover, preconcentration and rigorous clean-up of the extracts is also required before instrumental analysis can be carried out.

Uptake of analytes by SPMDs and determination of aqueous concentrations

The ambient water dissolved analyte concentration (C_w) can be estimated based on the amounts accumulated in the SPMD's lipid (C_{SPMD}), the effective sampling rate (R_s) and the deployment period (t) (Kot et al., 2000). TWA concentrations are determined using mathematical models previously developed by Huckins et al. (2006, 1993), and later on modified by Smedes et al. (2009) and Booij et al. (2010) are used. Uptake of chemicals into passive samplers is initially linear over time, then moves to a curvilinear stage and finally can approach equilibrium (Esteve-Turrillas et al., 2008; Booij et al., 2007; Vrana et al., 2005). In the initial stage of sampler deployment, analyte amounts increase linearly with time. This stage has therefore been named as the linear uptake stage, time-integrative sampling stage, or kinetic sampling stage. The term 'time-integrative sampling' arises because in cases where aqueous concentrations vary with time, the concentration in the SPMD is linearly proportional to the TWA concentrations (Booij et al., 2007). In this stage, an estimate of the water dissolved concentrations of the compounds is determined using equation 2.1.

$$C_{TWA} = \frac{C_{SPMD} V_{SPMD}}{R_s t} \qquad (2.1)$$

Where C_{TWA} is the time weighted average concentration, C_{SPMD} (ng) is the analyte concentration in the SPMD, V_{SPMD} (L) is the volume of SPMD, R_s is the sampling rate (L d^{-1}), and t (d) is the SPMD exposure time.

However, after an elongated field exposure period, the absorbed amounts attain their equilibrium levels giving rise to what is called equilibrium sampling. Here, equation (2.2) is used to calculate the aqueous concentrations of the analytes.

$$C_W \approx \frac{C_{SPMD}}{R_s t} \tag{2.2}$$

Where C_w is water dissolved concentrations of the compounds (ng L^{-1})

In between the linear and equilibrium stages is the curvilinear stage which results from intermediate exposure periods of a sampler. In such cases, the TWA concentrations can be determined using equation (2.3)

$$C_w = \frac{N_s}{K_{sw}V_s[1 - \exp(-R_s t/K_{sw}V_s)]} \tag{2.3}$$

Where K_{sw} is the SPMD-water partition coefficient, V_s is SPMD volume and N_s amount (ng) of analyte absorbed by the SPMD

Unlike equations (2.1) and (2.2) which provide approximated C_w concentrations, Booij et al. (2003) and Huckins et al. (2006) recommended the use of the curvilinear stage equation (equation 2.3) for determining water soluble analyte concentrations because of its superior accuracy.

Permeability reference compounds (PRCs)

The uptake rates of samplers towards specific analytes are often determined in the laboratory under controlled conditions of temperature and flow velocity around

the sampler, and the absence of biofouling (Rubio and Perez-Bendito, 2009). Such ideal conditions are rarely encountered in the field. Therefore, environmental conditions such as temperature fluctuations, biofouling and water turbulence can adversely affect the performance of SPMDs. This also poses a challenge when comparing estimated water concentrations of pollutants sequestered by SPMDs deployed in different sites experiencing different sets of environmental conditions. In order to account for such variations, PRCs are normally added to the devices prior to deployment. By doing so, the *in situ* sampling rates of target compounds can be determined more accurately as opposed to laboratory calibration. Moreover, by impregnating the SPMDs with PRCs, it is possible to deploy them for times that are too short to attain environment-sampler equilibrium (Fernandez et al., 2009)

PRCs are analytically non-interfering, non-native compounds with moderate to relatively high-fugacities, added to the lipid of SPMDs during sampler fabrication prior to deployment (Huckins et al., 2006). Usually, deuterated, isotope-labeled and sometimes, non-labeled or native compounds are used as PRCs. However, labeled compounds are mostly preferred because their existence at significant levels in the natural environment is seldom witnessed. Estimation of water sampling rates from the PRCs' dissipation parameters provides a means to evaluate the influence of the exposure variables on the uptake kinetics of the analytes by each sampler and thus calculate the sampling rates of the analytes by each SPMD (Augulyte and Bergqvist, 2007).

This approach to *in situ* SPMD calibration is premised on theoretical and experimental evidence that have shown that the rates of PRC loss and uptake of target compounds exhibit isotropic exchange kinetics (Huckins et al., 2002; Booij et al., 1998), (Figure 2.12). Therefore, information on the rate of PRC dissipation can be used to adjust SPMD-derived estimates of ambient concentrations to reflect site-specific environmental conditions of an exposure.

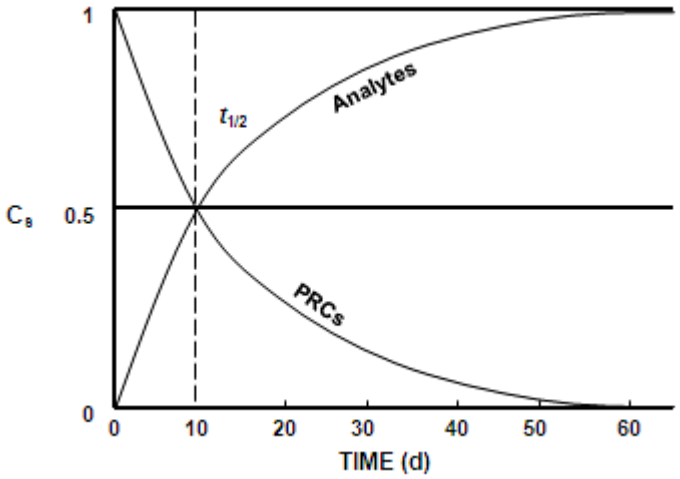


Fig 2.12: Illustration of isotropic exchange kinetics (Huckins et al., 2005)

2.3.6.2 The polar organic chemical integrative sampler

The Polar organic chemical integrative sampler (POCIS), shown in Figure 2.13, is a relatively recently developed device designed for sampling hydrophilic organic micropollutants in aquatic systems (Morin et al., 2012, Mazzella et al., 2010). Such polar compounds are characterised by the presence of one or more polar functional groups such as, hydroxyls and carboxyls, or a significant molecular dipole moment within it. Although other passive sampling devices have been tested for this group of compounds such as Chemcatcher and solid phase microextraction (SPME, POCIS has emerged superior.

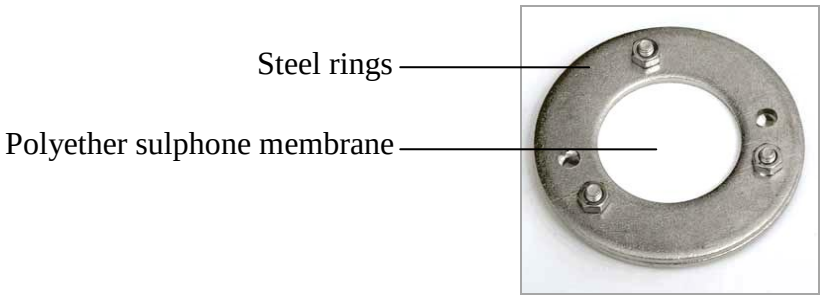


Figure 2.13: The polar organic chemical integrated sampler (POCIS)

It targets organic contaminants with log K_{ow} values between 3.0 and 4.0. Since its introduction in the late 1990s, POCIS has witnessed major milestones and has

proved to be an effective passive sampler for emerging pollutants such as PPCPs and polar organic pesticides (Mazella et al., 2007). POCIS has been used as a screening tool for determining the possible sources and relative amounts of organic contaminants in surface water and wastewater and drinking water (Morin et al., 2012).

Principle of POCIS

The POCIS is configured in a disk-like manner in which a solid-phase sorbent or mixtures of solid sorbents are held betwee Sorbent particles polyethersulphone (PES) diffusion-limiting membranes. PES is a porous membrane characterised by fixed pores of about 100 nm diameter which allow molecules to diffuse through it based on size exclusion limit. To prevent sorbent loss, two compression rings are used to firmly sandwich the PES membranes. The rings are made of stainless steel, but an inert polymeric material can also be used (Alvarez et al., 2007). The rings are firmly secured in place using a combination of thumb screws, bolts, nuts or clips. Figure 2.14 shows a POCIS disk and its component parts. A typical standard POCIS used in field studies is characterised by the parameters listed in Table 2.11.

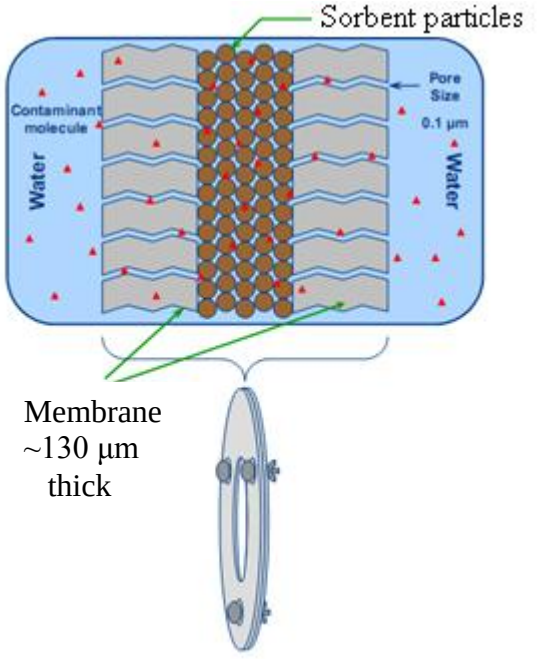


Fig 2.14: POCIS disks and its parts (Alvarez et al., 2004)

Table 2.11: Properties of a typical POCIS

Property	Dimension
Hydrated pore structure	76.5 %
Hydrated membrane thickness	130 μm
Effective surface area	41 cm^2
Mass of sorbent	200 mg
Surface area to sorbent ratio	200 cm^2g^{-1}
Compression ring dimensions	5.1 cm i.d, 8.9 cm o.d.

i.d = internal diameter, o.d. = outer diameter (Mazzella et al., 2010; Alvarez et al., 2007; Allan et al., 2006; Blom et al., 2002)

By acting as a semipermeable barrier between the sorbent and the surrounding environment, PES membrane selectively excludes particulates, microorganisms and macromolecules with cross-sectional diameters greater than 100 nm while allowing hydrophilic compounds such as PPCPs to pass through to the sorbent where they get retained. In addition, the PES membrane greatly reduces the risk of the sorbent material getting biofouled during the exposure period by creating a physical barrier.

Biofilm infestation of the sorbent is problematic as it is very difficult to directly remove it from the sorbent surfaces. PES is especially suitable for use as an effective barrier due to its good resistance to biofouling. Although, the water-filled transport corridors through the PES membrane are intricate and occasionally devious, unlike the linear structures of many microporous membranes (Alvarez et al., 2007), permeation of water through its pores into the solid sorbent still occur rapidly on sampler deployment in the aquatic system.

In order to enhance the detection of certain compounds that may occur at very low concentrations in the environmental waters, extracts from several POCIS disks may be combined into a single sample. This is possible due to the fact that a direct relationship exists between the quantity of the analyte sampled and surface area of the device.

The versatility of POCIS as a sampling technique is demonstrated by its ability to target specific compounds or groups of compounds by simply using the right sorbent. Currently, there are two "universally" accepted and commercially available types of sorbents recommended for use in all standard POCIS in field deployments. Each sorbent system is better suited for specific groups or types of polar organics. In order to maximize on the range of detectable polar organic compounds at a sample site, a number of POCIS devices, each having a different sorbent type, can be deployed in a single protective cage (Alvarez et al., 2007).

Types of sorbents used in POCIS

Hydrophilic-Lipophilic Balanced or "Pharmaceutical" sorbent

Hydrophilic-Lipophilic Balanced (HLB) sorbent is a water-wettable reversed phase sorbent constituting a specific ratio of two monomers namely N-vinylpyrrolidone (hydrophilic) and divinylbenzene (lipophilic). This mixture forms a macroporous poly(dinylbenzene-co-N-vinylpyrolidone) that exhibits both hydrophilic and lipophilic retention characteristics capable of sorbing both polar and non polar compounds. Oasis HLB is an example of the commercially available, universal polymeric reversed-phase sorbent system. Figure 2.15 gives the general structure of Oasis HLB sorbent.

Oasis HLB sorbent is characterised by a higher reversed-phase capacity with a neutral polar hook for enhanced retention of polar analytes. It possesses a number of key advantages that include stability at pH extremes and in a wide range of solvents, extraordinary retention of polar compounds and a relative hydrophobic retention capacity that is about three times higher than that of traditional silica-based SPE sorbents (Alvarez et al., 2007). Table 2.12 highlights some of the major physical properties of Oasis HLB sorbent.

Pharmaceuticals fall into the hydrophilic group of organics and their optimal sequestration in aqueous media is best achieved using HLB sorbents.

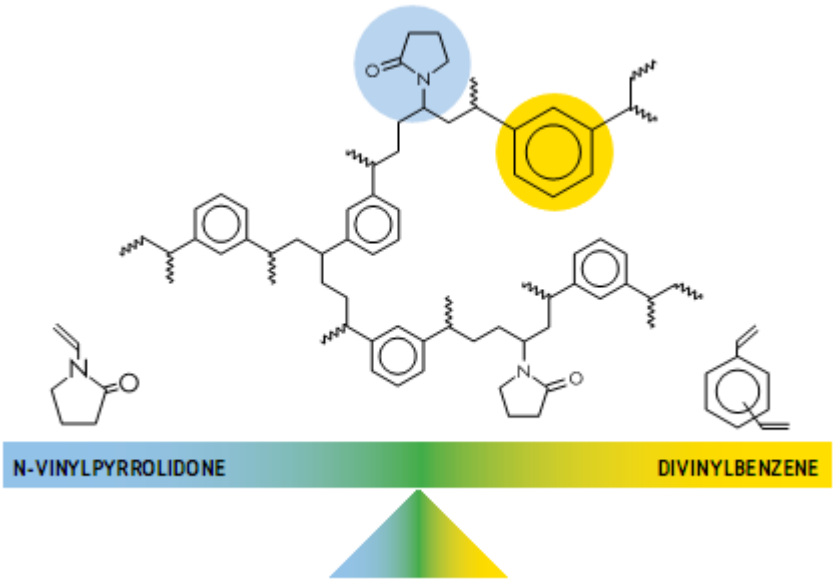


Fig. 2.15: Oasis Hydrophilic-Lipophilic Balanced co-polymer

Table 2.12: Some physical properties of Oasis HLB sorbent

Property	Dimension
Specific surface area	810 m^2 g^{-1}
Average pore diameter	80 Å
Total pore volume	1.3 cm^3 g^{-1}
Average particle diameter	5 µm, 15 µm, 25 µm, 30 µm or 60 µm

POCIS samplers that incorporate HLB sorbent systems as their sequestration medium are therefore referred to as the "pharmaceutical" POCIS (Morin et al, 2012). Oasis HLB has also found wide application as an SPE-based sorbent for sampling pharmaceuticals and other polar organics in water. Considerable data on the recoveries of sorbed analytes has resulted from its use (Miege et al., 2009).

Furthermore, solvents used to recover chemicals from the Oasis HLB are generally compatible with toxicity tests, precluding the need for rigorous solvent exchange (Alvarez et al., 2007). As a result, the "pharmaceutical" POCIS is often more frequently used because of the less toxic elution solvents required in addition to the ease of utilization of the HLB phase as compared with the triphasic mixture in "pesticide" POCIS (Li et al, 2010).

ENVI+ or "pesticide" sorbent

This sorbent system consists of a triphasic admixture of Isolute ENV+ polystyrene divinylbenzene resin (80% by weight) and Ambersorb 572 carbon, lightly dispersed on S-X3 Biobeads (20% by weight) (Alvarez, et al., 2007). Figure 2.16 displays the molecular structure of ENVI+ sorbent.

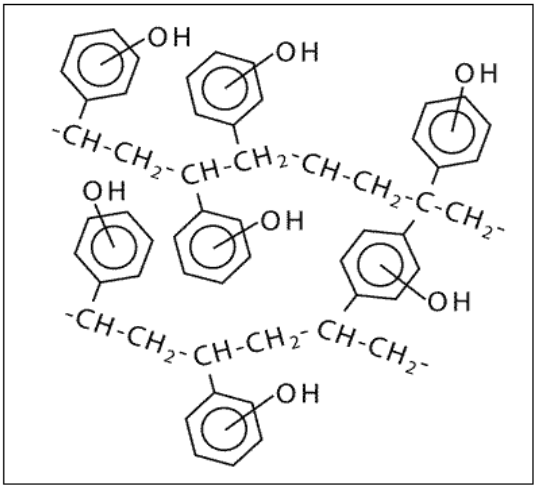


Fig 2.16: Isolute ENV+ sorbent

With this sorbent, the common preconditioning step can be skipped because the hyper cross-linking associated with it provides an excellent hydroxylated surface. Resulting from this superior capacity, the sorbent sequesters remarkably high amounts of waterborne hydrophilic organic compounds with particular efficient recovery of most pesticides, natural and synthetic hormones and other wastewater related hydrophilic organic contaminants.

Since ENVI+ has become the sorbent of choice in sampling pesticides, it has therefore been christened, the "pesticide" sorbent (Morin et al., 2012).

This sorbent type is characterised by the physical properties listed in Table 2.13 below.

Table 2.13: Some physical properties of Isolute ENV+ sorbent

Property	Dimension
Description	Hydroxylated polymeric material
Average pore diameter	80 Å
Total pore volume	1.3 cm^3 g^{-1}
Average particle diameter	5 µm, 15 µm, 25 µm, 30 µm or 60 µm

Accumulation of contaminants by POCIS

Passive diffusion of the analytes from the water phase through a microporous membrane into a selective receiving phase (sorbent) governs uptake of the compounds by POCIS. This sampler is mainly used in the linear regime to determine TWA concentrations. Based on results to date, POCIS remains in the integrative phase of sampling during exposure periods of at least 30 days (Morin et al., 2012).

Unlike samplers that rapidly achieve equilibrium, integrative samplers (like POCIS) can capture chemical residues from episodic release events at the end of the exposure period ensuring minimal analyte loss rates and elongated times to reach equilibrium (Morin et al., 2012). In other instances, POCIS may be used for screening purposes of contaminants in the sample sites. In such a scenario, the information obtained is qualitative and thus, the sampler can be used in any of the regimes.

As mentioned earlier, POCIS is suited for sampling polar organic compounds typically with log K_{ow} < 3. Figure 2.17 shows the barriers to chemical uptake in POCIS, whereas, a graphical representation of the sampling characteristics of POCIS and SPMDs as a function of their log K_{ow} values is presented in Figure 2.18.

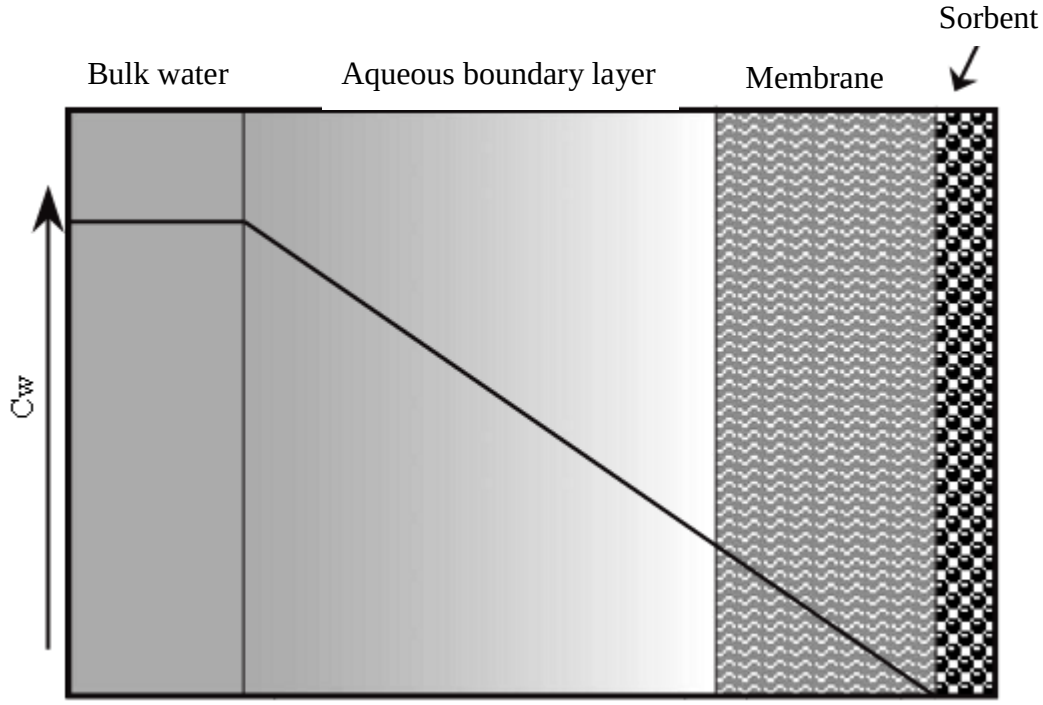


Figure 2.17: Representation of the barriers to chemical uptake into the POCIS (Alvarez et al., 2007)

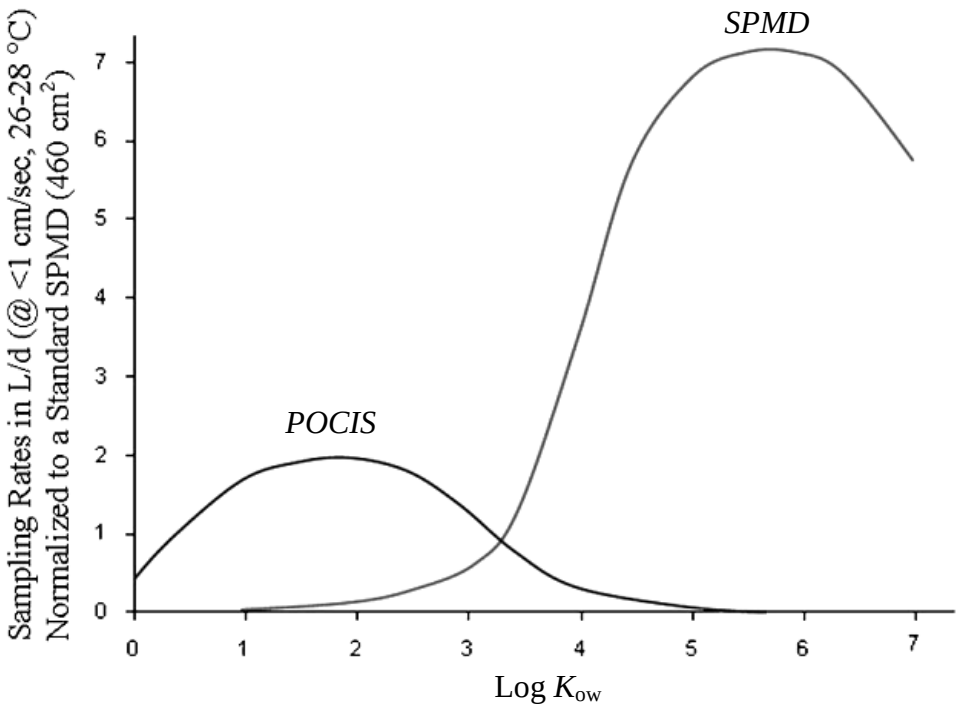


Fig 2.18: Comparison of POCIS and SPMD sampling rates (normalized to 460 cm^2 surface area) for a wide range of organic chemical log K_{ow} values (Alvarez et al., 2007)

Evaluation of TWA concentration

The correct determination of TWA concentrations of the analyte of interest in the bulk water is usually preceded by laboratory or *in situ* calibration of the POCIS. This exercise creates a link between the quantity of a compound accumulated in the sampler and its concentration in the sampled medium through the determination of its sampling rate, R_s (Morin et al, 2012). A reliable calibration of the sampler can only be achieved in the kinetic/integrative regime.

Alvarez and co-workers and Jones-Lepp and co-workers (Alvarez et al., 2004; Jones-Lepp et al., 2004), observed that laboratory experiments carried out under turbulent conditions using POCIS showed a number of pesticides and pharmaceuticals remaining in the integrative phase of residue accumulation for up to 56 days. This could justify the use of a linear uptake model for the determination of sampling rates and subsequent calculation of ambient water concentrations.

The concentration of a compound in the sampling device is linked to the concentration in the bulk medium via equation (2.4)

$$C_s = \frac{C_w}{k_u t} \qquad 2.4$$

Where, C_s is the analyte concentrations (µg g^{-1}) in the sorbent, C_w is analyte concentration (µg L^{-1}) in the bulk water, k_u is the uptake rate (L g^{-1} d^{-1}), t is exposure time (days)

On introducing sampling rate (R_s) and the mass of the sorbent, equation (2.4) translates to equation (2.5)

$$C_s = \frac{C_w R_s t}{M_s} \qquad 2.5$$

Where, R_s and M_s are the sampling rate (L d^{-1}) and the mass of sorbent in the POCIS (g), respectively.

Finally, analyte water concentrations (C_w) can be determined using equation (2.6)

$$C_w = \frac{C_s M_s}{R_s t} \qquad 2.6$$

R_s can be visualised as the volume of water cleared per unit time for a given molecule, and is usually influenced by water flow, temperature and biofouling (Vrana et al., 2005).

Although the parameters in a laboratory calibration set-up may not be completely identical to field conditions, R_s for many compounds are still being determined in this manner. Ideally, the incorporation of PRCs prior to deployment could yield more accurate *in situ* sampling rates. However, in this case, estimation of such sampling rates using the PRC approach is complicated by strong sorption of most compounds to the adsorbents, and desorption kinetics are generally not isokinetic with the uptake. So far, there have been very few PRCs for the POCIS, and only Mazzella and co-workers (2010) were able to successfully use PRCs for herbicides in river waters with POCIS having HLB sorbent (Morin et al., 2012). Suitable PRCs for many other polar compounds, and especially pharmaceuticals, remain a challenge that needs to be resolved.

2.3.6.3 Membrane Assisted Passive Samplers (MAPS)

This is a relatively novel passive sampler based on silicone hollow fibre membrane used for extracting ionisable organic compounds in aqueous media. It is a simple, inexpensive and very selective passive sampler that does not use organic solvents (Nyoni et al., 2011, Chimuka et al., 2008). It works on the principle that for the analyte compounds to diffuse into the silicone membrane from the sample media, they have to be unionised at the sample pH. The

compounds then diffuse into the acceptor phase where they get ionized and absorbed thus keeping the concentration of the non-ionised analyte molecules in the acceptor phase at zero and maintaining the concentration gradient between the two phases (Chimuka et al., 2008). Depending on the pH of the acceptor solution, MAPS can be configured to sample either acidic or basic compounds in environmental water.

MAPS' potential for the extraction of phenolic compounds under laboratory and field conditions is documented (Nyoni et al., 2010; Chimuka et al., 2008). More recently, Nyoni et al. (2011), in a study on triazine compounds demonstrated that MAPS can be successfully used to extract basic organic compounds, such as triazines by changing the pH of the acceptor solution from basic to acidic.

2.3.7 Sample preparation methods

Sample preparation is usually a laborious and time consuming process. An ideal scenario for any analyst is to have a method that combines sampling, sample preparation and analysis. However, this is not easily achieved except for few techniques like immunoassays (Nunes et al., 1998). Sample preparation is designed to eliminate contaminants from the analyte as well as enhance its enrichment which in turn ensures improved detection. Masking of the analyte may occur where matrix contaminants exist in conjunction with the analyte (Chimuka, 2001). This can create major challenges during instrumental analysis of the target compounds. Sample preparation is therefore geared towards eliminating excess matrix-related contaminants in order to produce clean signals. In most cases, the analyte of interest is found at trace or ultra-trace levels in the water sample rendering detection and subsequent measurement using common equipment difficult or even impossible. In addition to emphasising on methods that give high selectivity and enrichment, current approaches have also focussed on green techniques as well as those that are amenable to automation. Some of the commonly used sample preparation techniques include liquid-liquid extraction solid-phase extraction, solid phase micro-extraction, supercritical fluid extraction,

pressurised liquid extraction, microwave assisted extraction and passive samplers. Subsequent discussions will briefly touch on liquid-liquid extraction, solid-phase extraction and hollow fibre supported liquid membrane techniques.

2.3.7.1 Liquid-liquid extraction

Liquid-liquid extraction (LLE) is one of the oldest and most widely used sample preparation techniques in the extraction of organic compounds from aqueous samples. In LLE, separation of a sample is achieved through partitioning or distribution between two immiscible liquids or phases (organic phase and an aqueous phase) in which the analytes and the matrix differ in their solubilities. In principle, the hydrophilic (more polar) components of the sample are preferentially partitioned to the aqueous phase while hydrophobic (non-polar) compounds partition to the organic phase. This method is also best suited for extracting organic compounds that are to be analysed using gas chromatography (GC). This is because the compounds of interest are isolated in an organic solvent suitable for GC analysis either directly, or if need be, preconcentrated further prior to analysis. Moreover, analyte fractions in the aqueous phase can be analysed using high performance liquid chromatography (HPLC) either directly or after additional enrichment steps.

The main advantages of LLE are its wide applicability, availability of high purity organic solvents and the use of low-cost apparatus (Dean, 1998). Despite the many merits, LLE technique also has several disadvantages. For instance, it is a tedious and time consuming process, uses a lot of solvents (not environmentally friendly), formation of emulsions particularly when extracting samples that contain surfactants or those that are rich in fatty materials and possible loss of analytes during the process (Psillakis and Kalogerakis, 2003; Chimuka, 2001).

2.3.7.2 Solid-phase extraction

The popularity of solid phase extraction (SPE) as a sample preparation method

currently surpasses all other techniques (Chimuka, 2001). SPE is widely applied in the separation, preconcentration and/or clean-up of analytes of interest from aqueous samples. The principle of SPE is based on sorption of analytes onto a solid sorbent. Typically, a sample solution is brought into contact with a solid sorbent whereby the compound is selectively trapped or adsorbed onto the surface of the solid prior to elution (Moors et al., 1994) using a suitable solvent(s). Most sorbents are packed in cartridges, small tubes or disks (Sabik et al., 2000). SPE technology has continued to evolve such that production of new designs, new sorbents (e.g. silica or polymer-based media and mixed-mode media) and the development of automated and on-line systems (Somsen et al., 2002) has been witnessed in recent times.

Indeed, development and introduction of new sorbents into the market is witnessed every other year (Chimuka, 2001). Available sorbents can be categorised into two broad groups: selective and non-selective sorbents. Non-selective sorbents have a general advantage in that they are capable of extracting as many compounds as possible from different families or classes but lack selectivity when extracting analytes in complex matrices such as sediments, surface water, plant tissues and foodstuffs (Chimuka, 2001). On the other hand, selective sorbents are more specific and therefore more suitable for such matrices.

Irrespective of the design used, the sample-containing solvent is forced by pressure or vacuum through the sorbent. Careful selection of the sorbent is done so that the organic compound is retained by the sorbent in preference to other extraneous material present in the sample (Dean, 1998). By washing the analyte-containing sorbent with the right solvent, contaminants associated with the matrix can be removed. Eventually, the sorbent-bound analyte is eluted using an appropriate solvent or mixture of solvents and the eluate collected for analysis. If the need arises, further clean-up and/or preconcentration of the eluate can be done so as to improve on signal quality and detection. SPE technique therefore facilitates the simultaneous extraction and enrichment of the analytes.

2.3.7.3 Hollow fibre supported liquid membrane extraction

A hollow fibre supported liquid membrane (HF-SLM) is normally a triphasic liquid membrane system in which the pores of a piece of hollow fibre are impregnated with an organic solvent and its lumen filled with a given volume of an aqueous acceptor solution (Lamas et al., 2004; Rasmussen et al., 2004; Psillakis and Kalogerakis, 2003). The immobilised liquid is a membrane phase and a microporous film serves as a support for the membrane (Dzygiel and Wieczorek, 2000). Extraction of target compounds is done by immersing the hollow fibre in the aqueous sample solution (donor). After the extraction is done, the analyte-rich acceptor phase is then analysed by HPLC or electrophoresis directly without subjecting it to further preparative steps. In addition to exhibiting good selectivity, HF-SLM technique yields high enrichment factors. Extraction of macromolecules and particulates into the acceptor phase is not possible because of the small pore sizes of the hollow fibre and molecules that are not soluble in the organic solvent are also excluded (Pena-Pereira et al., 2010; Sarafraz-Yazdi and Amiri, 2010; Lee et al., 2008; Psillakis and Kalogerakis, 2003; Jonsson and Mathiasson, 2001). Figure 2.19 gives a diagrammatic representation of HF-SLM system.

Ionisable/polar organic compounds resident in aqueous solutions can be extracted using three-phase HF-SLM systems. The analytes are extracted from an aqueous sample (donor phase) to an aqueous acceptor solution placed in the lumen of the hollow fibre, and both aqueous phases are separated by the hollow fibre membrane which contains an organic solvent immiscible with water in its pores Sagrista, 2012). Equation (2.7) summarises this process (Pedersen-Bjergaard and Rasmussen, 2008; Rasmussen et al., 2004).

$$A_{sample} \longleftrightarrow A_{organic} \longleftrightarrow A_{acceptor} \qquad 2.7$$

Where A_{sample} is the target analyte in the sample solution, A_{org} is the analyte in the organic phase, and $A_{acceptor}$ is the analyte in the acceptor solution.

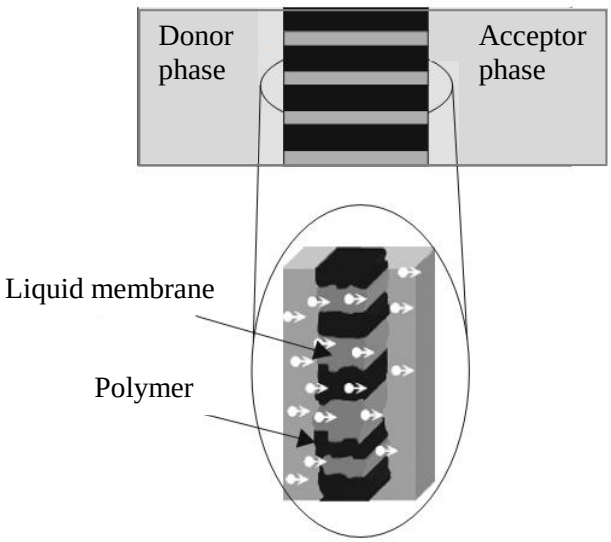


Figure 2.19: Scheme of a supported liquid membrane (Dzygiel and Wieczorek, 2000)

Two parameters, namely, the extraction efficiency and enrichment factor, characterise the performance of a HF-SLM. Extraction efficiency (E) measures the fraction of the analyte extracted from the donor phase to the acceptor phase, while the enrichment factor (E_e) reflects the increase in analyte concentration in the acceptor phase relative to the initial concentration of the donor solution (Chimuka et al., 2010). E and E_e are mathematically defined by equations 2.8 and 2.9, respectively.

$$E = n_{Ae}/n_{Di} \text{ x } 100\% \qquad 2.8$$

Where n_{Ae} is the total amount of analyte in the acceptor solution at equilibrium and n_{Di} is the amount of the analyte found in the donor phase.

$$E_e = C_{Ae}/C_{Di} \qquad 2.9$$

Where C_{Ae} is the concentration of the analyte in the acceptor phase at equilibrium and C_{Di} is the initial concentration of the analyte present extracted sample solution. As a prerequisite, the analytes to be extracted using this method must be unionised, in addition to being soluble in the organic solvent. In cases where the compounds are acidic, basic or exist in ionic form, pH adjustment of the sample

solution is important. As a rule, the pH of the donor solution must be kept at least 2 units lower that the pKa value for acidic analytes and 2 units higher for basic compounds. On the other hand, the pH in the acceptor phase should be at least 3.3 units lower than the pKa of the least basic analyte and vice versa for acidic analytes (Chimuka, 2001). Such conditions ensure that all the analytes in the donor phase are kept in their unionised state and extracted analytes are successfully stripped. Generally, buffers with high capacities are used as the acceptor phase because they are able to resist alteration of their pH by co-extracted compounds.

In other cases, an ion pairing or complexing agent can be added to the sample or in the organic membrane. Then, the analytes are back extracted from the organic phase where they are trapped as ions by pH adjustment or by adding a suitable stripping agent (Sagrista, 2012).

In the current study, extraction of acidic analytes by pH adjustment was carried out, whereby transport of analytes was achieved by a pH gradient between the donor and the acceptor phases. Extraction of analytes was however done in the absence of an organic membrane. Instead, water molecules were used to impregnate the hollow fibre pores, hence, forming an aqueous membrane. This was necessitated by long extraction periods (24 hours) coupled with continuous agitation of the sample solution. Such conditions are known to promote the loss of the organic solvent membrane.

2.4 Analytical techniques

A comprehensive assessment of a broad range of environmental organic micropollutants has been made possible through the use of gas chromatography (GC) and liquid chromatography (LC) combined with mass spectrometry (MS) for detection (Diaz-Cruz et al., 2009; Esteve-Turrillas, 2008; Fatta et al., 2007; Verweij et al., 2004). Although, ultra violet (UV) and fluorescence (FLD) detectors are also still applied in the identification of these contaminants, the

suitability of UV as a detection system is often limited by its poor selectivity and lower sensitivity. Therefore, this technique may not be useful for trace analysis.

2.4.1 Analysis of POPs

GC techniques are best suited for the analysis of hydrophobic, volatile or volatisable organic compounds that are thermostable, (Comerton et al., 2009), e.g. PAHs, PCBs and OCPs. In GC, separation of the components is achieved through partitioning between a liquid stationary phase and a gaseous mobile phase. Detection of separated compounds is commonly achieved using flame ionisation detector (FID), electron capture detector (ECD) or mass spectrometer. Coupling GC with MS gives the best analytical technique combination for POPs (PAHs, PCBs and OCPs). However, analysis of non-volatile compounds, such as PPCPs, often requires derivatisation to make them compatible for such analyses. This step may lead to significant losses of the analytes. In the present study, GC-MS/MS was applied for the analytical determination of PAHs, PCBs and OCPs.

2.4.2 Analytical methods for PPCPs

LC methods are typically applied to more polar, less volatile or thermodegradable compounds such as pharmaceuticals and personal care products. LC separation of such compounds involves partitioning of the analytes between a stationary phase and a liquid mobile phase. Transportation of the sample into the column is effected by a liquid mobile phase. Once in the column, analytes are retained according to their interaction with the stationary phase and thereby, sequentially eluted after some time (Dean, 1998). For such polar compounds, separation is normally achieved in a reversed phase mode with the stationary phase composed of either C_{18} (octadecyl) or C_8 (octyl) bonded silica material.

In LC, the ultraviolet-visible (UV-Vis) detector still remains the most common detection system found virtually in any laboratory set-up. The fluorescence (FLD)

detector is another appropriate alternative to the UV detector. However, it has a limitation in that its application is only possible for compounds that can undergo fluorescence. Selectivity is based on the fact that each compound has a unique excitation and emission wavelength.

Of late, LC-MS and LC-MS/MS techniques have increasingly been favoured as the best tools for the detection and identification of trace organic contaminants in environmental samples. Particularly, LC-MS/MS is highly sensitive, has the ability to confirm compounds and its analytical selectivity in complex matrices such as wastewaters is unrivalled (Fatta et al., 2007). Unfortunately, LC-MS/MS is susceptible to matrix effects which can cause suppression or even enhancement of analyte signals, especially when working in the Electrospray ionisation (ESI) mode. In such instances, a standard addition method or an internal standard with structurally similar unlabelled compounds or isotopically-labelled standards can be applied (Richardson, 2010; Radjenović et al., 2007). Furthermore, the instrument is still very expensive for many laboratories. In this work, analysis of PPCPs in wastewater was carried out using HPLC-UV and HPLC-FLD. Table 2.15 summarises some of the commonly used methods for the preparation and analysis of naproxen, ibuprofen and triclosan in aquatic samples.

2.5 South African legislation on POPs and PPCPs

2.5.1 POPs

Implementation of the Stockholm Convention is done through the Department of Environmental Affairs (DEA) in collaboration with other departments such as those of Agriculture Forestry and Fisheries, Water Affairs, International Relations, Trade and Industry, Science and Technology and Health. Several legislation targeting environmental pollution by various organic contaminants that include POPs have been enacted in the post 1994 South Africa, in line with the philosophical and structural reforms undertaken by the new political order.

Table 2.14: Comparison of methods used in the preparation and analysis of naproxen, ibuprofen and triclosan in aqueous samples

Compound	Matrix	Extraction technique	Analytical method	Recovery (%)	MLOQ (ng L^{-1})	Reference
Naproxen Ibuprofen	Wastewater	SPE	GC-MS	92 98	2.7 9.6	Samaras et al., 2011
Triclosan	Surface water and wastewater	SPE	GC-MS	89 - 104	3	Ying et al. 2007
Naproxen Ibuprofen	Wastewater	SPE	LC-ESI-MS/MS	34-81 63-111	7-9 8-12	Gros et al., 2006
Ibuprofen Triclosan	Wastewater	LLE	GC-MS	100 >90	6.7 17	Kanda et al., 2003
Naproxen Ibuprofen	Surface water and wastewater	SPE	LC-QqLIT	71-113 82-107	0.3-21 0.4-9	Gros et al., 2009
Naproxen Ibuprofen	Surface water and wastewater	SPE	LC-UV/FLD	92-97 79-100	UV:366-3333 FLD:6.67-1517	Camacho-Muñoz et al., 2009
Ibuprofen	Tap, surface and wastewater	SPE	HPLC-MS/MS	53 – 70	0.52	Nebot et al., 2007
Ibuprofen	Wastewater	Liquid-liquid-liquid	HPLC-UV	73.1	100	Wen et a., 2004
Naproxen Ibuprofen	Surface, drinking and wastewater	SPE	LC-MS/MS	76 – 103 90 - 124	49 642	Gracia-Lor et al., 2010
Naproxen Ibuprofen	Surface and wastewater	SPE	GC-MS/MS	112 64	0.5 0.8	Verenitch et al., 2006
Naproxen Ibuprofen	Wastewater	SPE	HPLC-DAD/FLD	98 89	20 250	Santos et al., 2005

Naproxen Ibuprofen	Wastewater	Dynamic HF-LPME	GC-MS	98 - 103 97 - 102	10 10	Zhang et al., 2009
Naproxen Ibuprofen	Surface water	SBME	HPLC-UV	44 – 50 47 - 52	900 900	Al-Hadithi et al., 2011
Naproxen Ibuprofen	Drinking water, surface water and Wastewater	Dynamic HF-LPME	GC-FID	90 – 108 89 - 95	1 2	Es'haghi, 2009
Triclosan	Surface water and wastewater	XAD bag samples	GC-MS	76	20	Yu and Wu, 2011
Triclosan	Surface water and wastewater	SPE	UHPLC-MS/MS	85 - 92	3 - 10	Pedrouzo et al., 2009
Triclosan	Wastewater	SPE	LC-MS	74 - 90	10 - 30	Heidler et al., 2009
Triclosan	Wastewater	SBSE	LC-DAD	78	100	Silva & Nogueria, 2008
Triclosan Ibuprofen	Surface water, drinking water and wastewater	SBSE	GC-MS	70 – 92 95 - 105	29 20	Quintana et al., 2007
Triclosan	Surface water and wastewater	SPME	GC-MS	100 - 104	2	Canosa et al., 2005
Triclosan	Surface water	SPE	LC-MS/MS	69 - 100	0.23 - 50	Singer et al., 2002

MLOQ = Method limit of quantification; HF-LPME = Hollow fibre liquid phase microextraction; SBSE = Stir bar sorptive extraction

Prior to 1994 environmental management regulations generally lacked adequate integration of all the environmental media, was reactive and addressed symptoms rather than focusing on proactive measures which went to the root causes of pollution (National implementation plan for Stockholm convention, 2011). The paradigm shift in environmental protection thus, started with the enactment of a new constitution in 1994 that recognized environmental management as a critical component in national development.

The overall environmental protection legislative framework is anchored in a number of policies, acts and regulations. Generally, this is accomplished through the following laws and regulations: the National Environmental Management Act (Act No 107 of 1998 and Regulations), the National Environmental Management: Waste Act (Act No 59 of 2008), the National Environmental Management: Air Quality Act (Act No 39 of 2004), Fertilizers, Farm Feeds, Agricultural Remedies and Stock Remedies Act, (Act No 36 of 1947 and Regulations), Hazardous Substances Act (Act No 15 of 1973 and Regulations), National Health Act (Act No 61 of 2003), Occupational Health and Safety Act, (Act No 85 of 1993 and Regulations), National Water Act (Act No 36 of 1998), National Road Traffic Act (Act No 93 of 1996 and Regulations), Foodstuffs, Cosmetics and Disinfectants Act (Act 54 of 1972), Customs and Excise Act (Act No 91 of 1964), and the International Trade Administration Act (Act No 71 of 2002) (National implementation plan for Stockholm convention, 2011).

2.5.2 PPCPs

As in the case of many other countries, no specific regulations that target pharmaceuticals and personal care product residues have been set up in South Africa to date. As mentioned previously, this class of pollutants are ‘emerging’ and most of their health effects on animals and humans still remain unknown. Research on these contaminants is on-going and hopefully, regulatory frameworks will be instituted by agencies and countries. On this issue, environmental regulatory agencies the USEPA are committed to investigating this topic and

developing strategies to help protect the health of both the environment and the public (USEPA, 2012). The maximum contaminant limits (MCL) of selected PAHs, OCPs, and PCBs according to USEPA and WHO standards are presented in Table 2.15.

Table 2.15: Maximum contaminant limits (MCL) for some PAHs and POPs

POP	**Compound**	**MCL ($\mu g\ L^{-1}$)**	**Reference**
PAHs	Chrysene	0.02	USEPA
	Benzo(a)anthracene	0.01	USEPA
	Benzo(b)fluoranthene	0.02	USEPA
	Benzo(k)fluoranthene	0.02	USEPA
	Benzo(a)pyrene	0.02	USEPA
	Indeno(1,2,3-cd)pyrene	0.04	USEPA
	Dibenz(a,h)anthracene	0.03	
PCBs	Polychlorinated biphenyls	0.05	USEPA
OCPs	HCHs	0.02	USEPA
	DDTs	0.5	USEPA
		2.0	WHO

Chapter 3:

Research objectives

3.1 General objectives

The main objective of this study was to develop passive sampler-based methods for determining the bioavailable concentrations of pharmaceuticals and personal care products (PPCPs) in wastewater, and persistent organic pollutants (PAHs, PCBs and OCPs) in environmental waters. Some of the developed methods were then applied to monitor the concentrations of PAHs, PCBs, OCPs and PPCPs in selected South African water bodies and in wastewater.

3.2 Specific objectives

(1) To develop and apply a membrane assisted extraction method in combination with HPLC-FLD and HPLC-UV for the simultaneous determination of naproxen, ibuprofen and triclosan in wastewater.

(2) To investigate the influence of temperature on mass transfer in an incomplete trapping single hollow fibre supported liquid membrane extraction of naproxen, ibuprofen and triclosan.

(3) To investigate the seasonal variation in the free dissolved PAH, PCB and OCP concentrations in Hartbeespoort dam, South Africa as derived from their accumulation in semipermeable membrane device (SPMD) passive samplers.

(4) To determine the water borne concentrations of PAHs, PCBs and OCPs in water bodies located around Johannesburg and Pretoria cities, South Africa, using semipermeable membrane devices

(5) To fabricate, calibrate and subsequently apply the polar organic chemical integrated sampler (POCIS) to estimate the water-borne concentrations of naproxen, ibuprofen and triclosan in wastewater emanating from wastewater treatment plants situated in Johannesburg, South Africa.

3.3 Research statement

PAHs and POPs such as PCBs and OCPs are known hazardous and ubiquitous organic micropollutants for which several regulations have been instituted to curb their production, distribution and/or use. Pharmaceuticals and personal care products (PPCPs) are an emerging group of pharmacologically active organic contaminants whose health effects on humans arising from environmental exposure generally remain unknown. In addition to being labour intensive, most conventional monitoring practices yield samples that are not well representative. Thus, development of sensitive methods that are inexpensive, selective and representative enough to sample especially, the bioavailable fraction of these compounds in aquatic ecosystems are still needed. Passive samplers offer a better alternative to traditional approaches. Therefore, in this study, passive samplers were developed and used in monitoring POPs and PPCPs in surface water and wastewater, respectively.

3.4 Justification

Aquatic systems are often exposed to contamination from both natural and anthropogenic sources and require continuous monitoring. Contamination of the water systems by POPs that include PAHs, PCBs and OCPs is a major environmental problem due to their widespread distribution and proven health effects (Levinson et al., 2008). Significant quantities of these contaminants mainly enter water systems through fossil fuel combustion, industrial and WWTP discharges, and agricultural activities. Wet deposition, surface water runoff, and remobilisation of POPs adsorbed onto soils and sediments due to heavy rainfall, are also other contributors. Most POPs are recalcitrant compounds that are extremely persistent in the environment. Thus, the need to constantly monitor them in water systems is critical.

PPCPs and their metabolites enter the aquatic environment through industrial, hospital and domestic effluents, landfills and veterinary discharges. Significant

concentrations of human PPCPs have been detected in municipal sewage effluents in several countries and some of these compounds have been found to be resistant to degradation during the sewage treatment processes (Lapen et al., 2008; Yu et al., 2006; Beausse, 2004). Treated effluent is usually discharged directly into the water systems: streams, rivers and wetlands.

Sampling is a very important stage in any analytical procedure and most traditional sampling approaches have major shortcomings. For instance, the methods are unsuitable where pollutants are present at trace or ultra-trace levels. Their reliability is also questionable as they only provide a snapshot of the pollutant levels at the time of sampling and may fail to detect fluctuations with time. Solutions to these problems such as increasing the sampling frequency or installing automatic sampling systems increases costs and may not be feasible in the long run.

Passive sampling techniques such as SPMDs and POCIS, used in this study, are attractive alternatives to conventional sampling methods. Passive samplers are generally known to considerably decrease costs associated with sample preparation (combines sampling, analyte isolation and pre-concentration into a single step) as well as significantly reducing the amount of solvents used. Moreover, SPMDs and POCIS sample the bioavailable fraction of the contaminants. This fraction is critical in environmental risk assessment of a pollutant.

Johannesburg is a major industrial hub in the region. South Africa also principally uses fossil fuels to generate its electricity. Most of the industrial, domestic and hospital effluents are normally discharged into the water bodies (dams, rivers and streams) in the vicinity either directly or after undergoing routine wastewater treatment procedures. Literature on the state of POPs and PPCPs in South African natural water systems and wastewater effluent emanating from WWTPs situated in and around Johannesburg city is scanty. Moreover, in spite of their many advantages, use of passive sampling techniques in these systems for monitoring POPs and PPCPs has so far not been reported.

Chapter 4:

Materials and methods

4.1 Semipermeable membrane devices (SPMDs)

4.1.1 Chemicals and reagents

The PAHs standard mixture that contained the 16 US EPA priority PAHs (all > 97% pure) was purchased from Sigma-Aldrich Chemie GmbH, Steinheim, Germany. Permeability 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. PCB121 and terphenyl (Dr Ehrenstorfer GmbH, Augsburg, Germany) were used as internal standards for PCBs and PAHs instrumental analysis, respectively. Pesticide residue analysis grade n-hexane, dichloromethane, trichloromethane, acetone and all other solvents (all > 97% pure) used were purchased from Sigma-Aldrich (Prague, Czech Republic). Sulphuric acid (99%) was purchased from Merck-Schuchardt (Darmstadt, Germany. Milli-Q water was obtained from the Millipore Simplicity 185 system (Millipore, Bedford, MA, USA).

4.1.2 SPMD sampler preparation

Layflat tubing made from low-density polyethene (LDPE) that was free from any additives was used to prepare the SPMD membranes. The tubing characterised by a 2.5 cm width and wall thickness of 70 µm was sourced from Brentwood plastics, MO, USA. Initially, 100 cm long portions of the tubes were cut off from the roll before inserting them into pre-cleaned, dry glass bottles using a pair of blunt tweezers. Cleaning was done twice by soaking them overnight in hexane with the aim of removing organic contaminants. After air-drying, the membranes were heat-sealed at one end to form a loop.

Membranes were filled with triolein (1,2,3-Tri(cis-9-octadecenoyl)glycerol) (Sigma, Munich, Germany) which had previously been cleaned six times by partitioning with HPLC-grade methanol (Lebo et al., 2004) and 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 final concentration of 2 µg g^{-1} triolein. 1 ml of the spiked triolein was introduced as close as possible into the sealed end of the SPMD membrane using a micropipette. Another heat seal was made to ensure that a distance of 91.4 cm from the first seal was created. This was done after squeezing out as much air as possible from the membrane. The process of expelling air from the membrane also produced a more even spreading of the triolein throughout the device. To safeguard against contamination after fabrication, the SPMDs were stored in air-tight sealed metal cans under freezing temperatures (-20^{0}C) until deployment. Control blanks were also prepared in the same manner.

4.1.3 Deployment of SPMDs

At the deployment site, the samplers, including the field controls, were unpacked from the metal cans and placed on a clean piece of aluminium foil. The samplers were then mounted onto the deployment devices in triplicate. The deployment device was a cylindrically shaped casing made of stainless steel and had the dimensions: 10cm diameter and 35 cm height. Once ready, they were quickly immersed in the water at between 1 and 1.5 metres depth from the water surface. The steel cages housing the samplers were tied using polyethylene ropes and anchored firmly to buoys. Finally, the field blanks were paced in air-tight tin cans and transported in cool boxes to the laboratory where they were stored at -20^{0}C.

4.1.4 Sampling sites

In total, deployment of the SPMDs was done at eight sampling sites situated around Johannesburg and Pretoria cities, South Africa. They were: Hartbeespoort

dam, Jukskei River, Centurion Lake, Centurion River, Homestead Lake, and the Airport River. Table 4.1 describes the sampling sites in the study area whereas Figure 4.1 is a map showing the sampling sites.

4.1.4.1 Hartbeespoort Dam (HD)

Two sampling sites were located in the Hartbeespoort dam: Ifafi (IFA) and Eagles (EGL). The dam is situated about 37 km west of Pretoria city and along the Crocodile River in North West Province of South Africa. The water body is a 20 km^2 water reservoir sandwiched between the Magaliesberg mountain range in the Highveld region of northern South Africa (Nyoni et al., 2011, Van Rei, 1987). The dam reservoir receives water from approximately 4100 km^2 area all the way from Johannesburg via the Juskei 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 Jukskei, the Hennops and the Swartspruit basin.

The Crocodile River accounts for about 90% of the dam's water inlet supply with rain water being the major source. This scenario dramatically changes during the dry season (winter) as the water of the dam is more than 50% treated wastewater from urbanised areas upstream (Harding et al., 2004) thus creating additional environmental problems for the water body.

Although the origins of the Crocodile River system can be traced to the highly urbanised north of the City of Johannesburg (Harding et al., 2004), extensive rural crop farming is still carried out within the dam's drainage area using its water. Considerable urban developments are also present along the shorelands of the basin, and a portion of the impounded water from the dam is utilized for domestic supply, both within the riparian community and in downstream urban centres (Department of Water Affairs, 2012).

Table 4.1: Description of sampling sites

No	Sampling site	Symbol	Water body	Longitude	Lattitude
1.	Ifafi, Hartbeespoort dam	IFA	Dam	25°45′09.97"S	27°53′04.39"E
2.	Juskei River 1	JR1	River	26°01′07.49"S	28°05′34.69"E
3.	Juskei River 2	JR 2	River	26°00′25.30"S	28°04′45.74"E
4.	Eagles, Hartbeespoort dam	EGL	Dam	25°44′56.29"S	27°50′06.18"E
5	Homestead Lake	HSL	Dam	26°10′25.64"S	28°17′04.71"E
6	Airport River	AUP	River	26°08′29.74"S	28°17′04.71"E
7	Centurion Lake	CL	Dam	25°51′55.41"S	28°12′23.36"E
8	Centurion river	CR	River	25°51′40.01"S	28°11′22.93"E

At IFA sampling site, temporal trends in analyte water concentration were also investigated by monitoring the water body for PAHs, PCBs and OCPs using SPMDs in each of the four seasons of the year: winter, spring, summer and autumn. Table 4.2 presents the deployment periods of the SPMDs and the associated water quality parameters in the sample site during deployment.

4.1.4.2 Juskei River (JR 1 and JR 2)

Two sampling sites were chosen in the Juskei River for the deployment of SPMDs (Figure 4.2). The Juskei is one of the river catchments in metropolitan Johannesburg that covers over 800 km^2 and its source can be traced upstream to Bruma Lake at the foot of the Witwatersrand area (Matowanyika, 2010). The river eventually empties its water into the Hartbeespoort dam after joining the Crocodile River downstream. The river meanders northwards through a number of residential areas such as the highly populated Alexandra Township. Juskei River catchment area is characterised by a warm and moderate climate with mean annual temperatures ranging from 10.1^0C in June to 20.1^0C in December and receives a mean annual rainfall of about 730 mm (Matowanyika, 2010).

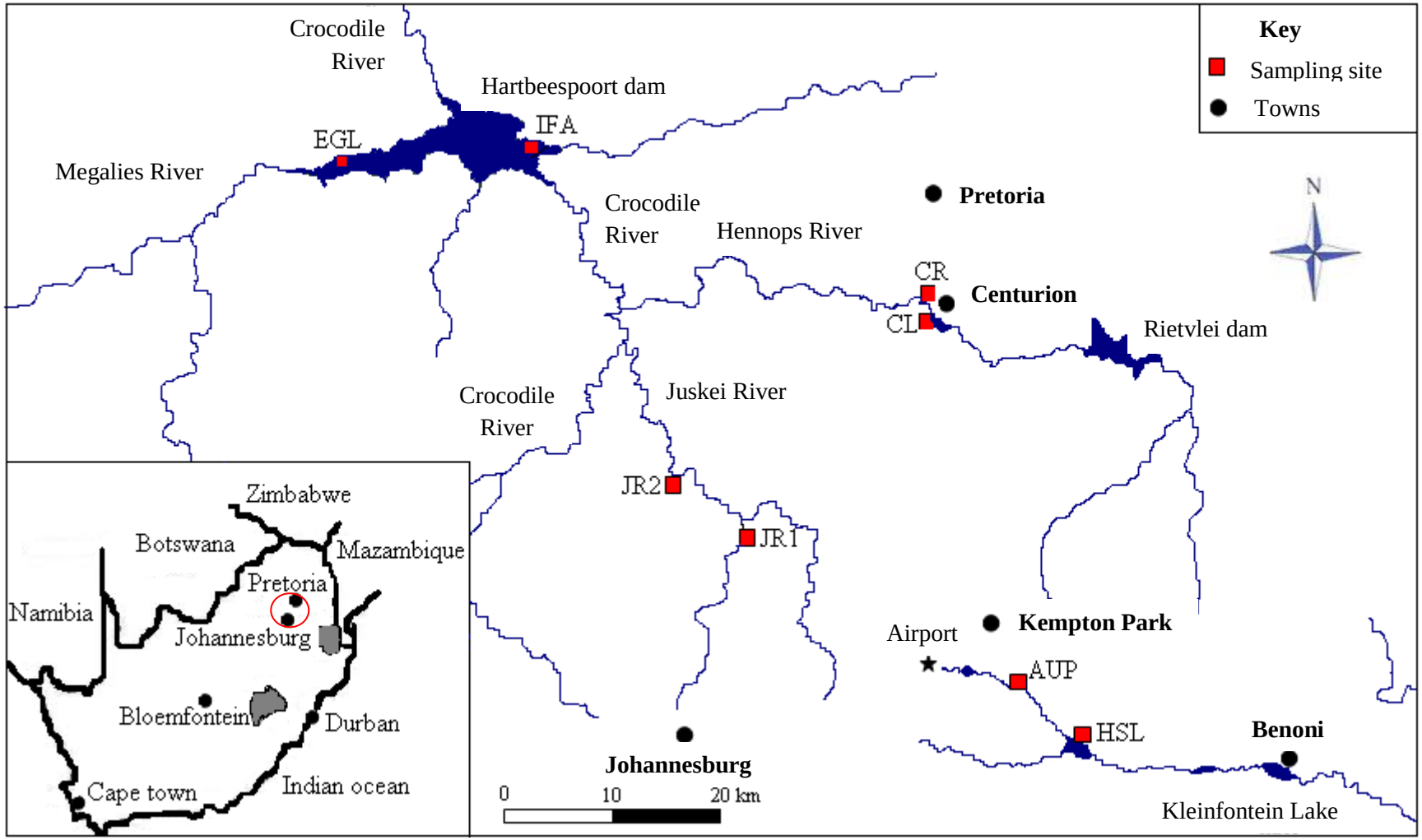


Figure 4.1: Sketch map showing the sampling sites

Table 4.2: Deployment periods and water quality parameters at IFA sampling site

	Sampling period	Water temperature (^{0}C)	pH	Conductivity ($\mu S\ m^{-1}$)
Winter	19-04-2011 to 04-05-2011	11.6	8.0	546
Spring	19-08-2011 to 02-09-2011	14.2	8.2	538
Summer	18-11-2011 to 02-12-2011	25.5	9.0	456
Autumn	24-02-2012 to 09-03-2012	19.7	8.6	482

4.1.4.3 Centurion Lake (LC) and Centurion River (RC)

Centurion lake (CL) and Centurion River (CR) form part of the Hennops, a relatively small perennial river, that originate from a marshy area situated a few kilometres east of Kempton Park. As it flows downstream, it passes through a swamp before receiving treated effluent from the Kempton Park WWTP. The Kempton park area is home to several industries which release their effluent to the river after treatment. Centurion Lake is surrounded by vibrant business installations such as shopping malls, hotels and recreational facilities. It also has several garages and a few small industries. The outskirts of the town is covered by many residential areas.

4.1.4.4 Homestead lake (HSL) and Airport River (AUP)

Both Homestead Lake (HSL) and Airport River (AUP) are located about 28 and 35 km, respectively, east of Johannesburg city and very close to the O.R. Tambo international airport. The source of the AUP River is right at the periphery of the Airport. It briefly flows downstream in a south east direction into a small man-made reservoir. It then continues its flow through a swampy area and meanders through several residential areas before discharging its water into a man-made reservoir called HSL. This dam is also surrounded by many residential developments. Industrial activities are a rare sight in the immediate vicinity of the dam. However, another stream originating from the southern part of the airport

located about 5 km west of the dam also discharges its water into HSL. Its source is a water reservoir that is surrounded by a number of industrial establishments. Both streams exit the dam as a single river and flows in an easterly direction towards Benoni and the east rand area.

4.1.5 Retrieval of SPMDs

After the 14-day exposure period, the SPMDs were retrieved from the sample sites. The field controls were removed from the metal cans and placed on a clean and firm aluminium foil away from sunlight and wind. After recording the time, the deployment devices containing the samplers were quickly removed from the water. This was followed by removal of the exposed SPMDs from the steel cages, briefly washing off excess biofouling (where found) and placing them in air-tight sealed metallic cans. Finally, the samplers were placed in a cool box and transported to the laboratory where they were stored at -20^{0}C awaiting processing.

4.1.6 SPMD processing

Once in the laboratory, remaining biofouling on the affected samplers was mechanically removed by brushing in water using a soft tooth brush. In order to get rid of adsorbed carbonates, the SPMDs were briefly immersed in diluted (10%) hydrochloric acid solution before flushing with sufficient quantities of tap water and subsequently dried using a soft paper tissue. The whole SPMD was then carefully rolled around a clean, pair of tweezers and gently transferred into a pre-cleaned, empty 250 mL glass bottle with a ground joint stopper. 100 ml of HPLC grade n-hexane was added and each sample 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}, PCB2 K19 and d_6-gamma HCH (0.5 μg sampler^{-1} of each compound added directly to the hexane containing the sampler). Extraction of the SPMDs was done twice for 24 hours in the dark at room temperature. The extracts were then combined and reduced to about 10 mL using a rotary evaporator (Heidolph Laborata4000, Germany) before

concentrating it further to about 0.5 mL and reconstituted using 1 mL of pesticide residue analysis grade trichloromethane (chloroform). This raw extract was then subjected to clean-up and fractionation by gel permeation and column chromatography.

4.1.6.1 Clean-up of SPMD extracts by gel permeation chromatography

To remove lipids that diffused into the extract during SPMD dialysis, gel permeation chromatography, also called size exclusion chromatography was employed. A high pressure pump (HPP5001) coupled to a BioBeads S-X3 200-400 mesh column (8 x 500 mm) was used with chloroform as the mobile phase. The flow rate of the mobile phase was maintained at 0.6 mL min^{-1}. The injection loop was initially washed with chloroform at least three times before 1 mL of the SPMD extracts obtained in step (2.45) was manually loaded into the injection port. A glass syringe (Hamilton Bonaduz AG, Switzerland) was used to introduce 1 mL of the extract into the injection loop.

Majority of the long chain lipids eluted before 18 minutes. The contaminants of interest (PAHs and PCBs) were collected as from 18 minutes 20 seconds to 41 minutes 40 seconds. After elution, the extract was divided into two parts at a ratio of 80:20 v/v. The 80 % portion was used for the determination of PCBs and OCPs whereas the 20% portion was used for PAH analysis. Each portion of the extracts was further reduced till the last drop using a gentle stream of nitrogen gas before reconstituting with 1 mL of n-hexane. The resulting extracts were thus ready for the next clean-up step using activated silica gel.

4.1.6.2 Clean-up of SPMD extracts by column chromatography

Preparation of activated silica gel

Silica gel was initially cleaned in a sohxlet extraction system using pesticide residue analysis grade dichloromethane for 8 hours. Afterwards, the clean silica

gel was spread on an aluminium foil and left to dry in a fume hood for 2 hours. Activation was achieved by heating the dry gel at 150^0C for 12 hours in a closed furnace and thereafter cooled in a desiccator.

Clean-up of PAHs

Preparation of the glass column was done by placing a small bunch of glass wool at the bottom of the column to prevent loss of the silica gel. 5 g of activated silica gel was then added into the column with constant tapping so as to ensure uniform packing as well as exclusion of air. Using a clean Pasteur pipette, the sample was introduced onto the silica gel in the column followed by slight tapping of the column. Elution of PAHs was done by first adding 10 mL of n-hexane to the sample then followed by 20 mL of DCM. The eluate was collected in a clean glass vial. The PAH-containing fraction was then reduced under a gentle stream of nitrogen gas to a final volume of 1 mL and quantitatively transferred into GC mini vial. 50 µL of an internal standard (terphenyl) was added to the extract. Analysis was performed by GC/MS. Where the extracts were not analysed immediately, they were stored in a freezer at -20^0C.

Clean-up of PCBs and OCPs

The modified activated silica gel used for the clean-up of PCBs and OCPs was prepared by mixing 33 mL of concentrated sulphuric acid (> 98%) with 50 g of the freshly prepared activated silica gel. Thorough homogenisation of the mixture was ensured before column packing effected in a similar manner as for PAH clean-up, albeit with small changes (Figure 4.2). To prevent direct contact between the modified silica gel and the cotton wool, about 1 g of unmodified activated silica gel was overlaid on the cotton wool, followed by addition of about 5 g of the sulphuric acid-modified activated silica gel. Finally, another 1 g thick layer of unmodified activated silica gel was added. Gentle, but constant tapping of the column was done during the process to ensure proper packing of the sorbent as well as expelling air from the gel.

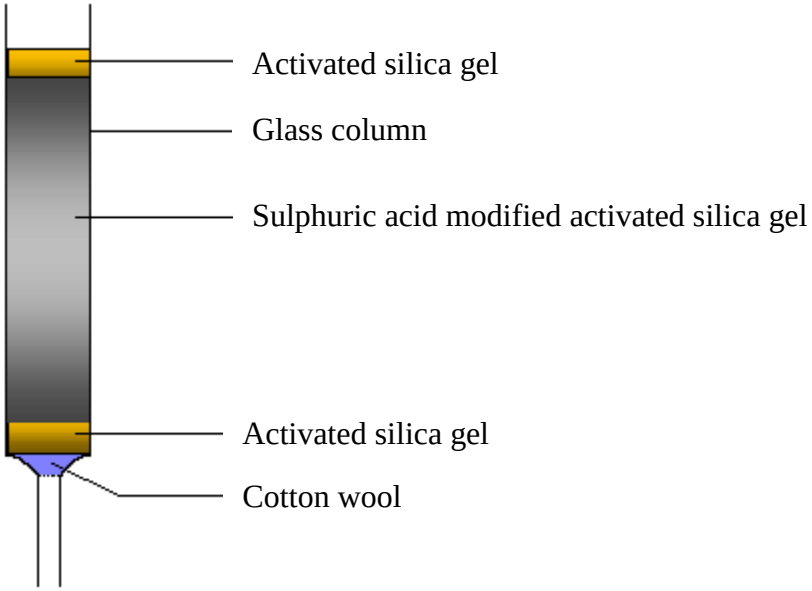


Figure 4.2: Column chromatography set-up used for PCB and OCP clean-up.

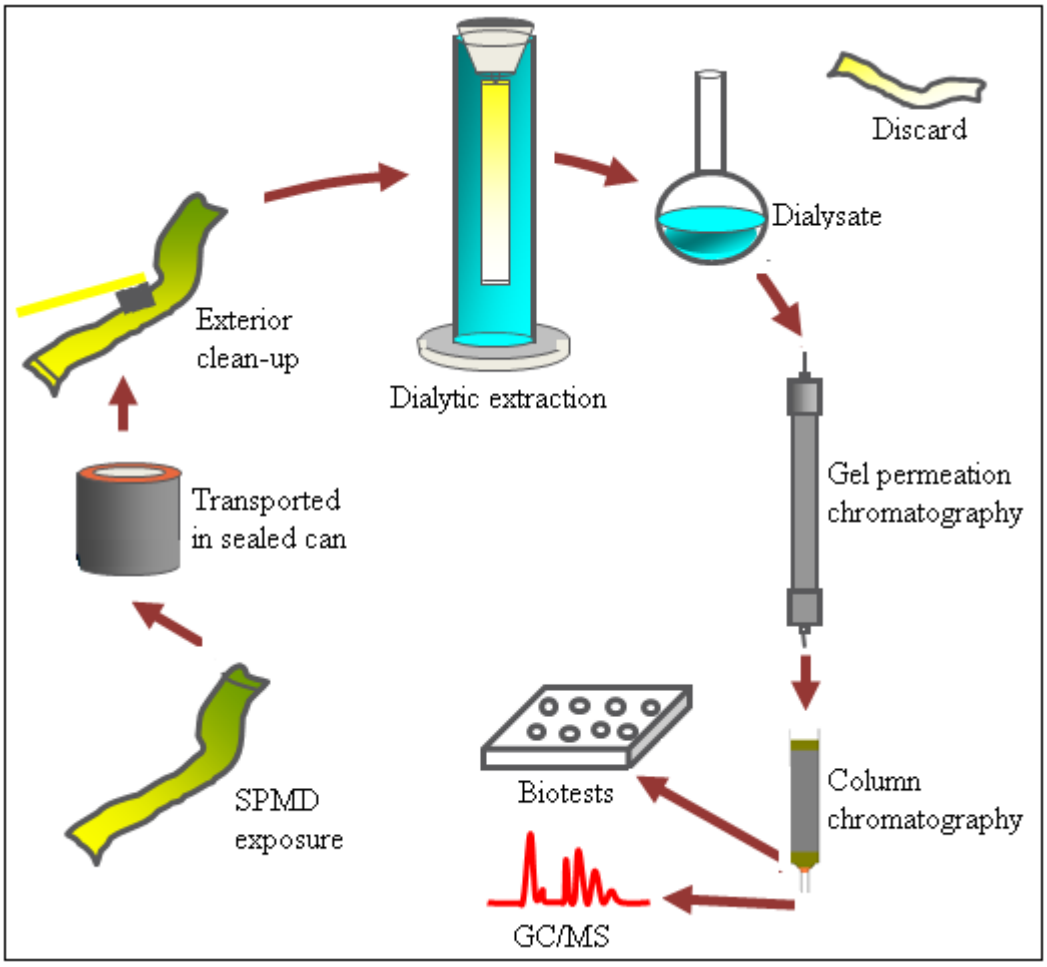


Figure 4.3: Schematic diagram showing steps followed in processing SPMDs

A summary of all the steps followed in processing SPMDs is presented schematically in Figure 4.3.

The PCB/OCP fractions obtained from GPC clean-up were then loaded into the column and eluted with 30 mL DCM. Reduction of the PCB/OCP-containing eluate to 1 mL was achieved using a gentle stream of nitrogen gas. Internal standard (PCB 121) was then added to the reduced eluate and subsequently, instrumental analysis by GC/MS/MS followed.

4.1.7 Instrumentation

The PAHs of interest were analysed using a 6890 GC system coupled with a 5971 mass selective detector (MSD) (Agilent technologies). Chromatographic separation of the components was done using a DB5-MS capillary column (30 m x 0.25 mm internal diameter, 0.25 µm film thickness) with a non-polar stationary phase and helium was used as the carrier gas flowing at 1.5 mL min^{-1}.

Conditions: Injector 250^0C; column 70^0C (0.5 min) - 25^0C/min - 150^0C - 3^0C/min - 200^0C - 8^0C/min -2800C (20 min). Detection of the separated PAHs was achieved using a MSD operated in selected ion monitoring mode with the electron impact ionisation auto-set at 70eV. The temperatures of the ion source, transfer line and the quadrupole were held at 230^0C, 280^0C and 150^0C respectively. Quantitation of the residues was accomplished using a seven-point standard calibration curve.

GC-MS/MS was used for indicator PCBs and OCPs analysis. 6890N GC (Agilent, USA) equipped with a 60m x 0.25mm x 0.25um DB5-MS column (Agilent J&W, USA) coupled to Quattro Micro GC/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). The GC method used in the analysis of PCBs and OCPs was optimised in the laboratory in order to get the best separation conditions.

4.1.8 Quality control

Fabrication controls and field blanks were used to account for contamination of the SPMDs during device construction and during sampler deployment and retrieval from the sampling site. Vapour-phase contamination during deployment of the SPMDs was factored in by the field blanks. These blanks were subjected to identical process treatment as the deployed devices (as described in 4.1.5).

4.2 Determination of naproxen, ibuprofen, and triclosan in wastewater using the polar organic chemical integrated sampler

4.2.1 Chemicals and reagents

Naproxen and ibuprofen (all > 98% pure), were purchased from Sigma Aldrich Chermie GmbH (Steinheim, Germany). Triclosan (> 97% pure) was sourced from Merck (Darmstadt, Germany). HPLC-grade methanol (MeOH) and acetonitrile (ACN) were purchased from Sigma Aldrich (Johannesburg, South Africa) and B& J brand (Honeywell, Germany). Formic acid, citric acid and disodium hydrogen phosphate (all > 97% pure) were obtained from Sigma Aldrich (Johannesburg, South Africa). PES membranes and Oasis HLB sorbent were purchased from Waters Corporation (Milford, MA, USA). Standard POCIS steel rings were fabricated at the Mechanical Engineering workshop (University of the Witwatersrand, South Africa). Deionised water was obtained using a Millipore Simplicity 185 system (Millipore, Bedford, MA, USA). All other reagents used were of the highest analytical grade.

Stock solutions were prepared in ACN at a concentration of 1000 mg L^{-1} for each of the compounds: naproxen, ibuprofen and triclosan. Working solutions (standards and calibration solutions) were prepared from the stock solutions in ACN and used in the development and validation of the analytical methods. In all cases, the stock solutions were stored at 4^0C for a maximum of one month, while the working standards were stored under similar conditions for a maximum of one week. After the expiry of such periods, new batches of stock solutions and working solutions were prepared.

4.2.2 Fabrication of POCIS

4.2.2.1 Cleaning of the adsorbent

5 g of HLB sorbent was weighed in a clean beaker and washed with 20 mL of dichloromethane (DCM) for 5 minutes in an ultrasonic bath (Transsonic 460, Elma, Singen, Germany) and then with 20 mL of HPLC-grade methanol (MeOH) for another 5 minutes. The clean sorbent was then transferred into a 100 mL round-bottom flask and excess solvent removed using a rotary evaporator (Heidolph Laborata 4000, Germany) set at a rotation speed and temperature of 120 r.p.m. and 50°C, respectively. The temperature was subsequently lowered (≤ 40°C) as the amount of the solvent remaining in the sorbent decreased. This was followed by drying of the sorbent in an oven at about 60°C for 3 hours. Complete drying was ensured by weighing a small portion of it after every round of drying. If not used immediately, the clean, dry sorbent was stored at 4°C for up to 4 weeks awaiting assembly of POCIS.

4.2.2.2 POCIS assembly

Stainless steel rings, bolts and screws, a 90 mm diameter PES membrane and 200 mg OASIS HLB sorbent were required to assemble the POCIS. 200 mg of the sorbent was weighed onto the PES membrane using a Precisa 180A (Dietikon, Switzerland) electronic weighing balance. The sorbent was carefully covered

using another PES membrane and both sandwiched between two stainless steel compression rings to safeguard against sorbent losses. Bolts and screws were used to tighten the rings. Prepared POCIS devices were eventually kept in the fridge at 4^0C until deployment.

4.2.3 Deployment of samplers

Items required during sampler deployment included sampler holders, transport containers, blunt tweezers, an aluminium foil sheet, ultra pure water, PE ropes, anchor, pH meter, thermometer, conductivity meter and rubber gloves. All listed materials were prepared prior to sampling. Once at the sample site, the field controls were unpacked and placed on a a piece of aluminium foil at a secure place so as to shield them from the elements of weather such as wind and sunlight. The time was registered. Samplers to be deployed were removed from their transport container and mounted to the deployment cage made of stainless steel. Each deployment device had triplicate samplers. The deployment device was then quickly immersed into the wastewater effluent at a depth of between 1 to 1.5 m and anchored using a PE rope in order to keep it at the required position. Finally, the field controls were packed, time registered and transportation of the devices to the laboratory followed. The field controls were stored in the fridge at 4^0C awaiting retrieval and eventual processing of the deployed POCIS.

4.2.4 Sample sites

Sampling for naproxen, ibuprofen and triclosan in wastewater was done at two

sample sites namely the Goudkoppies and Northern works WWTPs. Figure 4.4 shows a map of the two sampling sites, while Figure 4.5 shows some pictures of these sites.

4.2.4.1 Goudkoppies WWTP

Goudkoppies WWTP is located in Marshalltown, about 15 km south of Johannesburg city central business district (CBD). It treats domestic, industrial and hospital effluent discharged from Johannesburg CBD and the residential areas situated to the south east of the city. Sewage discharges emanating from clinic and hospital facilities found in the south of the city, for instance, the Baragwanath hospital, also end up in the facility. Treated effluent from the Goudkoppies WWTP is eventually discharged into the Klip River via a small stream bordering the plant.

The facility was commissioned in 1978 and is routinely treating between 120 and 150 million litres per day. It also produces about 15,804 tons of dry sludge per year. The plant consists of a new head of works with screening, degritting, primary sedimentation, raw sludge thickening/acid fermentation, flow balancing, activated sludge incorporating the five stage phoredox process, final clarification, chlorination, waste sludge thickening, digestion, dewatering and solar drying of sludge (Johannesburg Water, 2012). Interested farmers collect the dried sludge and utilize them on their privately owned farmlands.

2.2.4.2 Northern Works Treatment Plant

Northern Wastewater Treatment Works is the biggest WWTP in Johannesburg and also one of the largest in the country. The treatment plant located at Diepsloot, about 38 km north of Johannesburg CBD, was designed to handle up to 360 million litres of raw effluent per day and incorporates a 90 dry tonne per day composting unit as well. However the average flows treated daily stands at 323 million litres and 28,392 tons of dry sludge is produced annually by the plant.

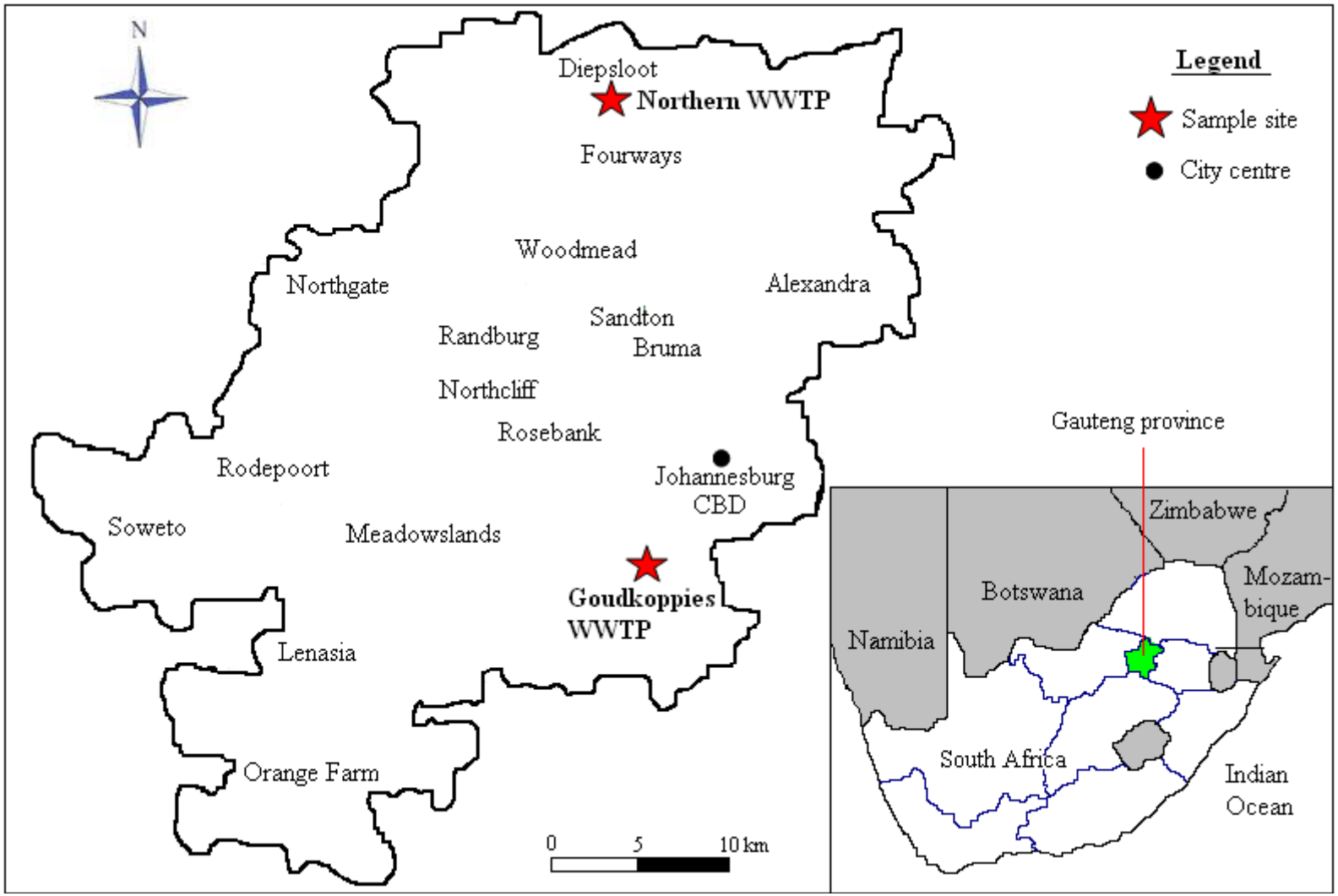


Figure 4.4: Map of Gauteng Province, South Africa indicating locations of Goudkoppies and Northern WWTPs



Figure 4.5: Pictures of the sampling sites

The treatment works mainly collects and treats household sewage from many residential areas including those situated in the northern parts of Johannesburg, Alexandra, Sandton, Randburg, Bedfordview and portions of Edenvale and Germiston. Treated effluent is ultimately discharged into the Juskei River.

The facility consists of four units that in total perform the following activities: Degritting, lime addition, primary sedimentation, primary and secondary biological filtration, primary humus removal, acid fermentation of raw sludge, flow balancing, activated sludge bioreacting, chlorination, sludge thickening, dewatering and composting (Johannesburg water, 2012). Additionally, in unit 4, about 30 million litres of the treated effluent is supplied as cooling water to the Kelvin Power Station each day. Moreover, raw sludge from this unit is thickened and fermented in dedicated thickeners to produce volatile fatty acids (VFA) (Johannesburg water, 2012).

4.2.5 Retrieval of samplers

The field controls were unpacked and placed on a firm aluminium foil sheet on a secure place and the time registered. This was followed by retrieving the sampler deployment device from the wastewater. The cable ties holding the POCIS to the deployment device were severed and biofouling infestation on the samplers wiped off as much as possible. The POCIS were then placed in air-tight, clean metal cans before closing the lids firmly and putting them in the appropriate transport container. Finally, the field controls were packed, the time registered and the samplers transported to the laboratory. Storage was done under freezing temperatures until processing time.

4.2.6 POCIS disassembly

Once in the laboratory, each POCIS was carefully opened and the sorbent washed off from the membrane with a small volume of ultrapure water using a Pasteur pipette into a 3 mL empty, pre-weighed SPE cartridge with a polyethylene frit at

the bottom. The transferred sorbent was packed in the cartridge under vacuum using a Visiprep SPE Manifold. To guard against losses, another PE frit was placed on top of the sorbent. Drying of the sorbent was done under mild vacuum for 30 minutes and the weight of each SPE cartridge containing the dried sorbent recorded. To ensure complete dryness, changes in weight after additional drying of the sorbent were monitored until a constant weight was achieved. Thereafter, the cartridges were kept at 4°C in the fridge awaiting elution.

4.2.7 Elution of analytes from adsorbent

After adding recovery standards, analytes were eluted with two 3-mL volumes of eluent: firstly 100% Acetonitrile (ACN) followed by ACN:MeOH, 50:50 (v/v). Sample dilution was performed where necessary and internal standards added before reducing the solvent under a stream of nitrogen to the last drop. Injection solvent was added to the extract to make up 1 mL sample. Samples were finally transferred into a 2-mL GC-vial and stored at 4^0C awaiting instrumental analysis.

4.2.8 POCIS calibration

In this study, the calibration process was determined according to the methods developed by Macleod et al. (2007) and Li et al. (2010). Modifications of certain aspects of the method were made during optimisation process.

Information on the decrease in analyte concentration in the bulk solution (C_w) over time is used to determine the sampling rate, R_s, as shown in the following equations.

$$C_w(t) = C_w(0)\exp[-(k_U + k_D)t] = C_w(0)\exp[-kt] \quad 4.1$$

Where k_U and k_D are uptake and dissipation rate constants, respectively (L d^{-1}) and

$C_w(0)$ and $C_w(t)$ are the initial water concentration (time = 0) and concentrations at time t (time = t), respectively (μg L^{-1}).

Equation 4.2 arises from the rearrangement of equation 4.1:

$$\text{Ln}[C_w(t)/C_w(0)] = -kt \qquad 4.2$$

From the above equations, the sampling rate, R_s, can thus, be determined as follows:

$$R_s = k_U V_T \qquad 4.3$$

Where V_T is the total volume of the bulk water being extracted.

When (Ln[$C_w(t)/C_w(0)$]) is plotted against exposure time, its slope gives a close estimate of the *k* value. The corrected uptake rate constant for the target compound can be obtained by subtracting the dissipation rate constant from the average rate constant, *k*.

The experimental set-up involved static exposure of POCIS to the target compounds for a given period of time. Initially, a mixture containing 15 μg of each compound (naproxen, ibuprofen and triclosan) was constituted in about 2 mL acetonitrile solvent and transferred to the bottom of a pre-cleaned 3 L capacity beaker. The solvent was allowed to evaporate completely before 3 litres of milli-Q water was added to the beaker and left to equilibrate for about one and a half hours. The resulting solution gave a nominal concentration of 5 μg L^{-1} of each compound. After equilibration was achieved, the solution was vigorously stirred briefly before sampling 20 mL of the water and to be used for determining of the initial analyte concentrations. Extraction of the analytes in the water sample was subsequently done using SPE technique as described in the next section.

Prior to introducing the POCIS into the solution, the samplers were initially soaked in milli-Q water for about 12 hours. This action was aimed at reducing the reported possibility of sudden increase in flux across the membrane during the wetting stage at the beginning of the experiment (Mazzella et al., 2007; Alvarez, 1999). Thereafter, a single POCIS configuration was vertically suspended in the solution for the required period. All experiments were carried out in triplicates at an average temperature of 25^0C. Studies were also conducted under both stirred and quiescent conditions to investigate the influence of turbulence on uptake of analytes.

Under stirred conditions, agitation of the analyte-fortified solution was achieved using a C-MAG HS 10 magnetic stirrer (Staufen, Germany) at a stirring speed set to approximately 400 rpm. In order to prevent the development of a concentration gradient in the vessel in the quiescent experimental set-up, the solution was slowly agitated at the bare minimum speed (60 rpm) of the magnetic stirrer.

The POCIS devices were exposed to the analyte solution for 7 and 14 days. Similar experiments were conducted for 7 and 14 days using solutions with analyte nominal concentrations of 10 μg L^{-1}. All vessels containing the analyte solution were covered with aluminium foil in order to reduce exposure to light and to minimise losses arising from volatilisation.

20 mL aliquots of the bulk solution were excised from the beaker after every 24 hours to monitor the decrease in water concentration over time. The water extract was then processed using the SPE method as described in the 4.2.6. Ultimately, analysis of the SPE extracts was done using HPLC-UV and HPLC-Fl as described in section 4.2.7. Since dissipation of target compounds in the positive blanks was not evident in this study, k_U was assumed to be equal to k. The sampling rates, Rs, for individual compounds were then calculated using the k_U value obtained and the volume of the water (3 L) used, as shown in equation 4.3.

Positive control experiments i.e. those containing only fortified water without the

POCIS, were carried out in order to account for possible analyte degradation, sorption or volatilisation processes during exposure. In addition, negative control experiments in which the POCIS was exposed to milli-Q water devoid of the analytes aimed at checking for analyte contamination were done. All experiments ran concurrently. The quality fit for the regressions was characterised by the correlation coefficient, and consistency was evaluated based on the standard deviations of the k_U values from triplicate experiments. The paired t-tests were applied in statistical comparisons and were considered significant at $p < 0.05$.

4.2.9 Solid phase extraction (SPE)

Analytes of interest in spiked water and wastewater samples were extracted by SPE based on the methods used by Li et al. (2010), albeit, with a number of in-house optimisations. The 20 ml aliquots from the laboratory experiments and 500 mL aliquots each of influent and effluent grab samples from the WWTPs were extracted by solid phase extraction (SPE). Initially, wastewater samples were passed through 1.0 μm mesh size pre-cleaned glass fibre filters that had previously been cleaned with dichloromethane by soxhlet extraction. Oasis HLB cartridges were conditioned basing on the methods by Sagrista (2012) but with some modifications. 3 mL of ethyl acetate, 3 mL acetonitrile (ACN), and 3 mL of milli-Q water were passed through the cartridge sequentially ensuring that the cartridge did not dry out between any loadings. The pH of the laboratory-derived water samples and wastewater samples were adjusted to pH 4 using 1 M sulphuric acid solution. With the aid of a vacuum pump (Gilson, Williers Le Bel, France), 500 mL of the field samples were then passed through the cartridge at about 3 mL min^{-1}. Washing of the loaded cartridge was done using 3 mL of ACN:H_2O (5:95, v/v) followed by 3 mL of n-hexane at a flow rate of 1 mL min^{-1}. After washing, the cartridges were dried under mild vacuum conditions for 20 minutes. The cartridges were then eluted sequentially with 3 mL ACN and then 1 x 3 mL of 2% formic acid in ACN. Finally, the extracts were evaporated to dryness and then reconstituted in 0.5 mL ACN. Procedural blanks were extracted concurrently with the water and wastewater samples.

4.2.10 Instrumentation

Analysis of the compounds was done using a Metrohm Bischoff AG HPLC system (Herisau, Switzerland) and a Waters 530 (LA, California, USA) HPLC system equipped with UV-Vis and Fl detectors, respectively. Separation was achieved using a Phenomenex C_{18} reversed-phase column (Supelco, Bellefonte, PA, USA) with the dimensions: 250 mm x 4 mm, 5 µm i.d. The photochemical behaviours of the compounds were investigated in isocratic mode at a flow rate of 0.8 mL min^{-1} with the mobile phase composing ACN:H_2O (0.2% Formic acid), 70:30 v/v. The mobile phase was degassed offline using a Transsonic 460 ultrasonic bath (Elma, Singen, Germany) for 15 minutes and the injection volume set at 20 µL.

Detection for naproxen and ibuprofen was achieved using a RF-10xL fluorescence detector (Shimadzu Corporation, Japan) with the excitation/emission wavelengths set at 333/540 (Naproxen) and 220/400 (Ibuprofen), while triclosan was detected using a Bischoff Lambda 1010 UV-Vis detector (Leonberg, Germany) at an optimum wavelength of 280 nm.

4.2.11 Quality control

Fabrication blanks

200 mg of clean sorbents were transferred into 3 mL empty SPE tubes and secured with PE frits. Three replicates of these were prepared and used as blank laboratory controls. The cartridges were stored at 4°C until the simultaneous elution and analysis with the POCIS extracts.

Field blank

Another triplicate set of POCIS, each with 200 mg of clean sorbent, were prepared and used as field controls. These controls were transported to the sample

site and brought back to the lab after brief exposure to atmospheric conditions at the sampling site. Once in the lab, they were kept at 4°C until the simultaneous elution and analysis with the extracts of the deployed POCIS. The entire process of preparing, deploying and processing POCIS is presented schematically in figure 4.6.

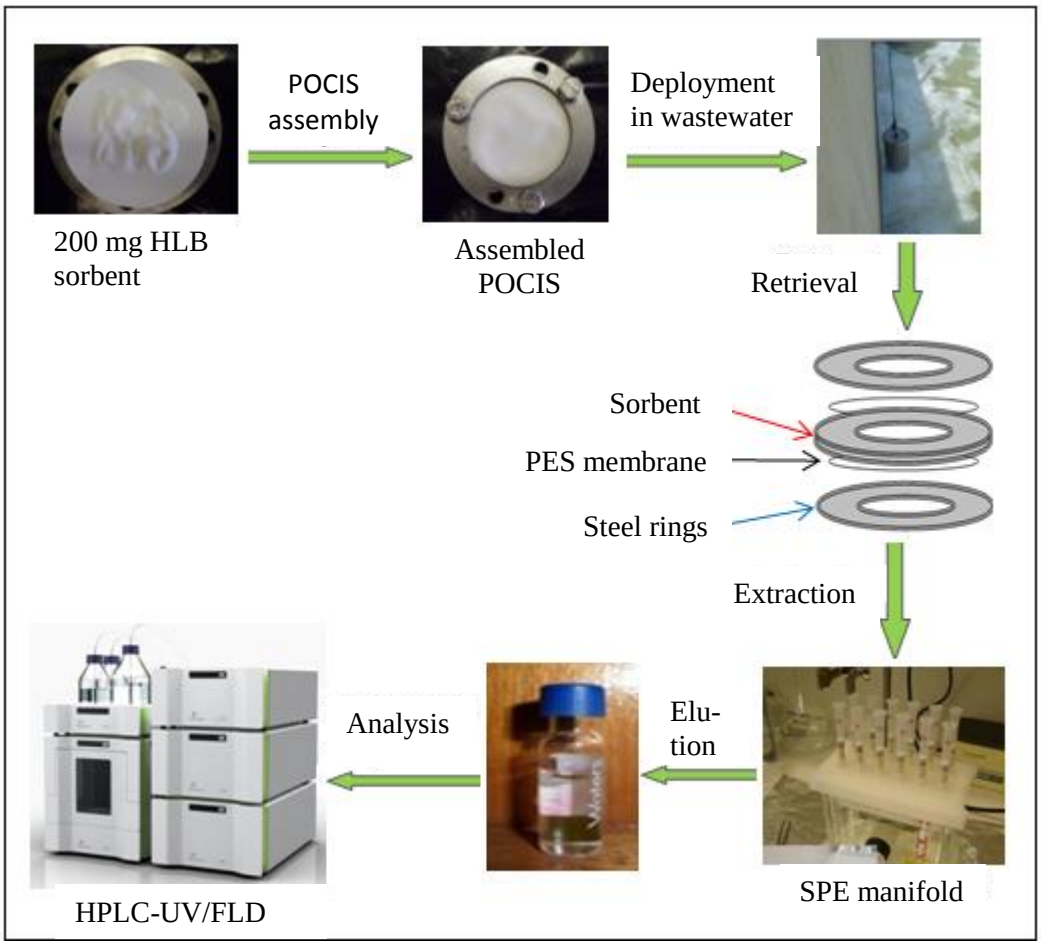


Figure 4.6: A summarised schematic diagram showing the assembly, deployment and processing of POCIS

4.3 Hollow fibre assisted extraction method

4.3.1 Chemicals and reagents

The standards of the following compounds: naproxen (> 98%), ibuprofen (> 98% pure) and triclosan (> 97%) were purchased from the suppliers described in 4.2.1. Acetone, MeOH (> 99.9%), ACN (> 99.9%) and disodium hydrogen phosphate

were bought from Sigma Aldrich (Steinheim, Germany). Sulphuric acid (99%), hydrochloric acid and formic acid were sourced from Fluka (Buchs, Switzerland. Dihexyl ether (> 99%) was purchased from Sigma Aldrich (Steinheim, Germany). Deionised water was obtained using a Millipore Simplicity 185 system (Millipore, Bedford, MA, USA). All other reagents used were of the highest analytical grade.

Stock solutions of all the three PPCPs naproxen, ibuprofen and triclosan were prepared in ACN at 1000 mg L^{-1} and stored in the refrigerator at 4^0C. Fresh stock solutions were prepared monthly. Working solutions, including calibration standards were prepared in ACN from the stock solutions. Upon preparation, standard solutions were stored at 4^0C and used within one week.

4.3.2 Hollow fibre membranes

Hollow fibres made from silicone rubber used in this study were sourced from Technical Products Inc. (Georgia, USA). Long tubes of the membranes were purchased and later on cut to appropriate sizes so as to give a volume of about 1 mL. Their dimensions are summarised in table 4.3

4.3.3 Chromatographic conditions

Separation of the PPCPs was achieved using a mobile phase made up of 70% ACN and 30% Water at a flow rate of 0.8 mL min^{-1} operated in an isocratic mode. A reversed-phase C_{18} column with dimensions 4.6 mm x 250 mm, 5µm (Supelco, Bellefonte, PA, USA) was used. Analysis of analytes was done using a Waters HPLC 510 system (Waters corp. Milford, USA) operated using Clarity chromatographic software and a Metrohm Bischoff AG HPLC system (Herisau, Switzerland) operated using Peak Simple (version 3.29). Each of the systems was equipped with a Rheodyne Series 7725i manual injector valve with a 20 µL injection loop.

Table 4.3: Summary of the dimensions of silicone rubber used in the study

I.D (cm)	O.D. (cm)	Thickness (cm)	Length (cm)	Surface area (cm^2)	Volume (cm^3)	Pore diameter (μm)
0.1575	0.2413	0.04	51.5	39.0	1.0	0.2

Detection of triclosan was done with a Bischoff Lambda 1010 UV-Vis detector (Leonberg, Germany) set at 280 nm whereas a RF-10xL fluorescence detector (Shimadzu Corporation, Japan) was used for naproxen and ibuprofen. Detector parameters for naproxen and ibuprofen were set at excitation/emission wavelengths of 333/540 and 220/400, respectively.

Quantification of the compounds was done using an external calibration curve. The calibration curve was made from the standards ranging from 0.01 to 0.1 mg L^{-1} (naproxen), 0.05 to 0.5 (ibuprofen) and 0.1 to 5 mg L^{-1} (triclosan). The mobile phase was filtered and degassed offline before use. A 20 μL injection volume was used.

4.3.4 Quantification and quality assurance

Quantification of the PPCP extracts was performed using external calibration curves. Linear calibration curves were obtained in concentration range of 0.01 to 0.1 mg L^{-1} for naproxen, 0.05 to 0.5 mg L^{-1} for ibuprofen and 0.1 to 5 mg L^{-1} for triclosan. Figures 4.7 and 4.8, present the typical calibration curves and standard chromatograms for the PPCPs. Good precision was obtained, as depicted by the linearity constant.

To ensure that good quality results were obtained in any experimental part, several strategies that included replication of experiments (at least three), use of certified reference standards and control blanks, were adopted.

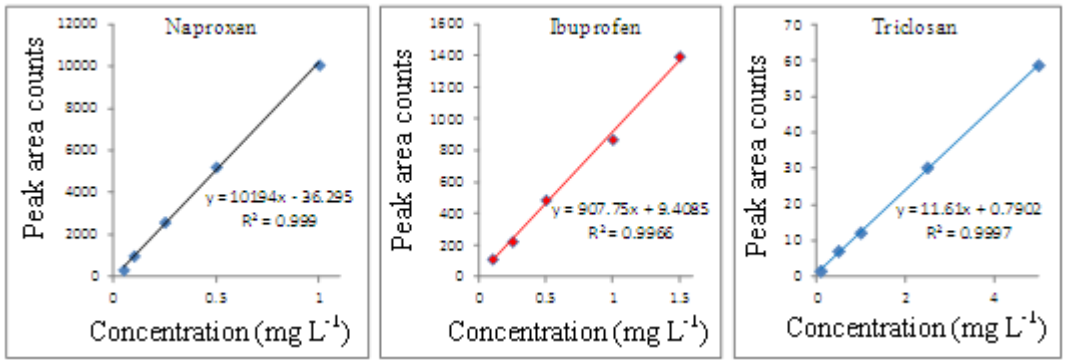


Figure 4.7: Typical calibration curves for naproxen, ibuprofen and triclosan

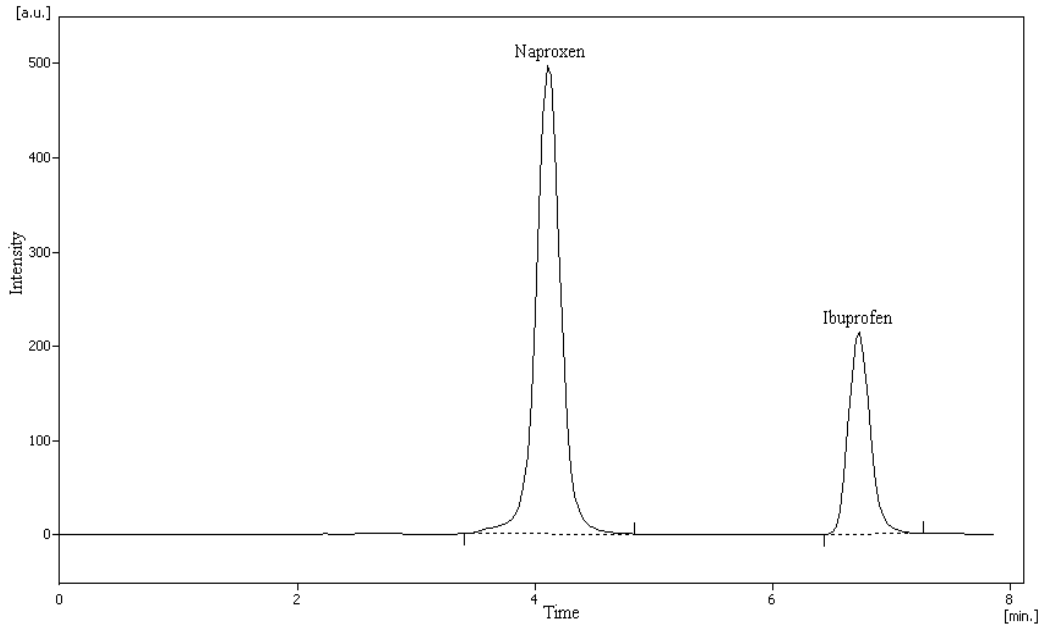


Figure 4.8: Typical chromatograms of 1.0 mg L^{-1} naproxen and ibuprofen standard injection using HPLC-Fl. The chromatographic conditions are described in 4.3.3.

4.3.5: Calibration procedure

4.3.5.1: Hollow fibre preparation

The hollow silicone fibre membranes, measuring about 51.5 cm, were cut off from the roll. The lumens of the membranes, initially soaked in deionised water for 24 hours, were filled with acceptor solution using a 1 mL micropipette. After optimisation, the most suitable acceptor phase for trapping the PPCPs consisted of a 0.25 M disodium hydrogen phosphate buffer (Na_2HPO_4) at pH 11.

The buffer-filled membranes were tied together at both ends in the form of a loop each measuring about 3 cm in diameter (Figure 4.9). This was followed by thoroughly rinsing of their exterior surfaces using deionised water in order to remove any buffer spills. Eventually, the prepared membranes were deployed in the target sample solution under stirred conditions (400 r.p.m.) and left hanging for 24 hours. Figure 4.10 shows the experimental set-up of the membrane assisted extraction system.



Figure 4.9: A prepared hollow silicon fibre membrane

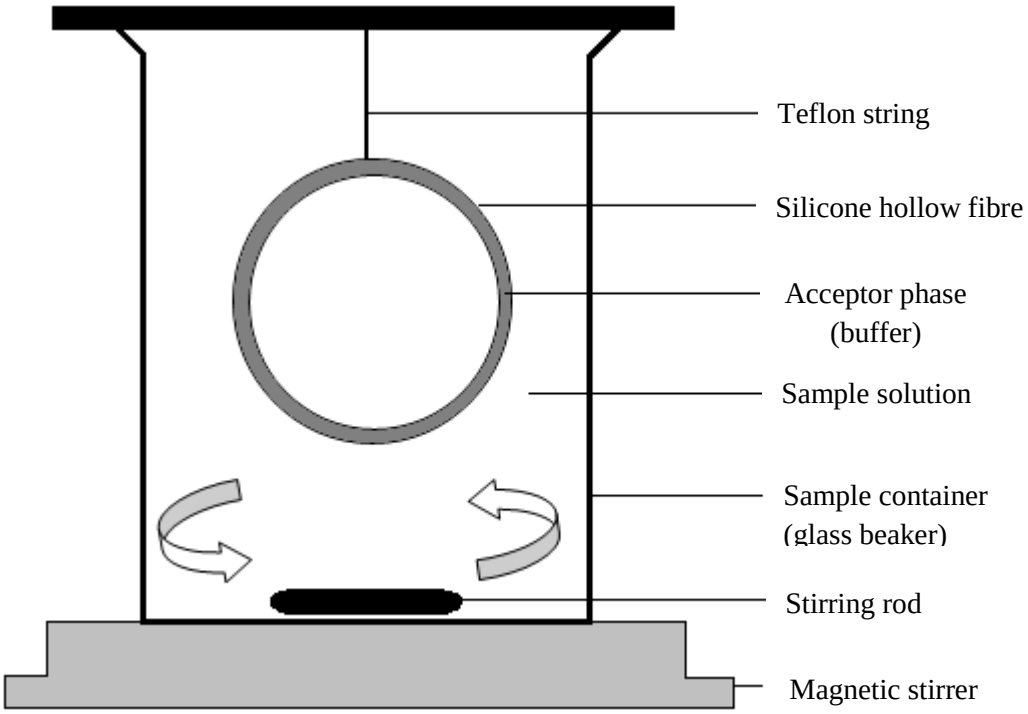


Fig 4.10: Experimental set-up of membrane assisted extraction with silicone hollow fibre

4.3.5.2: Extraction procedure

After the expiry of the exposure period, the membranes were retrieved from the sample vessel and their outer surfaces flushed with deionised water to remove any sample solution. The contents were transferred into 2 mL GC vials, and the pH of the acceptor solution adjusted to between 2 to 3 units using a drop of 1 M hydrochloric acid solution. Instrumental analysis of the extracts followed immediately. However, in cases where it was not possible, extracts were kept refrigerated at 4^0C awaiting analysis. As a quality control measure, unspiked deionised water samples that were used in the preparation of the sample solution were also extracted to check for the presence of the target analytes. Moreover, all experiments described hereafter were performed in three replicates, unless otherwise stated.

4.3.6: Optimisation of the membrane assisted extraction for uptake of PPCPs

Several parameters are known to influence the extraction efficiency of the SLM system as they affect the mass transfer of the compounds and hence, its extraction efficiency (Michel et al., 2009). The influences of some of these parameters on analyte extraction by SLM were investigated as described in the following section.

4.3.6.1 Buffer type

Two buffer types: 0.05 M ammonium carbonate [$(NH4)_2CO_3$] and 0.05 M Na_2HPO_4, were compared for their effectiveness in trapping naproxen, ibuprofen and triclosan. Here, two sets of triplicate hollow fibre membranes were prepared as described previously. Each of the samplers were subsequently immersed in a 0.1 mg L^{-1} solution composing all the three PPCPs and extraction carried out for 24 hours with stirring (450 r.p.m.). Afterwards, the samplers were retrieved, rinsed thoroughly on the outside with de-ionised water and the contents transferred into 2 mL GC vials. Prior to analysis, pH adjustment of the basic

extract was carried out using 1.0 M HCl solution. Finally, Naproxen and Ibuprofen were analysed by HPLC-Fl whereas Triclosan was analysed by HPLC-UV at the conditions described in 4.3.3.

4.3.6.2 Buffer concentration

The performance of Na_2HPO_4 buffer at three concentration ranges: 0.05, 0.25 and 0.5 M with respect to PPCP uptake was compared. After preparing the membranes as described in section 4.3.5.1, one was filled with 0.05 M Na_2HPO_4, while two other membranes were filled with 0.25 and 0.5 M Na_2HPO_4 solutions, respectively. Each of the membranes was then immersed in 3 L of 1 μg L^{-1} PPCP solutions containing all the three target compounds. Exposure of the membranes in the sample solutions took 24 hours under stirred conditions (450 r.p.m.). As stated in section 4.3.5.2, all the experiments were done thrice.

4.3.6.3 Extraction time

The influence of exposure time on the uptake of the acidic ionisable compounds in the sampler was studied by deploying the silicon hollow fibre membranes in spiked solutions containing the analytes of interest for 2, 4, 6, 8 and 24 hours. 3 L of the sample was used with each extraction being carried out in triplicates. Extraction was performed using deionised water spiked with a mixture of the three PPCPs so as to yield a sample solution with a concentration of 1 μg $L^{-1.}$ Two other parallel extractions were done using spiked solutions containing 5 μg L^{-1} and 100 μg L^{-1} of the analytes. Before exposure, hollow fibres were first soaked in deionised water overnight and then filled with 1 mL 0.25 M Na_2HPO_4 buffer (pH 11). Agitation of the solutions was effected using a magnetic stirrer at a speed of 450 r.p.m.

4.3.6.4 Use of dihexyl ether (DHE) as an organic membrane

In a three phase supported liquid membrane extraction, an organic solvent is usually immobilised in the pores of an inert support material separating the

aqueous donor and the acceptor phase (Chimuka, 2001). Agitation of the sample solution as well as long extraction times can decrease the stability of the organic solvent. Therefore, the influence of using DHE solvent on uptake of naproxen, ibuprofen and triclosan was investigated. The hollow fibre membranes were prepared in a similar fashion as described earlier, except that instead of soaking them overnight in deionised water, they were impregnated with DHE by using a 1 mL micropipette. Excess solvent was removed by immersing the fibres in deionised water. The hollow fibres were filled with 1 mL Na_2HPO_4, tied at both ends, looped, immersed in the sample (0.1 mg L^{-1} PPCP mixture) for 24 hours magnetic stirring (400 r.p.m). After extraction, the steps described in 4.3.5.2 were followed. For comparison, a parallel experiment in which the fibres were soaked in reagent water overnight instead of DHE was set up to run concurrently.

4.3.6.5 Donor and acceptor phase pH

Ideally, for extraction to occur, all the analytes of interest should diffuse into the membrane from donor solution and eventually into the acceptor phase. The pH of the sample should therefore be adjusted accordingly, depending on the pKa of the target compounds. Likewise, complete stripping by ionisation of the analyte into the acceptor phase is critical. Therefore, the acceptor phase is kept at a pH that encourages complete ionisation of the target compounds in order to avoid their re-extraction into the donor phase.

In this study, extraction of analytes was compared when the donor phase was kept at pH 2 and pH 4. To achieve this, adjustment of the pH was done by adding a few drops of 1 M HCl to the sample solution. The pH influence on the acceptor phase was also studied using two pHs: 9 and 11, with 0.25 M Na_2HPO_4 as the buffer solution.

4.3.6.6 Agitation of donor phase

Agitation of the sample solution is expected to improve extraction of analytes by

increasing their mass transfer through the membrane. In this work, a comparison was made between an extraction set-up in which the sample was stirred at 400 r.p.m. for 24 hours and another one in which the sample was kept static for the same exposure period. In both cases, the donor phase pH was maintained at pH 4 and the acceptor phase consisted of 0.25 M Na_2HPO_4 solution (pH 11).

4.3.6.7 Temperature

Changes in temperature of the donor phase can influence the uptake of compounds in an SLM system. In the current study, temperature influence was investigated by carrying out experiments at 298 K, 313 K and 333 K with the single hollow fibres. The appropriate temperature of the sample solution was ensured using a water bath. Preceding the permeation studies, the donor phase was kept in the water bath for 2 hours to allow for temperature equilibration.

A hollow fibre was filled with 1 mL of the acceptor phase (0.25 M Na_2HPO_4), as previously described, and subsequently immersed in the sample solution (pH 4) maintained at 298 K in a water bath. Because of its small size and volume (in comparison to the donor solution) temperature equilibration of the fibres was not deemed necessary as temperature changes associated with its immersion in the sample solution were assumed to be negligible. At this temperature, extraction of analytes was done in four parallel set-ups for 2, 4, 6 and 8 hours under stirred conditions (400 r.p.m.). At the end of each exposure period, a hollow fibre was retrieved from the sample solution and processed as described in section 4.3.5.2. Similar protocols were followed in extractions where the bulk donor solutions were kept at 313 and 333K, respectively.

4.3.7: Application to monitoring wastewater

Samples were collected from two different sewage treatment installations: Goudkoppies and Northern WWTPs. Both of them are located within Johannesburg metropolis. Because these same sample sites were used for

monitoring similar compounds using POCIS, their complete descriptions are given in section 4.2.4. Treated effluent and raw influent were analysed for the three PPCPs using the developed sample preparation method based on hollow fibre membrane. 3 L grab samples were taken from both the influent and effluent wastewater and quickly transported to the laboratory in brown bottles. In most cases, extraction of the analytes was commenced immediately the samples arrived in the laboratory. However, in instances where it was not possible, the samples were refrigerated at 4^0C awaiting extraction. Storage of such samples rarely exceeded one week. 3 L of the waste water samples were acidified to pH 4 and extracted and processed for naproxen, ibuprofen and triclosan as previously described in sections 4.3.5.1 and 4.3.5.2. As was the norm, all analyses were done in triplicates. Instrumental analysis of naproxen and ibuprofen was done using HPLC-Fl and HPLC-UV was used for triclosan as described in 4.3.3. A summary of the entire preparation, extraction and analytical process is schematically shown in Figure 4.1.1.

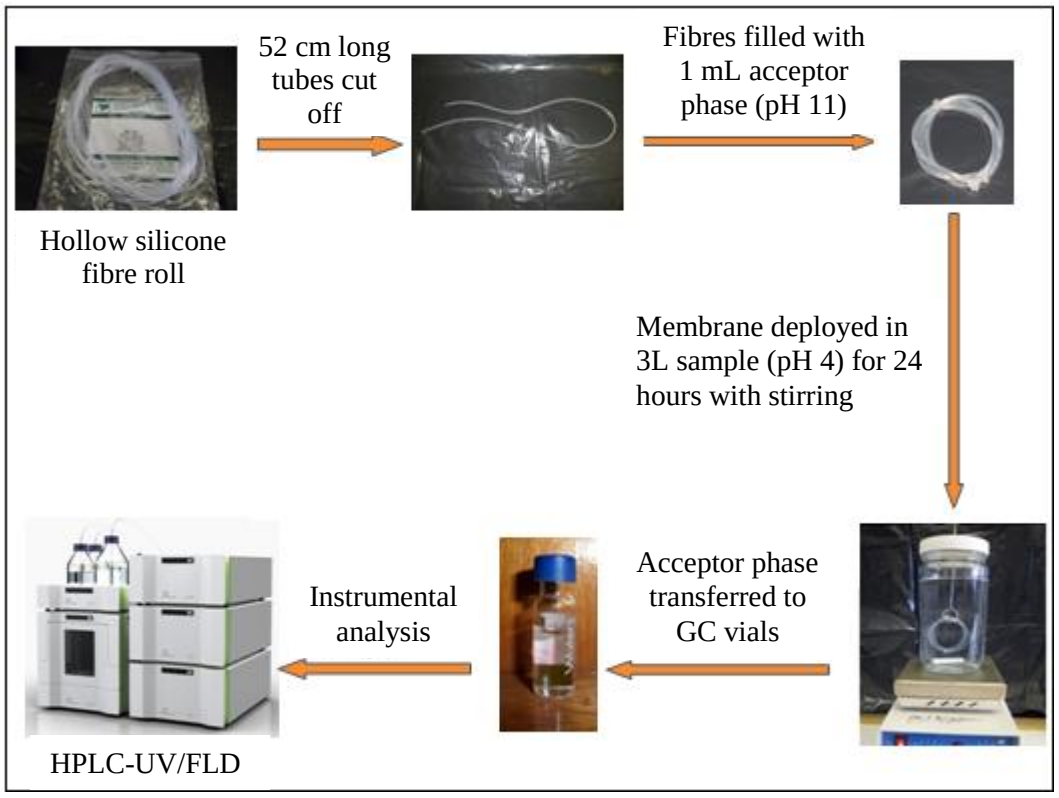


Figure 4.11: A summarised schematic diagram showing the preparation and use of the membrane assisted extraction system

Chapter 5:

Results and discussion

5.0 Results and discussion

5.1 Use of semipermeable membrane devices: Determination of water borne PAHs, PCBs and OCPs in water bodies situated around Johannesburg and Pretoria cities, South Africa.

5.1.1 Occurrence of PAHs, PCBs and OCPs in the SPMDs

Concentrations of the PAHs sequestered by the SPMDs deployed for 14 days at different sampling sites are shown in Table 5.1. Field blank SPMDs were devoid of quantifiable amounts of PAHs, PCBs and OCPs. Prior to the dialytic extraction of the target compounds in the exposed SPMDs, surrogate standards were introduced. Information obtained from their recoveries was used to adjust the concentrations of the analytes. In general, the analytes of interest showed good recoveries that ranged from 55% to 115% for PAHs, 57% to 102% for PCBs and 67% to 115% for OCPs. More details are given in Table A1 (Appendix). Comparable quantities of the analytes were obtained from triplicate SPMDs deployed in the same site. The percent relative standard deviation (%RSD) between such replicates in all sample sites were not greater than 25% for PAHs, except for anthracene at sampling site JR 1 (29%) and benzo[k]fluoranthene at sample site CL (40%). For all PCBs, the RSDs did not exceed 25%. Except for α-HCH obtained from sampling site JR 1 (34%), all OCPs of interest showed a relative percent difference of less than 21% between replicates.

5.1.2 Absolute PAH, PCB and OCP concentrations in SPMDs

5.1.2.1 PAHs

The sites can be ranked from highest to the lowest concentrations of total PAHs (Table 5.1) as follows: HSL, EGL, AUP, CR, IFA, JR 1, CL and JR 2.

Table 5.1: Mean concentrations of PAHs in SPMDs (ng sampler^{-1}) sequestered from different sample sites (n = 3)

Compound	Sampling site							
	IFA	***JR 1***	***JR 2***	***EGL***	***HSL***	***AUP***	***CL***	***CR***
Naphthalene	268 ± 41	247 ± 56	262 ± 16	283 ± 61	389 ± 88	307 ± 26	338 ± 71	148 ± 22
Acenaphthylene	156 ± 30	156 ± 18	158 ± 29	150 ± 12	164 ± 26	197 ± 28	132 ± 11	55 ± 4
Acenaphthene	34 ± 5	38 ± 7	124 ± 6	32 ± 7	38 ± 9	334 ± 6	47 ± 4	74 ± 8
Fluorene	84 ± 15	77 ± 4	355 ± 8	65 ± 11	82 ± 20	71 ± 11	36 ± 8	213 ± 22
Phenanthrene	144 ± 12	246 ± 5	1192 ± 97	132 ± 15	138 ± 18	174 ± 18	1220 ± 98	425 ± 13
Anthracene	308 ± 14	287 ± 83	198 ± 11	102 ± 14	49 ± 10	179 ± 22	121 ± 9	31 ± 5
Fluoranthene	127 ± 10	424 ± 47	999 ± 35	156 ± 37	61 ± 15	83 ± 21	118 ± 3	260 ± 19
Pyrene	96 ± 13	367 ± 38	825 ± 91	115 ± 12	42 ± 5	97 ± 19	279 ± 35	260 ± 22
Benz[a]anthracene	32 ± 8	62 ± 7	119 ± 6	32 ± 2	29 ± 0	31 ± 2	189 ± 14	18 ± 4
Chrysene	44 ± 9	133 ± 18	203 ± 28	46 ± 8	34 ± 4	42 ± 5	11 ± 2	31 ± 4
Benzo[b]fluoranthene	38 ± 3	57 ± 4	86 ± 4	34 ± 1	39 ± 6	36 ± 2	17 ± 4	9 ± 0
Benzo[k]fluoranthene	25 ± 5	62 ± 3	86 ± 17	38 ± 4	37 ± 2	71 ± 5	5 ± 2	5 ± 1
Benzo[a]pyrene	30 ± 4	37 ± 13	55 ± 4	79 ± 12	48 ± 6	ND	11 ± 1	4 ± 1
Indeno[1,2,3-cd]pyrene	38 ± 3	41 ± 2	48 ± 10	38 ± 5	37 ± 3	38 ± 0	4 ± 1	8 ± 0
Dibenz[a,h]anthracene	ND	ND	ND	ND	ND	ND	ND	ND
Benzo[ghi]perylene	40 ± 4	45 ± 3	56 ± 5	36 ± 2	36 ± 5	37 ± 2	18 ± 3	ND
ΣPAHs	**1464 ± 60**	**2279 ± 121**	**4766 ± 147**	**1335 ± 79**	**1223 ± 98**	**1394 ± 57**	**2543 ± 128**	**1541 ± 46**

ND: not detected

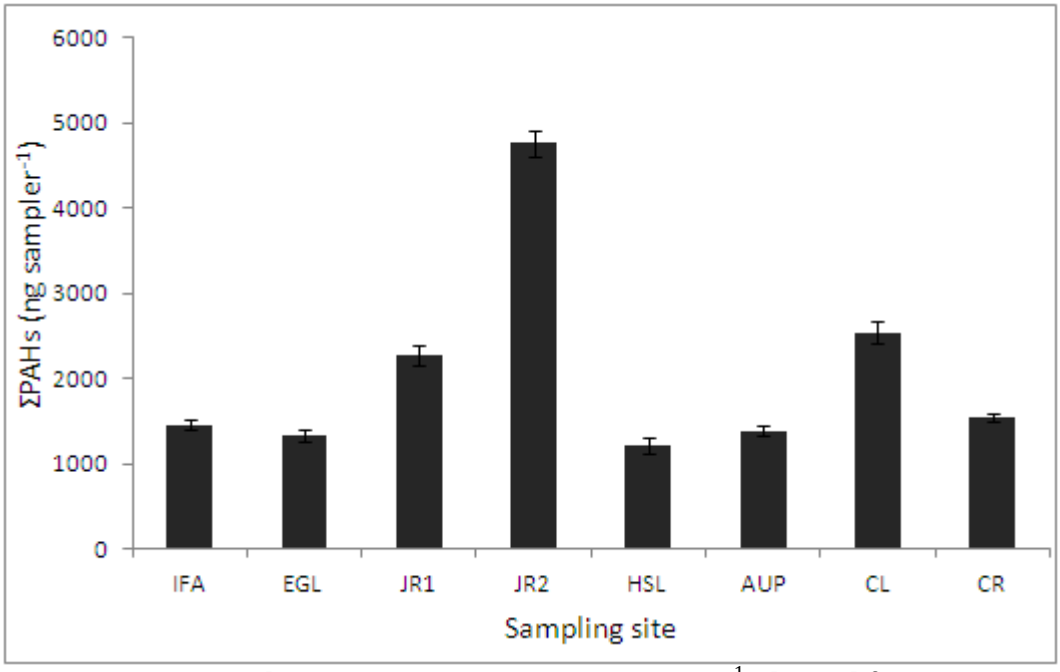


Figure 5.1: Summed up PAH concentrations (ng $SPMD^{-1}$) derived from SPMDs deployed at each of the sampling sites.

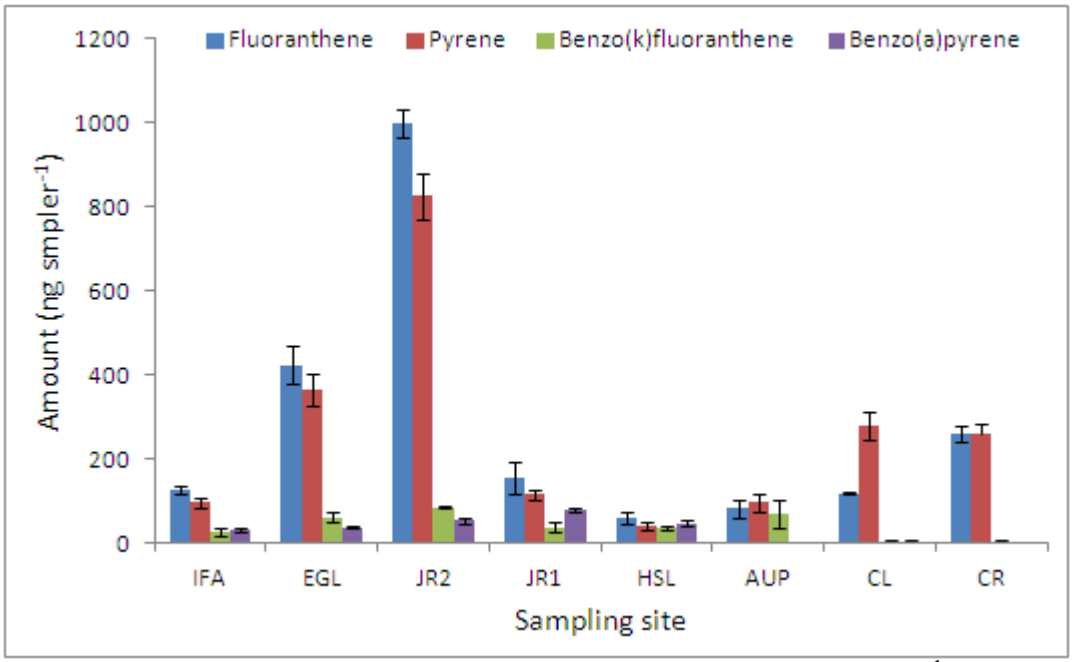


Figure 5.2: Accumulated amounts of some selected PAHs (ng $SPMD^{-1}$) derived from SPMDs deployed at each sampling site.

The average concentrations of individual PAHs (Figure 5.2) at the sampling sites generally followed the same pattern as the totals (Figure 5.1). The most prevalent

PAHs in all the eight sampling sites were naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and Pyrene. The origins of such small molecular weight (Mw) PAHs can be ascribed to combustion and industrial activity (Manoli and Samara, 1999). Among other sources, these PAHs are ubiquitous contaminants found in the runoff from urban and industrialised areas. Their elevated water solubility makes them more available in the water phase than their larger molecular weight counterparts. Many samples indicated that larger molecular weight PAHs such as benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, indeno[1,2,3-cd]Pyrene, dibenz[a,h] anthracene and benzo[g,h,i]perylene were either present at low concentrations or below limits of quantification. These compounds are more hydrophobic and predominantly partitioned to suspended particles and colloids in water column and only a small percentage is available as truly dissolved.

The mean PAH levels sequestered by SPMDs in this study were comparable on the order of magnitude to amounts found in SPMDs deployed in other areas of the world as shown in Table 5.2 (Karacik et al., 2013; Shaw et al., 2004; Vrana et al., 2001).

It was not unexpected that the highest concentration of total PAHs was recorded in SPMDs deployed at site JR 2. This is because the major tributaries of the Juskei River can be traced to the north and north eastern parts of the city of Johannesburg. In addition to extensive human settlement, some of these areas are characterised by major industrial activities. Moreover, the river receives substantial quantities of treated effluent from neighbouring WWTPs. Of significance is the Northern wastewater works that discharges its treated wastewater into the Juskei River, a few kilometres upstream of the sampling site JR 2. Its contribution is evident given that the site JR 1, also located in the same river further upstream from the WWTP's discharge point, showed lower concentrations of total PAHs. It is also worth noting that this WWTP is the biggest in Johannesburg and treats both domestic and industrial sewage originating from the entire northern areas of the city.

Table 5.2: Comparison of PAH concentrations (ng $SPMD^{-1}$) obtained in the current study and those reported in the literature

Compound	Current study (South Africa)	Vrana et al., 2001 (Austria/Slovakia)	Shaw et al., 2004 (Australia)	Karacik et al., 2013 (Turkey)
Naphthalene	148 - 389	117 – 711	ND	< LOD - 34
Acenaphthylene	55 - 197	ND	< LOD - 44	1.15 - 8.6
Acenaphthene	32 - 334	31 – 314	< LOD - 3.1	1.1 - 29.3
Fluorene	36 - 355	90 – 603	< LOD - 17	20.0 - 39.0
Phenanthrene	132 - 1220	227 – 1163	< LOD - 180	47.0 - 135.0
Anthracene	31 - 308	16 – 775	< LOD - 36	1.6 - 41.7
Fluoranthene	61 - 999	155 – 7420	30 - 370	26.1 - 228.0
Pyrene	42 - 825	92 – 8420	7.7 - 720	3.8 - 227.6
Benz[a]anthracene	18 - 189	20 – 1198	< LOD - 110	0.2 – 19.3
Chrysene	11 - 203	< 50 – 2918	1.4 - 200	3.8 - 48.5
Benzo[b]fluoranthene	9 - 86	< 20 – 747	ND	0.3 - 9.3
Benzo[k]fluoranthene	5 - 86	< 5 – 343	<LOD - 230	0.5 - 6.6
Benzo[a]pyrene	ND - 79	< 5 – 470	< LOD - 69	0.1 - 6.1
Indeno[1,2,3-cd]pyrene	4 - 48	< 15 – 21	< LOD - 100	< LOD - 2.5
Dibenz[a,h]anthracene	ND	< 15 – 165	< LOD - 100	< LOD - 2.3
Benzo[ghi]perylene	ND - 56	< 25 – 153	< LOD - 140	< LOD - 0.5
ΣPAHs	**1223 - 4766**	**815 – 25621**	**39.1 - 2319.1**	**106.6 - 787.8**

<LOD: below detection limit

Elevated concentrations of total PAHs were also found in the sampling site CL. This relatively small man-made dam is found in the Centurion area surrounded by several commercial installations and residential areas. The lake is part of the Hennops River whose source can be traced to Kempton Park, east of Johannesburg. This part of the city is home to a coal-powered power plant as well as several industries, shopping centres/malls and residential settlements. The river receives treated effluent emanating from Kempton Park WWTP on its way to Centurion. It is also likely that the water quality at CL is negatively affected by the many commercial and residential activities situated in the Centurion area. This is indicated by the relatively lower amounts of PAHs found at sample site CR (Centurion River) which drains its water to the lake.

In general, total PAH concentrations at all the sampling sites were comparable and none was more than one order of magnitude lower or higher than the concentrations obtained at the other sampling sites. However, the lower amounts sequestered by samplers at HSL may be deceptive with regard to the actual concentrations in the water body. Water sampling rates of PAH by SPMDs is known to be influenced by environmental factors such as turbulence, temperature, and biofouling (Stuer-Lauridsen, 2005; Vrana et al., 2005; Booij et al., 1998). The extent of their influence in all these sample sites was unequal. Unlike most of the other sites, HSL was characterised by very quiescent conditions which may have affected the rate of analyte uptake by the SPMDs.

5.1.2.2 PCBs

On the basis of total PCB residues, ranking of the sampling sites from lowest to highest was as follows: HSL, AUP, IFA, JR 1, EGL, and JR 2. Table 5.3 presents the mean PCB concentrations (ng $SPMD^{-1}$) in samplers deployed in the various sites. The sequestered amounts of PCBs were up to three orders of magnitude lower than PAH values. However, inter-site PCB concentration difference did not exceed one order of magnitude. Their summed up concentrations ranged from 6.5 to 76.1 ng $sampler^{-1}$. These fairly low analyte concentrations are probably a

consequence of the relatively high log K_{ow} values (4.3 to 8.26) of individual PCBs which makes solubility in water very low and in the range of 5.5 x 10^{-6} g g^{-1} to 1.2 g g^{-1} (Mackay, 1991). Hence, the analyte fraction available for SPMD uptake in the water phase is usually extremely small.

PCB levels recorded in the present study were comparable to those detected in an industrial region of Bitterfeld, Germany (Vrana et al., 2001) as well as those obtained from 10 fresh water sites in Amsterdam, Netherlands (Verweij et al., 2004). However, they were evidently lower by up to 4 orders of magnitude than those reported by both, Degger et al. (2011) in some South African marine environments such as Saldanha Bay and Cape Town, and Richardson et al. (2002) in Hong Kong coastal waters. This information is summarised in Table 5.4. Although further information exists on PCBs in soil and sediments (Quinn et al., 2009), breast milk from lactating mothers (Okonkwo et al., 2008) and human blood (Röllin et al., 2009), SPMD-derived data still remain scanty in South African-related literature.

Table 5.3: Mean total concentrations of PCBs in SPMDs (ng $sampler^{-1}$) accumulated by the samplers in the various sites (n = 3)

	Sample site					
Compound	**IFA**	**JR 1**	**JR 2**	**EGL**	**HSL**	**AUP**
PCB 28	34.3±5.5	44.1±7.8	68.1±12	32.0±6.3	5.9±1	3.2±0.2
PCB 52	1.2±0.2	2.3±0.5	2.4±0.4	0.8±0.1	0.3±0.0	2.4±0.1
PCB101	0.6±0.1	1.1±0.3	1.1±0.1	0.3±0.0	0.1±0.0	2.0±0.0
PCB 118	0.2±0.0	0.5±0.1	0.8±0.3	0.2±0.0	ND	ND
PCB 138	0.6±0.0	0.9±0.2	1.3±0.2	0.5±0.1	0.2	3.1±0.1
PCB 153	0.6±0.1	1.2±0.1	1.4±0.2	0.4±0.1	ND	5.1±0.1
PCB 180	0.7±0.1	0.5±0.1	1.0±0.1	0.4±0.0	ND	4.3±0.0
ΣPCBs	**38.2±0.5**	**50.6±0.9**	**76.1±0.6**	**34.6±0.6**	**6.5±0.1**	**20.1±0.2**

ND: not detected

Table 5.4: Comparison of total PCB levels in SPMDs (ng sampler^{-1}) from the current study with some literature values obtained using the same technique

Source	Concentrations (ng SPMD^{-1})	Country	Exposure time (days)
Current study	6.5 to 76.1	South Africa	14
Verweij et al., 2004	2.1 to 40	Netherlands	21
Vrana et al., 2001	< 6.0	Germany	43
Degger et al., 2011	29000 to 158000	South Africa	70
Richardson et al., 2001	43000 to 184000	Hong Kong	28

The elevated analyte concentrations detected at site JR 2 were not entirely unexpected. These compounds are of anthropogenic origin and their presence at higher levels in the sampling site can be linked to heavy industrial activity, urbanisation and human settlement upstream of the river and in the catchment area.

As described earlier, the roots of this river are traceable to Johannesburg city and its surroundings. Surface runoff from the urban areas characterised by heavy human population (more sources of PCBs), may be a contributory factor. As observed in the case of PAHs, treated wastewater input from Northern WWTP may account for the increased contaminant load at site JR 2 relative to site JR 1.

Although sites IFA and EGL were expected to exhibit higher levels of the contaminants than JR 1 and JR 2 (because both Juskei and Hennops Rivers eventually drain into Hartbeespoort dam where IFA and EGL were located), this was not evident. It should be noted that apart from the two rivers, the dam also receives water from other smaller, but potentially, less polluted rivers such as the Megalies and Crocodile (Figure 4.1). These rivers originate from less urbanised environments and mainly pass through agricultural areas. It is postulated that dilution effects of the contaminants due to increased volumes of less polluted water may have happened. Moreover, as the river water flows downstream

towards IFA and EGL, and considering the strong hydrophobicity of the compounds, it is a real possibility that the water phase fraction of the compounds may be lost to particulates and sediments in the river system due to sorptive interactions. It is, however, interesting to note that PCB levels at IFA and EGL were almost similar despite the two sites being over 20 km apart, but in the same water body. This uniformity in contaminant levels suggests that atmospheric deposition may be playing a major role in introducing the compounds to the dam.

Amounts of PCBs sequestered by SPMDs deployed at HSL and AUP were significantly lower than those from all other sampling sites. As mentioned earlier, AUP is a stream situated in close proximity to the airport while HSL (Figure 4.2) is a water reservoir surrounded by large residential establishments but also located a few kilometres from the airport. AUP drains its water to HSL. PCBs are universally banned compounds (UNEP, 2001) and since they are of exclusive industrial origin, their presence in aquatic systems is mainly due to recycling in the environment of what was previously released. Therefore, as observed in the sample sites, history of PCB application in an area (and to a lesser extent, current uses) may be determining concentration levels detectable in the environmental waters. It is also possible that accidental spills and illicit releases of these compounds from, say, leaking transformers and cooling systems in the nearby airport or even from the residential areas may be a contributory factor.

Among the PCB congeners, PCB 28 was the most prevalent in all the sample sites. These elevated levels may be related to the congener's comparatively higher water solubility (log K_{ow} = 5.67) than the others.

5.1.2.3. OCPs

The spatial trends in the summed-up OCP concentrations ranged from a minimum of 4.5 ng sampler^{-1} at site HSL to a maximum of 921.6 ng sampler^{-1} at site JR 2. Average concentrations of individual OCPs as well as their totals are displayed in Table 5.5).

Table 5.5: Mean concentrations of OCPs in SPMDs (ng sampler^{-1}) sequestered from different sample sites (n = 3)

	IFA	JR 1	JR 2	EGL	HSL	AUP
HCHs						
α-HCH	44.4 ± 7.7	120.4 ± 41.1	131.5 ± 25.6	43.2 ± 6.9	0.8 ± 0.2	1.2 ± 0.3
β-HCH	127.9 ± 6.4	626.8 ± 98.2	630.2 ± 82.3	114.1 ± 20.0	0.8 ± 0.1	0.7 ± 0.1
γ-HCH	7.0 ± 1.1	16.5 ± 3.7	13.6 ± 2.2	5.9 ± 1.2	1.4 ± 0.2	1.2 ± 0.2
δ-HCH	2.6 ± 0.4	46.5 ± 4.0	65.9 ± 13.4	2.3 ± 0.0	ND	ND
ε-HCH	6.7 ± 1.3	11.4 ± 1.9	28.8 ± 5.6	7.5 ± 1.3	ND	ND
ΣHCHs	**188.5 ± 10.2**	**821.6 ± 106.6**	**870.0 ± 87.4**	**173.0 ± 21.2**	**3.0 ± 0.3**	**3.1 ± 0.4**
DDTs						
o,p'-DDE	0.7 ± 0.1	0.8 ± 0.2	1.5 ± 0.2	0.6 ± 0.1	0.1 ± 0.0	0.1 ± 0.0
p,p'-DDE	7.6 ± 1.3	8.0 ± 1.6	14.4 ± 2.7	5.5 ± 1.0	0.5 ± 0.1	2.1 ± 0.4
o,p'-DDD	20.3 ± 4.8	3.2 ± 0.5	5.2 ± 0.5	28.6 ± 5.5	0.1 ± 0.0	0.6 ± 0.1
p,p'-DDD	55.8 ± 3.4	17.7 ± 3.0	26.6 ± 1.4	47.2 ± 8.1	0.5 ± 0.0	1.5 ± 0.2
o,p'-DDT	1.5 ± 0.0	3.0 ± 0.7	1.8 ± 0.4	1.8 ± 0.3	0.3 ± 0.0	0.5 ±0.1
p,p'-DDT	0.6 ± 0.1	11.1 ± 2.6	2.1 ± 0.2	0.6 ± 0.0	ND	0.6 ± 0.1
ΣDDTs	**86.5 ± 6.0**	**43.8 ± 4.4**	**51.6 ± 3.1**	**84.3 ± 9.8**	**1.5 ± 0.1**	**5.4 ± 0.5**

ND: not detected

Several HCH isomers were found in the samples and they included α-HCH (0.8 to 131.5 ng sampler^{-1}), β-HCH (0.7 to 630.2 ng sampler^{-1}), γ-HCH (1.2 to 16.5 ng sampler^{-1}), δ-HCH (below detection limit to 65.9 ng sampler^{-1}) and ε-HCH (below detection limit to 28.8 ng sampler^{-1}). On the other hand, the following DDX components were found in the samples: o,p'-DDE (0.1 to 1.5 ng sampler^{-1}), p,p'-DDE (0.5 to 14.4 ng sampler^{-1}), o,p'-DDD (0.1 to 28.6 ng sampler^{-1}), p,p'-DDD (0.5 to 55.8 ng sampler^{-1}), o,p'-DDT (not detected to 3.0 ng sampler^{-1}), p,p'-DDT (not detected to 11.1 ng sampler^{-1}). Trends of individual OCP compounds were generally similar to those of the ΣOCP concentrations.

Ranking of the sampling sites from the lowest to the highest in terms of total OCP residues accumulated by the SPMDs was as follows: HSL, AUP, EGL, IFA, JR 1 and JR 2. This was closely related to the trend witnessed for total PCB concentrations in the samplers. However, ΣOCP levels were 2 to 3 orders of magnitude higher than for PCBs except in sites HSL and AUP where they were comparable. Site JR 2 still yielded the highest amounts of OCPs in the SPMDs, just like for the other studied compounds. The same reasons advanced for the higher PCB concentrations at the site may apply to the OCP levels in the same sampling site. Total OCP amounts in the samplers from the studied areas were generally in agreement with what was reported by Vrana et al. (2001) but higher than those reported by Verweij et al. (2004) and lower than those reported by Röllin et al. (2009) as shown in Table 5.6 below.

Table 5.6: Total amounts of OCPs in SPMDs (ng SPMD^{-1}) from the current study as compared with literature values

	Present study	Verweij et al., 2004	Vrana et al., 2001	Röllin et al., 2009
Country	South Africa	Netherlands	Germany	South Africa
ΣHCHs	3.0 - 870.0	<1.4 - 20	74 - 10440	1.7 - 3181.3
ΣDDTs	1.5 - 86.5	<1.4 - 22	60 - 8097	17.5 - 20424.1
ΣOCPs	**4.5 – 956.5**	**<2.8 - 42**	**134 - 18537**	**19.2 - 23605.4**

5.1.3 Estimation of contaminant water concentration

Dissolved water concentrations of target analytes were calculated from amounts accumulated in SPMDs as described below. 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}:

$$C_w = \frac{N_s}{K_{sw}V_s[1 - \exp(-R_s t/(K_{sw}V_s))]} \qquad 5.1$$

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 non-linear least squares method by Booij and Smedes (2010), considering the fraction *f* of individual PRCs (D_{10}-acenaphthene, D_{10}-fluorene, D_{10}-phenanthrene and D_{10}-pyrene, PCB 30, PCB 185 and d_6-gamma HCH) 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. Deuterated PAHs were used as PRCs for PAHs, PCB 30 and PCB 85 for PCBs and d_6 HCH for HCHs.

$$f = \exp\left(-\frac{R_S t}{K_{SW} V_S}\right) \qquad 5.2$$

Here, $f = N_{PRC}/ N_{0,PRC}$; $N_{0,PRC}$ is the initial amount of the PRC at $t = 0$, N_{PRC} is amount of each PRC remaining after exposure, and *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

Equation 5.3 derived by Rusina et al. (2010) into Equation 5.2.

$$R_S = FAM^{-0.47} \quad 5.3$$

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 nonlinear least squares method for estimating sampling rates. The necessary K_{sw} values were intrapolated from the empirical equation (Huckins et al., 2006) below:

$$\text{Log } K_{sw} = \text{-01618}(\log K_{ow})^2 + 2.321 \log K_{ow} \text{-2.61} \quad 5.4$$

$$\log K_{SPMD} = 1.21 \text{ x } \log K_{ow} - 0.92 \quad 5.5$$

As observed by Booij et al. (2003), there was no significant change in the SPMD-water partition coefficients (K_{sw}) with temperature in the range from 2°C to 30°C. Therefore, there was no need to correct for the effect of temperature in calculating partition coefficients in this study. Site-specific R_s values for all the compounds were derived using equation 5.3, which estimates a slight decrease in R_s with increasing molecular mass. For instance, the R_s values obtained for phenanthrene ranged from as little as 1.0 L d^{-1} at sample site HSL to a high of 24.8 L d^{-1} at site JR 2. R_s values for all the target compounds in the various sites are presented in Tables A3, A4, and A5 (Appendix).

Transfer through the water boundary layer is the rate limiting step for uptake of highly hydrophobic compounds such as PAHs, PCBs and OCPs and as such, R_s values for these compounds depend on the hydrodynamic conditions at the exposure site (Booij et al., 2007). Based on this assumption, different R_s values were obtained at each of the sample sites corresponding to differences in water flow velocities at those water bodies. Mass transfer of analytes may also be affected by other factors such as temperature, biofilm infestation, and deposition of particulates on the SPMD's surface. Table 5.7 describes the sampling campaign and the water conditions during the sampling period.

Table 5.7: Description of the sampling campaign and the sampling sites

Sampling site	Exposure period (days)	Water temperature (^{0}C)	SPMD-sampling rate (L d^{-1})
IFA	14	18	11.4
JR 1	14	20	18.3
JR 2	14	19	26.3
EGL	14	18	8.7
HSL	14	21	1.1
AUP	14	21	18.4
CL	10	18	5.7
CR	10	18	16.6

5.1.4 Water dissolved concentrations of the analytes

The estimated water-borne concentrations of PAHs, PCBs and OCPs are presented and discussed in the following section.

5.1.4.1 PAHs

Estimation of the freely dissolved water concentrations of the PAHs based on the amounts acquired from deployed SPMDs in the various sample sites are presented in Table 5.8. The sample sites can be ranked in ascending order as follows: CR, EGL, JR 1, IFA, AUP, JR 2, CL, and HSL. Summed up analyte concentrations by site ranged from about 33.5 ng L^{-1} at RC to 126.8 ng L^{-1} at HSL. These concentrations were higher than what was reported by Allan and Ranneklev (2011) (0.033-9.3 ng L^{-1}) in Alna river, Oslo, Norway. It is also evident that water phase PAH concentrations of individual compounds (Figure 5.3) generally reflects the trend exhibited by the cumulative concentrations at any given sampling site (Figure 5.4).

Table 5.8: Estimated water dissolved PAH concentrations, C_w, (ng L^{-1}) at the various sample sites

Compound	**IFA**	**JR 1**	**JR 2**	**EGL**	**HSL**	**AUP**	**CL**	**CR**
Naphthalene	37.205	34.705	36.813	38.92	61.185	43.135	47.491	20.795
Acenaphthylene	3.832	3.795	3.828	4.084	13.307	4.777	3.279	1.338
Acenaphthene	1.037	1.154	3.764	0.941	3.194	1.017	1.439	2.247
Fluorene	1.349	1.157	5.280	0.905	6.422	1.063	0.595	3.200
Phenanthrene	1.198	1.699	7.487	0.900	10.465	1.171	11.773	2.942
Anthracene	2.838	1.656	1.306	0.581	3.743	0.918	1.200	0.224
Fluoranthene	0.755	1.938	3.757	0.483	4.753	0.363	0.909	1.194
Pyrene	0.579	1.694	3.152	0.429	3.265	0.427	2.164	1.207
Benz[a]anthracene	0.185	0.276	0.423	0.130	2.409	0.131	1.470	0.081
Chrysene	0.256	0.592	0.726	0.179	2.822	0.178	0.086	0.139
Benzo[b]fluoranthene	0.268	0.263	0.317	0.151	3.370	0.157	0.139	0.042
Benzo[k]fluoranthene	0.141	0.284	0.313	0.198	3.182	0.319	0.041	0.023
Benzo[a]pyrene	0.195	0.171	0.200	0.189	2.023	ND	0.089	0.019
Indeno[1,2,3-cd]pyrene	0.236	0.196	0.182	0.172	3.361	0.174	0.034	0.039
Dibenz[a,h]anthracene	ND	ND	ND	ND	ND	ND	ND	ND
Benzo[ghi]perylene	0.247	0.214	0.212	0.165	3.27	0.167	0.152	ND
ΣPAHs	**50.319**	**49.794**	**67.76**	**48.427**	**126.771**	**53.997**	**70.861**	**33.488**

ND: Not detected

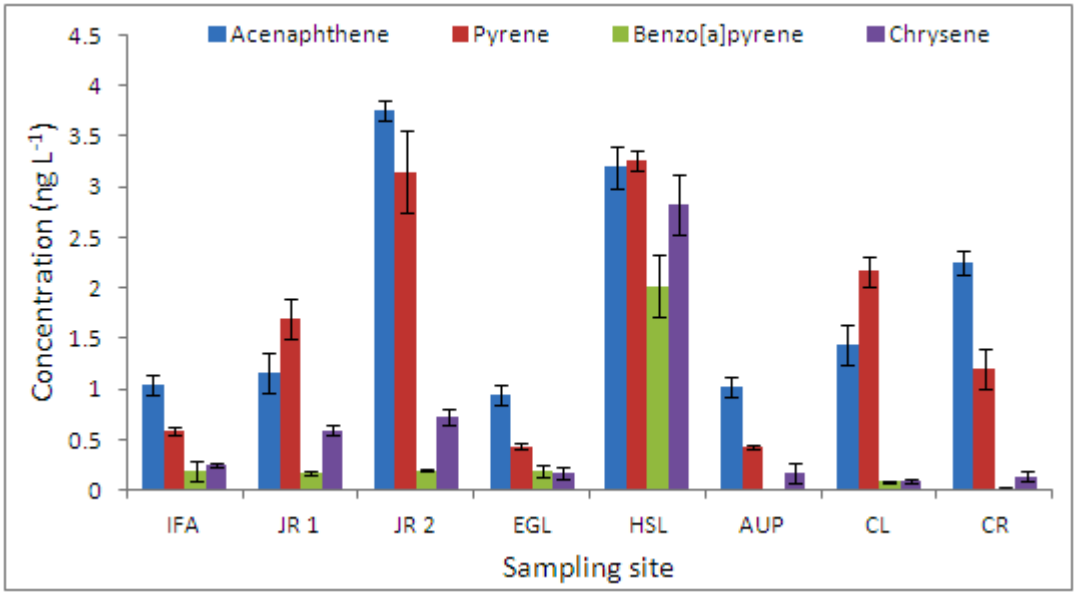


Figure 5.3: Estimated water dissolved PAH concentrations of some individual PAHs in the sampling sites

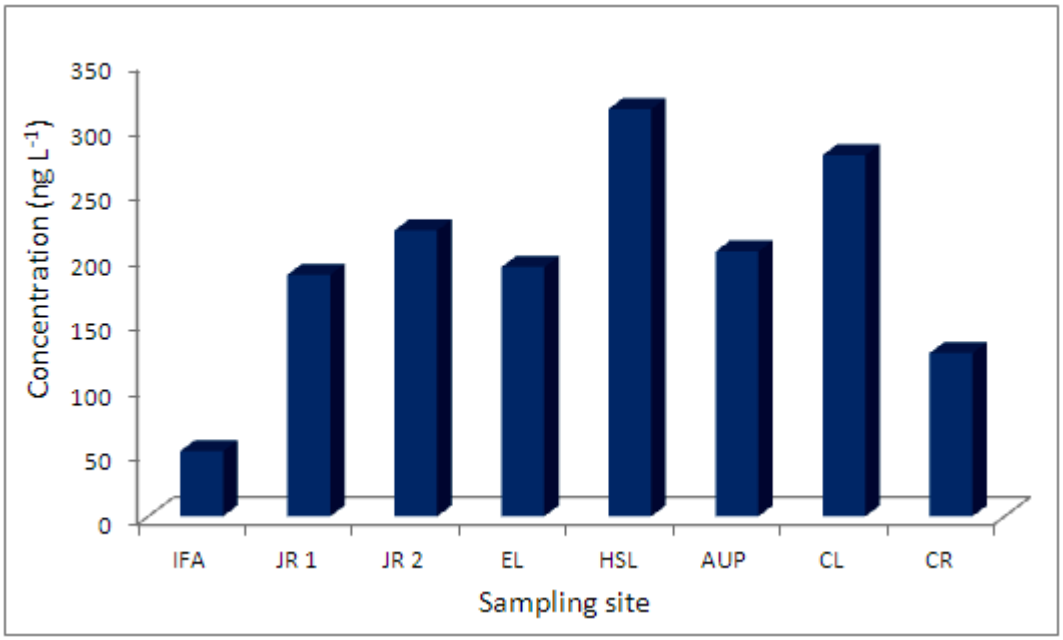


Figure 5.4: Estimated water dissolved concentrations of total PAHs in each sampling site

Estimated water-borne PAH concentrations obtained in the current study were closely comparable to what was reported by Karaćik et al. (2013), and Wang and co-workers (2009). Table 5.9 presents these values.

Table 5.9: Comparison of PAH concentrations (ng L^{-1}) recorded in the present study with selected literature values obtained using similar methods.

Compound	Current study (South Africa)	Karacik et al., 2013 (Turkey)	Wang et al., 2009 (China)
Naphthalene	20.79 - 61.19	ND -15.10	0.96 - 16.75
Acenaphthylene	1.34 - 13.31	0.14 - 1.10	0.09 - 0.53
Acenaphthene	0.94 - 3.76	0.18 - 3.30	0.16 - 4.84
Fluorene	0.91 - 6.42	2.10 - 7.00	0.46 - 6.20
Phenanthrene	0.90 - 10.47	3.90 - 21.00	1.78 - 18.75
Anthracene	0.291 - 3.74	0.12 - 3.30	0.31 - 1.51
Fluoranthene	0.36 - 8.75	1.40 - 10.50	1.32 - 18.96
Pyrene	0.43 - 5.95	0.23 - 10.70	2.48 - 16.65
Benz[a]anthracene	0.05 - 2.41	0.02 - 0.94	0.21 - 1.67
Chrysene	0.18 - 2.82	0.21 - 2.30	1.97 - 6.25
Benzo[b]fluoranthene	0.04 - 3.37	0.02 - 0.50	0.38 - 1.35
Benzo[k]fluoranthene	0.04 - 3.18	0.03 - 0.35	0.30 - 0.75
Benzo[a]pyrene	ND - 2.02	0.01 - 0.31	0.17 - 1.67
Indeno[1,2,3-cd]pyrene	0.07 - 3.36	ND - 0.13	0.15 - 2.30
Dibenz[a,h]anthracene	ND	ND - 0.12	0.24 - 3.93
Benzo[ghi]perylene	0.03 - 3.27	ND - 0.03	0.03 - 0.42
ΣPAHs	**33.5 - 126.8**	**8.36 - 76.68**	**19.14 - 97.17**

ND: not detected

Predictably, smaller molecular weight compounds (with carbons < 3) accounted for the highest PAH concentrations (77.6% at HSL to 92.7% at CR) in the water phase. Their relatively higher solubilities in water as indicated by lower log K_{ow} values enhance their availability for uptake by the samplers. On the other hand, the strong hydrophobicity of larger molecular weight PAHs makes them to readily sorb to particles and colloids in water phase resulting in diminished concentrations in the water phase.

Interestingly, sampling site HSL which had the lowest quantities of total PAHs yielded the highest water soluble concentrations of the compounds. As mentioned earlier, R_s values are site specific and are influenced by prevailing environmental conditions at the site. The low R_s (1.0 L d^{-1}) values obtained from this quiescent water body implied that subdued mass transfer of analytes could only have been possible. This in turn led to accumulation of smaller amounts of the compounds by the SPMDs by the end of the exposure period.

The significantly higher estimated water soluble concentrations of PAHs at HSL may be explained as follows: As shown in Figure 4.1, there exists a small river that drains its water to the dam and whose origins can be traced to a fairly industrialised area to the south eastern part of the airport. The river passes through the southern tip of the airport. Considering its origin, it is reasonable to suspect this river as a source of PAH pollution in the dam. It is also possible that the water body receives some of the PAHs from several other diffuse sources, especially of domestic origins through combustion activities. Presence of extensive residential establishments surrounding the lake in all directions may justify this observation.

Accidental hydrocarbon spills and surface runoff emanating from the airport situated only a few kilometres upstream may also be finding their way into the dam. The less turbulent conditions experienced in the water mass encourages loss of PAHs from the water phase to particulates through sorption processes. These particle-associated analytes can later on be remobilised when the environmental conditions become favourable.

Sampling site CL was also found to contain significantly high analyte concentrations in spite of the river that supplies it (Centurion River, CR) recording little pollution. This observation points to presence of localised input sources, and as discussed earlier, CL is situated in a vibrant urbanised set-up. Several non-point sources of the pollutants that include small-scale combustion

activities in homes and hotels, water runoff from garages, vehicular emissions, and accidental oil and sewerage spills may be responsible.

5.1.4.2 PCBs

Estimated water-phase concentrations of total PCBs are presented in Table 5.10 and concentrations for selected individual PCB congeners are shown in Figure 5.5. Calculated water phase PCB residues were in the sub ng L^{-1} range and close to the method's limit of quantification (Table A1). Sum of 7 indicator PCB congeners captured by the samplers at the sampling sites ranged from 20.9 pg L^{-1} at AUP to 120.9 pg L^{-1} at HSL. Ranking of the sites according water soluble total PCB concentrations followed the trend: AUP < EGL < IFA < JR 1 < JR 2 < HSL.

Of the many PCB congeners that are known, 7 of them were quantified in most of the sites. The highest percentage of these congeners was predominantly (over 70%) of lower chlorinated PCBs resulting from their relatively higher water solubilities.

Table 5.10: Mean estimated water concentrations of PCBs in SPMDs (pg L^{-1}) sequestered from different sample sites

Compound	IFA	JR 1	JR 2	EGL	HSL	AUP
PCB 28	16.2	24.7	37.3	12.0	52.6	4.1
PCB 52	5.5	10.7	15.9	4.2	27.8	2.4
PCB101	2.5	5.6	3.9	1.9	9.8	2.5
PCB 118	0.6	2.5	2.7	2.9	ND	ND
PCB 138	2.7	6.4	5.2	2.0	30.7	4.6
PCB 153	3.3	4.8	4.8	2.0	ND	3.6
PCB 180	2.8	2.8	3.8	2.1	ND	3.8
ΣPCBs	**33.6**	**57.5**	**73.6**	**27.1**	**120.9**	**20.9**

ND: not detected

PCB levels obtained in this study were in general agreement with what was reported by Wang et al. (2009) in an investigation of the water of the Three

Gorges Reservoir in China. Table 5.11 shows this compoarison.

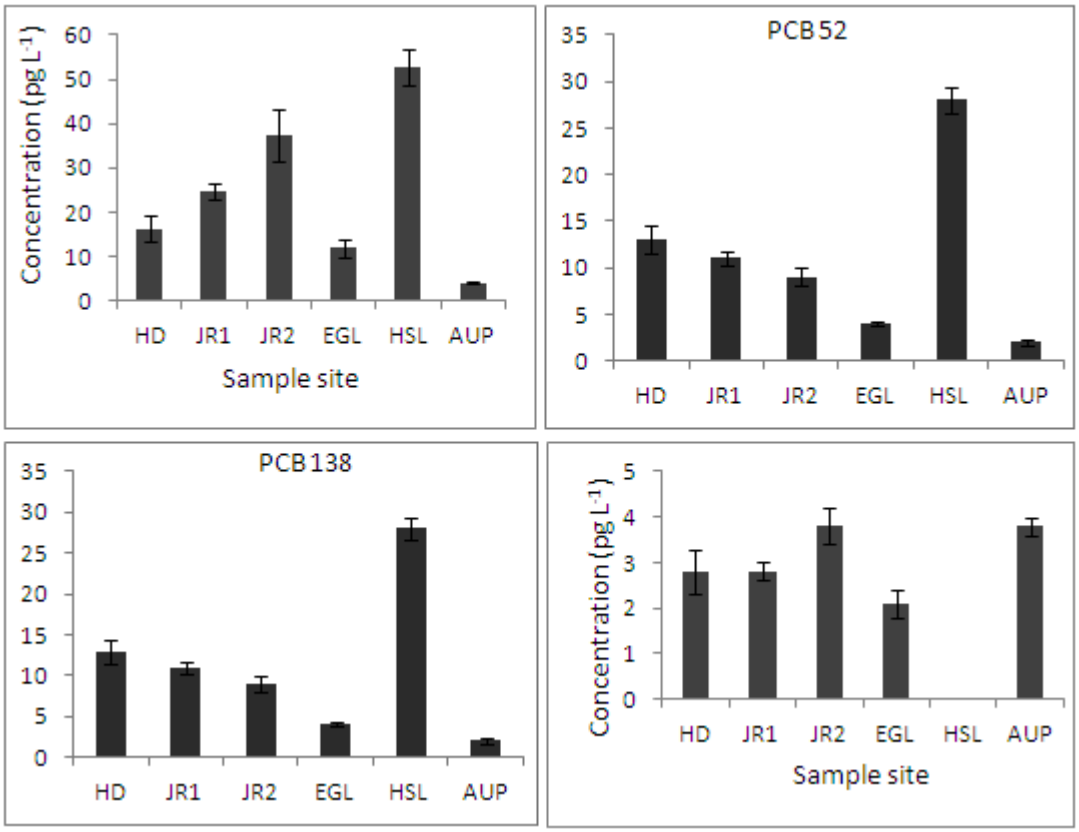


Figure 5.5: Water dissolved concentrations of some individual PCB congeners as estimated from SPMDs deployed in several sample sites

Table 5.11: Comparison of average PCB concentrations (pg L^{-1}) detected in the present study with values reported by Wang et al. (2009).

Compound	Present study	Wang et al., 2009
PCB 28	4 - 53	17 - 38
PCB 52	2 - 28	20 - 48
PCB101	3 - 10	21 - 109
PCB 118	ND - 3	ND - 91
PCB 138	3 - 31	8 - 45
PCB 153	ND - 5	ND - 45
PCB 180	ND - 4	ND - 143
ΣPCBs	**20.9 – 120.9**	**66 - 519**

ND: not detected

It is surprising that sampling site AUP that recorded the least PCB concentrations drains its water directly into HSL, which apparently exhibited the highest analyte levels. Several propositions are advanced for this observation. Firstly, since AUP originates right from the airport, accidental spills of the compounds emanating from the facility may have been washed downstream and deposited in the lake where they get sorbed to particulates and sediments. This is mainly favoured by the generally quiescent conditions (as shown by the low R_s values) experienced in the lake. Under favourable environmental conditions, such as rain events, remobilisation of the sorbed compounds may occur. Secondly, the same stream that was suspected to have introduced more PAHs into HSL may also be having a stake in the elevated PCB residues. As mentioned previously, this stream originates from some industrial area neighbouring the airport. Thirdly, illicit and/or accidental PCB releases (in electrical transformers, cooling systems e.t.c.) from the vast residential area surrounding the lake may have also contributed.

Although these compounds were never produced in South Africa, PCB oils as well as equipment containing such oils were imported for use mainly for electricity generation and in manufacturing industries. However, use of PCBs is outlawed in South Africa and their presence in the environment may be resulting from old stock.

Despite the sampling sites IFA and EGL being located in an area devoid of major industrial activities, it still recorded relatively high quantities (33.6 and 27.1 pg L^{-1}, respectively) of water soluble contaminant concentrations. Apparently, most of the water at the Hartbeespoort dam (HD) is supplied by the Crocodile River (Harding et al., 2004) whose major tributaries include the Juskei and Hennops Rivers. As elaborated previously, the origins of the two rivers can be traced to the industrialised city of Johannesburg - a probable major source of PCBs. Considering the large surface area of the water body, reintroduction of atmospheric PCBs through wet and dry deposition may not also be ignored.

In addition to the smaller weight PCB congeners, larger molecular weight congeners such as PCB 118, PCB 138, PCB 153 and PCB 180 were also detected. The lighter congeners are more prone to atmospheric transport (Ockenden et al., 2003) and volatilisation (Wang et al, 2007). The presence of the dioxin-like PCB 118 (Quinn et al., 2009) in the water body is a likely result of previous application in the immediate surrounding area. Although they exist at very low levels in the water phase, their high lipophilicity and biomagnification effects through the food web may be a cause of concern (Degger et al., 2011). Typically, heavier PCB molecules are known to deposit close to the main source, resulting in relatively increased levels in the areas, even decades after initial use, whereas their lighter counterparts can travel for long distances from their sources.

5.1.4.3 OCPs

The ambient water concentrations of OCPs as estimated from amounts accumulated by the SPMDs in the various sampling sites are shown in Figure 5.6. They ranged from a low of about 0.17 ng L^{-1} at AUP to a high of 37.14 ng L^{-1} at JR 2. The major OCP compositions registered in the sites were HCH and DDX.

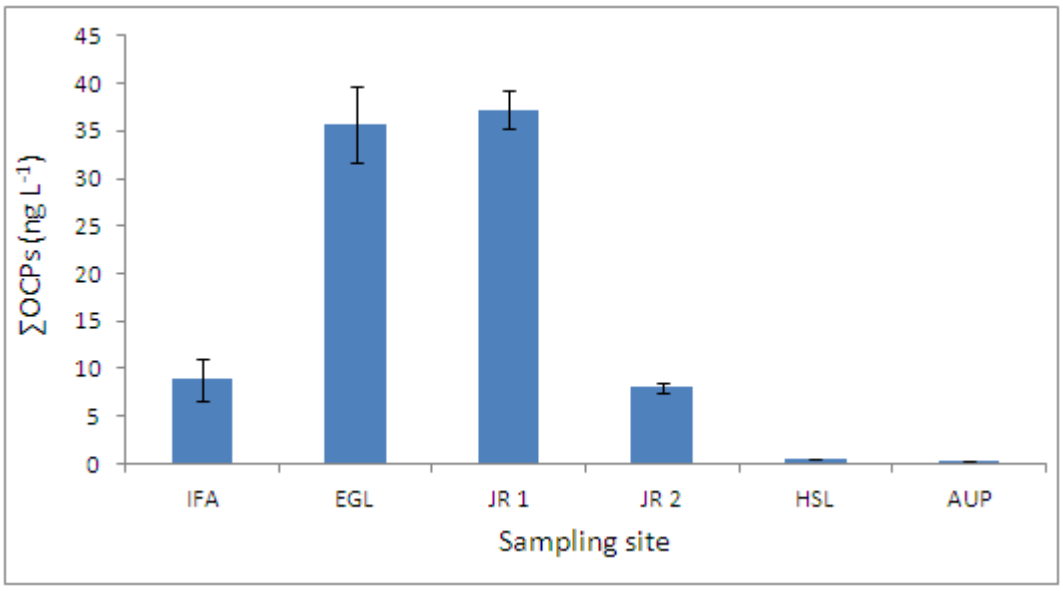


Figure 5.6: Estimated water soluble total OCP concentrations in the various sites

The proportion of HCHs in the water phase was found to be higher than for DDTs and their metabolites. Table 5.12 shows estimated water concentrations of HCH isomers. ΣHCHs ranged from 0.146 ng L^{-1} (AUP) to 36.937 ng L^{-1} at JR 2.
Basing on these estimated water borne concentrations of the analytes, ranking of the sampling sites was as follows: AUP < HSL < EGL < IFA < JR 1 < JR 2. Individual HCH concentrations generally followed a similar trend as the totals.

Table 5.12: Estimated water concentrations, C_w, of HCHs (ng L^{-1}) in various sampling sites.

Compound	**IFA**	**JR1**	**JR2**	**EGL**	**HSL**	**AUP**
α-HCH	1.884	5.106	5.576	1.832	0.092	0.051
β-HCH	5.737	28.103	28.254	5.116	0.094	0.031
γ-HCH	0.371	0.874	0.721	0.313	0.170	0.064
δ-HCH	0.046	0.790	1.095	0.039	ND	ND
ε-HCH	0.301	0.511	1.291	0.336	ND	ND
ΣHCHs	**8.339**	**35.385**	**36.937**	**7.635**	**0.356**	**0.146**

ND: not detected

Table 5.13: Comparison of concentrations of HCHs (ng L^{-1}) detected in the current study with selected literature values obtained using similar methods.

Compound	**Present study** (South Africa)	**Karacik et al., 2013** (Turkey)	**Wang et al., 2009** (China)
α-HCH	0.051 -5.576	35 – 73	0.032 – 0.225
β-HCH	0.031 - 28.254	130 – 250	0.008 – 0.031
γ-HCH	0.064 - 0.874	ND – 56	0.061 – 0.345
δ-HCH	ND - 1.095	ND	0.002 – 0.025
ε-HCH	ND - 1.291	ND	ND – 0.003
ΣHCHs	**0.146 – 36.937**	**165 - 379**	**0.103 – 0.629**

ND: not detected

A comparison of the HCH concentrations obtained in the present study was made against existing literature values. As Table 5.13 shows, average analyte concentrations were broadly comparable to those reported by Wang et al. (2009) in the waters of the Three Gorges Reservoir in China, but, were significantly less than what Karacik et al. (2013) detected in a Turkish study.

The summed-up water concentrations of individual HCH isomers from all the sites sampled increased in ascending order as follows: δ-HCH (1.970 ng L^{-1}), ε-HCH (2.439 ng L^{-1}), γ-HCH (2.513 ng L^{-1}), α-HCH (14.541 ng L^{-1}), and β-HCH (67.335 ng L^{-1}) (Figure 5.7). On the other hand, Figure 5.8 shows the percent composition of each isomer in the various sites. In most sites, analyte water phase concentrations were dominated by two isomers, α-HCH and β-HCH, accounting for over 91% of the total HCH amounts. β-HCH is characterised by higher water solubility, lower volatility and enhanced environmental stability (Wang et al., 2009). These properties are attributable to the isomer's structure and spatial orientation of its chlorine substituents (all in the equatorial position) (shown in Figure 2.7). Such a configuration is thought to impart in the molecule its recalcitrant properties and, hence, environmental resistance to physical, chemical and biological degradation (Willet et al., 1998).

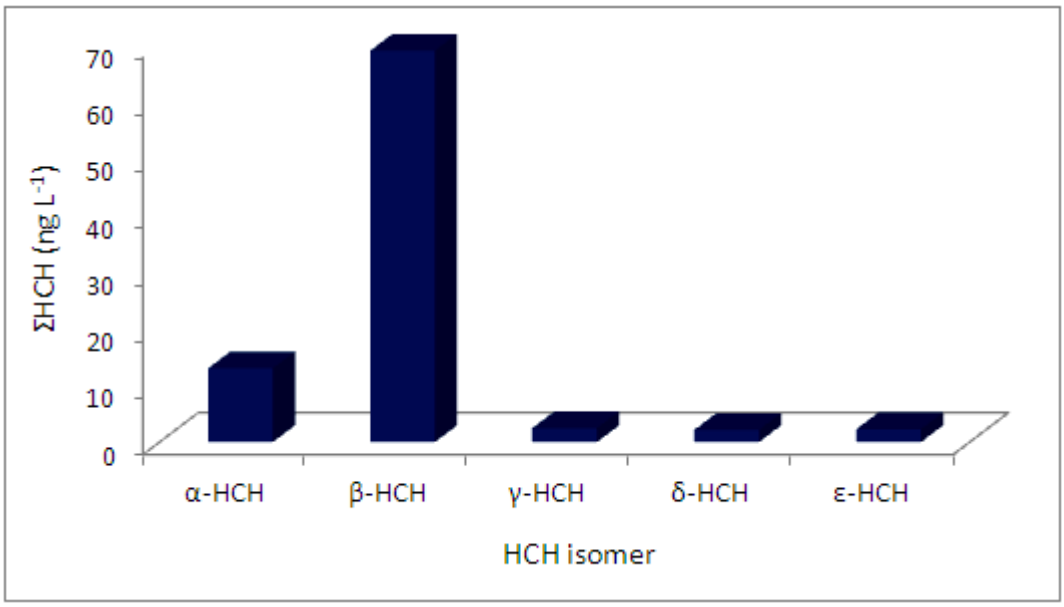


Figure 5.7: Sum total concentrations of water-borne HCH isomers in all the sampling sites

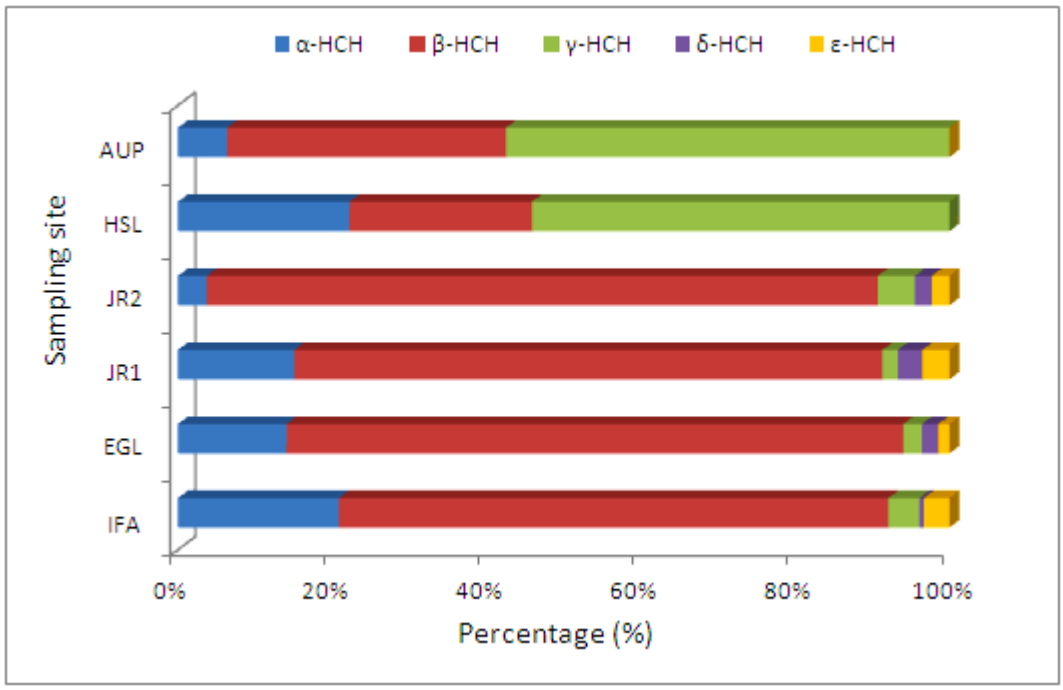


Figure 5.8: Percent composition of HCHs in the water of the various sites

Concentrations of α-HCH were also significantly high compared with the γ-, δ- and ε-isomers. Generally, technical HCH contains the isomers in the following percentages: α, 60-70%; β, 5-12%; γ, 10-12%; δ, 6-10%; ε, 3-4% (Li and Macdonald, 2005; ATSDR, 1995b). This implies that for every quantity of the pesticide used, a reasonably large percentage constitutes α-HCH, which eventually ends up in the environment. Moreover, α-HCH is a volatile compound which is prone to long-range transportation to regions afar.

Technical HCH was widely used as an insecticide, and together with its accompanying isomers, it is still readily found in the environment because of its persistence. However, the lower concentrations of γ-HCH (lindane) observed in all the sampling sites suggests no recent applications of the insecticide in the catchment areas of the studied water systems. As a signatory of the Stockholm Convention, South Africa has phased out the production and use of these compounds. Whatever exists in the environment is mainly due to previous applications, losses from dumpsites or trans-boundary introduction.

In the sites JR 1 and JR 2, total HCH concentrations showed slight spatial variations in that contaminant levels increased from upstream (JR 1) to downstream (JR 2). The high levels of the contaminants in both sites may be related to urban runoff, sewage discharges and dumpsite leakages. Further downstream (JR 2), an observed marginal increase in HCH contamination is likely resulting from additional input from agricultural activities, domestic sources and more effluent discharges.

Sampling site IFA showed high levels of β-HCH followed by the α-isomer while the rest of the isomers constituted less than 9% of the totals. Two sources of the pollutants may be enriching the dam: discharge from Juskei and Hennops Rivers, and atmospheric deposition (wet and dry). Interestingly, sampling site EGL also located in the same dam had its β-HCH levels being about 11% less than for IFA. The closer proximity of the Crocodile River entry point into the dam to IFA than to EGL may explain this slight discrepancy. Overall, the closeness in β-HCH values from the two sites that are situated several kilometres apart, but, in the same water body, suggest a significant analyte contribution from atmospheric sources. Contrary to expectation, these two sites registered lower contaminant levels than JR 1 and JR 2 that are situated upstream in the Juskei River. It is possible that losses of the compounds through processes such as volatilisation and sorption may have happened as the river flowed downstream and into the dam. It is also possible that dilution of the contaminants occurs at the confluence of the Juskei and Crocodile Rivers and/or in the dam itself where water from different sources mix. Good mixing of the water in the water body may also have contributed to lowering the analyte concentrations.

The sums of the water borne DDT and its metabolites in each sampling site are presented in Table 5.14. ΣDDX ranged from 0.026 ng L^{-1} in AUP to 0.549 ng L^{-1} in IFA. Ranking by site followed the trend: IFA > EGL > JR 1 > JR 2 > HSL > AUP. Total DDX concentrations were at most two orders of magnitude lower than HCH values. IFA and EGL sampling sites recorded significantly higher contaminant concentrations of at least two-fold as compared to all the other sites.

Table 5.14: Estimated water concentrations, C_w, of DDTs and its metabolites (ng L^{-1}) in various sampling sites.

	IFA	JR 1	JR 2	EGL	HSL	AUP
o,p'-DDE	0.004	0.004	0.006	0.003	0.010	ND
p,p'-DDE	0.048	0.040	0.055	0.026	0.048	0.010
o,p'-DDD	0.129	0.016	0.020	0.133	0.010	0.003
p,p'-DDD	0.354	0.090	0.102	0.227	0.048	0.007
o,p'-DDT	0.010	0.016	0.007	0.009	0.030	0.003
p,p'-DDT	0.004	0.059	0.008	0.003	ND	0.003
ΣDDX	**0.549**	**0.225**	**0.198**	**0.401**	**0.146**	**0.026**

ND: not detected

DDX levels from this study were broadly comparable to those reported by Wang et al. (2009) (2.33 - 3.60 ng L^{-1}), but lower by several orders of magnitude than those reported by Karacik et al. (2013) (126 - 1537 ng L^{-1}). These comparisons are illustrated in Table 5.15.

Table 5.15: Comparison of concentrations of DDX (ng L^{-1}) detected in the current study with selected literature values obtained using similar methods.

Compound	**Present study** (South Africa)	**Karacik et al., 2013** (Turkey)	**Wang et al., 2009** (China)
o,p'-DDE	ND - 0.007	22 - 130	0.033 - 0.190
p,p'-DDE	0.01 - 0.059	ND - 47	0.133 - 0.190
o,p'-DDD	0.003 - 0.046	54 - 440	0.05 - 0.104
p,p'-DDD	0.007 - 0.364	15 - 540	0.096 - 0.190
o,p'-DDT	ND - 0.021	15 - 240	0.063 - 0.092
p,p'-DDT	ND - 0.061	20 - 140	0.149 - 0.171
ΣDDX	**0.024 - 0.554**	**126 - 1537**	**0.524 - 0.937**

ND: not detected

In the current study, the detected DDT and its metabolites (DDD and DDE) may be attributed to historical applications, possible current use or releases from obsolete stocks (Wang et al., 2007). It is worth noting that regulated use of DDT for controlling mosquito vectors that transmit malaria is still being practiced in South Africa and some of the neighbouring countries. Although this mainly happens in the northern, north eastern and eastern parts of the country, far away from the sampling sites, atmospheric transportation of the pollutants and eventual deposition in the sites is a real possibility. Indeed, this factor may account for the significantly higher DDX levels recorded at sites IFA and EGL relative to JR 1 and JR 2. Atmospheric transportation and eventual deposition into the water body may be happening. This is encouraged by the dam's relatively large surface area.

Ultra violet radiation as well as microbial activity can convert DDT to its degradation products - DDD and DDE. These metabolites are representative of historic use of DDT, while DDT itself indicates possible recent use (Wang et al., 2009). The percent contributions of DDT and its metabolites in each of the sampling sites are shown in Figure 5.9.

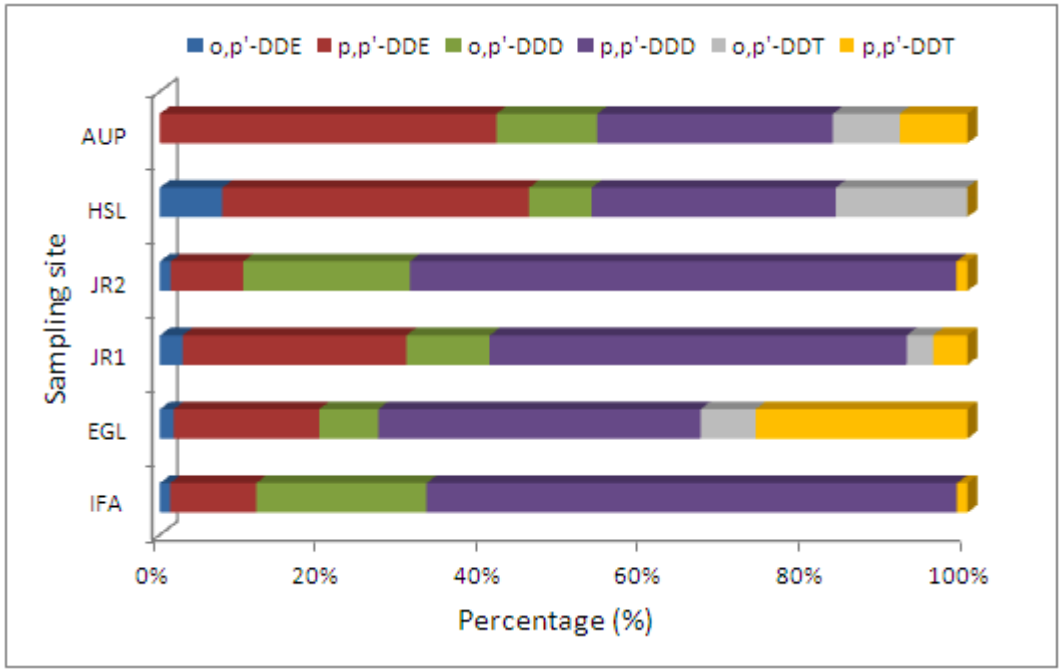


Figure 5.9: Percent composition of DDX in the waters of the various sample sites

A cursory look at these values shows that most of the DDX exist in the form of DDD and DDE, with the former constituting the highest percentage in the majority of sites (IFA, 88%; JR 1, 47%; JR 2, 62%; EGL, 89%; HSL, 40% and AUP, 38%). This was more pronounced at IFA and EGL sampling sites (both located in the same water mass).

Two inferences can be made from the observations. Firstly, contamination of the sites is mainly due to past application of DDT and the contribution of current use(s) appears limited. Secondly, reductive dechlorination mechanisms (Baxter 1990) of DDT are more prevalent in these aquatic systems, and especially, at IFA and EGL.

5.1.5: Source apportionment of PAHs in the sampling sites

The principal sources of PAHs in the environment can be classified as either pyrogenic or petrogenic, with the pyrogenic input predominating in aquatic environments (Ekpo et al., 2012). Using the SPMD-obtained PAH concentrations, identification of their probable sources was attempted. Reports by many authors on the apportionment of PAH sources in the environment using molecular ratios of certain PAHs can be found in the literature (Allan and Raneklev, 2011; Brandli et al., 2008; Zhang et al., 2004; Vrana et al., 2001). Variations in the ratios of the thermodynamically less stable PAHs are used as indices in apportioning such sources. With respect to passive sampling, ratios of PAHs must be for compounds with near to identical sampling rates to minimise bias as a result of the mode of calculation of the sampling rates for compounds with widely differing log K_{ow} (Allan and Raneklev, 2011). 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. In the current study, identification of the possible sources of PAHs in each sample site was done using ratios of Anthracene/(Anthracene + Phenanthrene) against Fluoranthene/(Fluoranthene+Pyrene) [Ant/(Ant + Phe) vs Flt/(Flt+Pyr)].

In the majority of the sites, the ratios of Flt/(Flt+Pyr) were found to be greater than 0.5, indicating pyrogenic origins. This occurs mainly through combustion of biomass and coal. PAHs at sampling sites AUP and LC were clearly inclined towards petroleum combustion sources. A small ratio (<0.1) of Ant/Ant+Phe indicates dominance of petrogenic sources. It is proposed that since AUP is in very close proximity to a busy international airport, aircraft, vehicular and other machinery exhaust products rich in PAHs may be finding their way into the waters of the sampling site.

PAHs detected at sites CL and CR also seem to point to petrogenic origins. As mentioned earlier, CL is situated in a busy urban setting defined by a myriad of human activities that include combustion of petroleum products. On the other hand, since CR is part of the Hennops River that has its origins near Kempton Park area, its contamination may be happening upstream through point sources such as wastewater discharges as well as through several diffuse sources such as vehicular emissions and power generation activities. The use of Ant/Ant+Phe ratio in differentiating petrogenic from pyrogenic sources is at times limited by photolytic degradation of anthracene which can result in lowered ratios (Liu et al., 2009; Kamens et al., 1988).

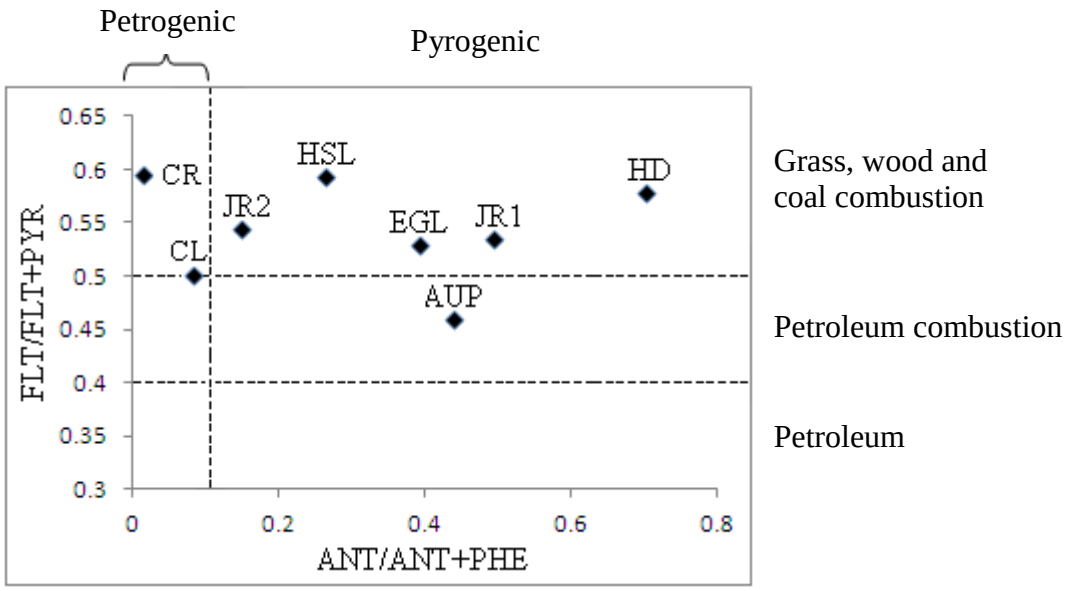


Figure 5.10: PAH cross plots for the ratios Ant/(Ant+Phe) vs Flt/(Flt+Pyr)

5.1.6 Conclusions

SPMDs are potentially effective tools for monitoring hydrophobic contaminants in aqueous systems. These samplers were able to detect concentrations of PAHs, PCBs and OCPs in the toxicologically most relevant dissolved phase in the water bodies. In general, total PAH concentrations sequestered by the samplers varied from 1223 to 4766 ng $SPMD^{-1}$, whereas the summed up PCB and OCP levels in the SPMDs were in the range of 6.5 to 76.1 ng $sampler^{-1}$ and 4.5 to 921.9 ng $sampler^{-1}$, respectively.

Estimation of water phase analyte concentrations yielded total PAH amounts by site that ranged from about 33.5 ng L^{-1} at CR to 126.8 ng L^{-1} at HSL. On the other hand, water phase PCB residues were in the pg L^{-1} region and close to the LOQ. Total water soluble OCP concentrations ranged from a low of 0.17 ng L^{-1} at AUP to 37.14 ng L^{-1} at JR2. HCHs and DDTs were the only constituents of the OCPs detected with the former being obtained at higher concentrations than the latter. Presence of the analytes in the water systems was attributed mainly to anthropogenic sources. The principle modes of introduction of these contaminants to the sample sites were proposed as atmospheric deposition (wet and dry), surface runoff and remobilisation of adsorbed compounds in soils and sediments due to heavy rain events.

Diagnostic ratios of PAHs measured in SPMDs were used to identify the possible sources of these compounds in the water. Apart from PAHs at sampling sites AUP and LC that indicated petroleum combustion sources, ratios from all the other sites were inclined towards pyrogenic origins.

5.2 Seasonal variation in the free dissolved PAH, PCB and OCP concentrations in Hartbeespoort dam

5.2.1 Occurrence of PAHs, PCBs and OCPs in the SPMDs

In this part of the study, temporal trends of dissolved water-borne PAHs, PCBs and OCPs were assessed using SPMDs over a period of one year in 2011. Exposure of the passive samplers was done for 14 days at a single sampling site, IFA (Figure 4.2) in the Hartbeespoort dam, South Africa. Monitoring for the compounds was done at the site in each of the four seasons of the year.

Table 5.16 and 5.17 presents the absolute contaminant concentrations (ng $SPMD^{-1}$) of PAHs and PCBs/OCPs, respectively, sequestered by SPMDs deployed at the site. Analyte concentrations were adjusted with respect to their recoveries obtained from surrogate standards introduced prior to the dialytic process. The SPMD field blanks showed no quantifiable concentrations of the target 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 percent differences between co-deployed triplicate samplers did not exceed 22% for PAHs, 24% for PCBs and 17% for OCPs.

5.2.2 Estimation of the analyte concentrations in water phase

Concentrations of water-borne PAHs, PCBs and OCPs were obtained from their amounts accumulated in the SPMDs in exactly the same way as described in section 5.1.3. Seasonal variability of these compounds is based on their water phase concentrations. As elaborated earlier, SPMD uptake of organic compounds in the actual field is influenced by several environmental factors that include temperature, water flow rates and membrane biofouling. The individual and/or combined effect of these factors on sampling rates (Rs) is site and time specific.

Table 5.16: Mean concentrations of PAHs (ng $SPMD^{-1}$) sequestered by SPMDs in the various seasons

	Season			
Compound	Winter	Spring	Summer	Autumn
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	**2117 ± 57**	**905 ± 21**	**984 ± 21**	**1450 ± 29**

ND: not detected

Table 5.17: Mean concentrations of PCBs and OCPs in SPMDs (ng $SPMD^{-1}$)

	Season			
Compound	Winter	Spring	Summer	Autumn
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
ε-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

This gives rise to differences in the uptake of target compounds by the sampler over the exposure period. Therefore, seasonal variability of contaminant levels in a sampling site is better understood by utilising the estimated water dissolved analyte concentrations as opposed to the amounts accumulated in the sampler. Seasonal trends in water borne PAH, PCB and OCP concentrations at IFA are discussed in the subsequent sections.

5.2.3 Temporal trends in water dissolved contaminant concentrations

Analyte estimated water soluble concentrations generally followed the trend: PAHs > OCPs > PCBs. PAHs are ubiquitous organic pollutants characterised by several natural and anthropogenic sources, unlike OCPs and PCBs (industrial products). As described earlier, the dam receives over 90% of its water from the Crocodile River whose source is Johannesburg city, and it is possible that a good portion of the pollutants sampled at the site are of industrial origin.

PCB concentrations were on average 2 to 3 orders of magnitude lower than PAHs and OCPs. This is because most of the compounds have long been banned and their use stopped, in line with the Stockholm Convention. Whatever was captured by the samplers is attributable to their environmental persistence due to slow degradation. The sum total water soluble 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 individual compounds mirrored the total amounts. An observed dominance of smaller molecular weight PAHs was visible in all the four seasons. This may be due to their higher solubility in water arising from their lower hydrophobicity and hence, more efficient transportation in water phase from point sources.

5.2.3.1 PAHs

Remarkable seasonal variability in the amounts of sequestered PAHs was shown by the SPMDs deployed at IFA in the four seasons of the year (Table 5.18).

Table 5.18: Estimated PAH water dissolved concentrations (ng L^{-1}, n = 3)

	Season			
Compound	**Winter**	**Spring**	**Summer**	**Autumn**
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**

ND: Not detected

Estimated total analyte concentrations ranged from about 30.2 ng L^{1} (in summer) to a high of 60.8 ng L^{-1} (in winter). The trend of total concentrations of PAHs dissolved in water was as follows: winter > spring > autumn > summer.

The observations of the current study are generally agreeable with findings reported by Vrana et al. (2013) (5-72 ng L^{-1}) in a one year monitoring exercise of the Danube River, Slovakia/Austria (Table 5.19). It should be noted that similarities are only with respect to the overall seasonal variation, but the PAH profiles are very different.

Table 5.19: Comparison of PAH concentrations from the current study with those reported by Vrana et al. (2013)

Compound	Winter		Spring		Summer		Autumn	
	Present study	Vrana et al., (Submitted)	Present study	Vrana et al., (Submitted)	Present study	Vrana et al., (Submitted)	Present study	Vrana et al., (Submitted)
Naphthalene	43.2	ND	43.2	ND	24.0	ND	38.5	ND
Acenaphthylene	3.9	0.7	3.9	0.4	3.2	0.1	4.4	0.2
Acenaphthene	1.1	1.3	1.2	1.7	0.8	0.9	1.1	0.8
Fluorene	1.2	2.9	1.9	1.5	0.7	0.6	1.6	1.4
Phenanthrene	1.3	7.2	1.3	2.4	0.4	1.3	1.8	2.9
Anthracene	7.3	0.4	2.2	0.3	0.3	0.2	1.5	0.3
Fluoranthene	0.8	3.0	1.3	1.6	0.2	1.6	0.6	2.0
Pyrene	0.7	2.9	1.0	0.8	0.2	1.0	0.6	1.3
Benz[a]anthracene	0.2	0.3	0.3	0.4	0.1	0.2	0.2	0.3
Chrysene	0.2	0.7	0.4	0.7	0.1	0.4	0.3	0.5
Benzo[b]fluoranthene	0.2	0.2	0.5	0.7	0.1	0.3	0.3	0.2
Benzo[k]fluoranthene	0.2	0.1	ND	0.4	0.1	0.3	0.3	0.1
Benzo[a]Pyrene	0.2	0.1	0.3	0.5	0.1	0.2	0.2	<0.1
Indeno[1,2,3-cd]Pyrene	0.2	< 0.1	0.4	0.4	0.1	0.1	0.3	0.1
Dibenz[a,h]anthracene	ND	< 0.1	ND	0.4	ND	0.1	ND	0.1
Benzo[ghi]perylene	0.2	ND	0.4	0.2	0.1	<0.1	0.3	0.1
ΣPAHs	**60.768**	**19.8**	**58.225**	**12.4**	**30.199**	**7.3**	**52.082**	**8.3**

Individual PAH concentrations obtained in the various seasons also generally adopted the same pattern as the totals (Figure 5.11).

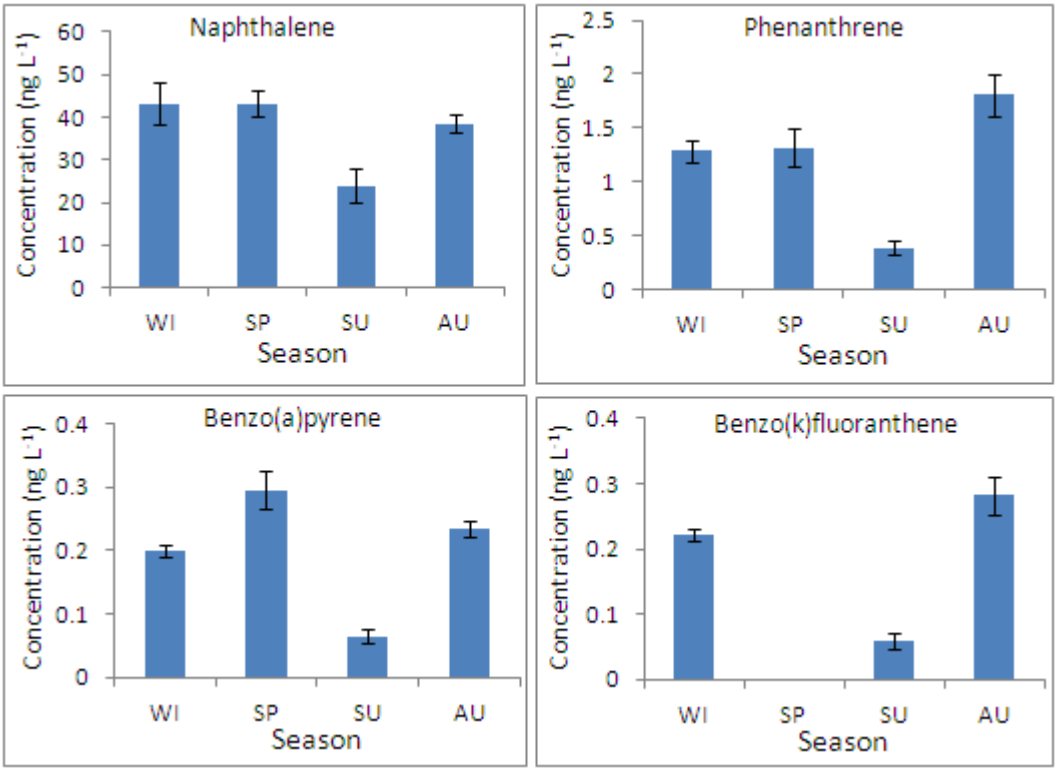


Fig 5.11: Water dissolved concentrations of some individual PAHs as affected by seasonal change

Expectedly, smaller molecular weight PAHs (naphthalene, acenaphthylene, phenanthrene, anthracene, fluoranthene and pyrene) formed the highest percentages (winter, 97.6%; spring, 96.2%, summer, 98.5% and autumn, 96.2%) of the sequestered compounds in all the sampling exercises. In addition to being more volatile (Table 2.2), the said compounds also defined by higher water solubility. Hence, their transportation in both atmospheric and water phases for longer distances is very possible. Conversely, heavier PAHs are significantly more hydrophobic and would rather sorb to particulates in the water column, hence, limiting their transportation and availability.

The elevated concentrations recorded during winter may be a consequence of a number of factors. During the winter months, very little precipitation is witnessed

and since the dam depends on river water for replenishment, its water volume drastically drops. This in turn increases the percentage of the dam's water attributed to treated wastewater sources, which can exceed 50% of the total volume (Harding et al., 2004). These sources originate from wastewater treatment plants located in the industrialised areas, north of Johannesburg city. Furthermore, average water temperatures substantially drop during this period which in turn discourages analyte losses via volatilisation.

Atmospheric deposition of PAHs represents an important introduction pathway of the compounds to aquatic ecosystems. During winter, temperatures drop significantly. Such conditions discourage PAH losses via volatilisation. Increased combustion of fossil fuels (for energy purposes) that lead to more PAH emissions is also more pronounced in winter. The higher activity of emission sources in combination with climatic conditions such as temperature inversion, that limit the vertical dispersion and less intensive atmospheric reactions, create favourable conditions for PAH deposition to water phase. Moreover, Henry's law constant increase with increasing temperature and thus higher equilibrium concentrations in water are expected at lower temperatures even when atmospheric concentrations remain constant (Staudinger and Roberts, 2001).

Summer months experience a lot of rainfall which are usually accompanied by high temperatures. Resuspension of sediment-immobilised PAHs, in addition to input from surface run-off and rivers, originating from polluted areas upstream, were expected to increase analyte water phase concentrations in the study area.

Although these factors may have been at play, it appears that dilution effects (larger water inputs from less polluted sources) as well as losses through volatilisation (as a consequence of high temperatures) may have tempered the expected increase in contaminant concentrations.

The autumn season is characterised by less precipitation and dropping temperatures. These conditions encouraged decreased contaminant losses via volatilisation as well as enhancement of concentrations due to decreased bulk water volumes as well as an increase in pollutant sources.

5.2.3.2 PCBs

In this study, it was found that PCB amounts accumulated in the deployed SPMDs were generally lower by about 3 orders of magnitude than PAHs and OCPs. PCBs are organic contaminants of purely anthropogenic origin as contrasted to PAHs that have both natural and anthropogenic sources. In addition, most of the PCBs were banned more than 3 decades ago and the remnants captured by the samplers are attributable to their strong persistence 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 sorb strongly to particulate matter, colloids and sediments. Moreover, their emissions are likely much lower than those of PAHs because, unlike the western industrialised countries, South Africa may not have utilized PCBs heavily during its economic growth in 1980s or later on when usage of PCBs had already been outlawed (Ogata et al., 2009).

Estimated water concentrations of the sum total PCBs are shown in Table 5.20 whereas Figure 5.12 gives the dissolved concentrations of some PCB congeners. When ranked in an increasing order, water-borne analyte levels followed the trend: winter < autumn < spring < summer. Concentrations of the compounds in water phase in all the seasons ranged between 38 and 150 pg L^{-1}. Winter concentrations were the least while contaminant levels obtained in summer were highest.

Table 5.20: Mean water concentrations of PCBs (pg L^{-1}, n = 3)

	Season			
Congener	**Winter**	**Spring**	**Summer**	**Autumn**
PCB 28	19	29	67	20
PCB 52	6	12	25	10
PCB 101	3	5	14	7
PCB 118	1	1	3	ND
PCB 153	3	6	13	5
PCB 138	4	5	18	4
PCB 180	2	4	12	3
ΣPCBs	**38**	**62**	**150**	**49**

ND: not detected

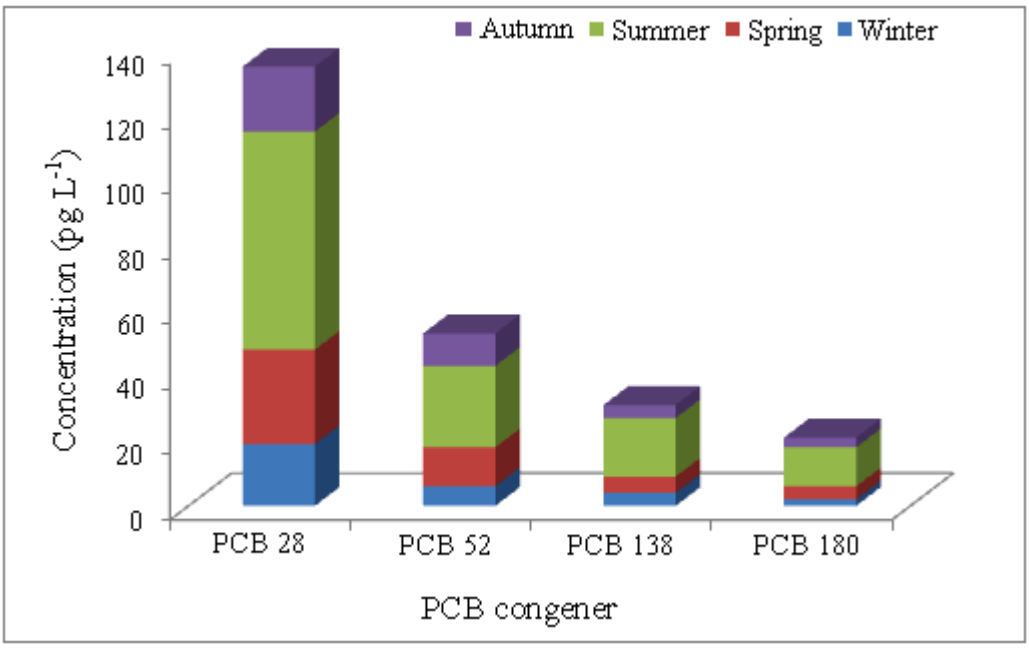


Figure 5.12: Water dissolved concentrations of some PCB congeners

The concentrations obtained in the present study were broadly agreeable to those obtained by Vrana et al (submitted) at the Danube River, Slovakia/Austria (5 to 16 pg L^{-1}) and Allan and Ranneklev (2011) in the Alna River, Norway (0.7 to 85 ng L^{-1}). Figure 5.13 shows the comparison of our values with the ones reported by Vrana and co-workers (submitted).

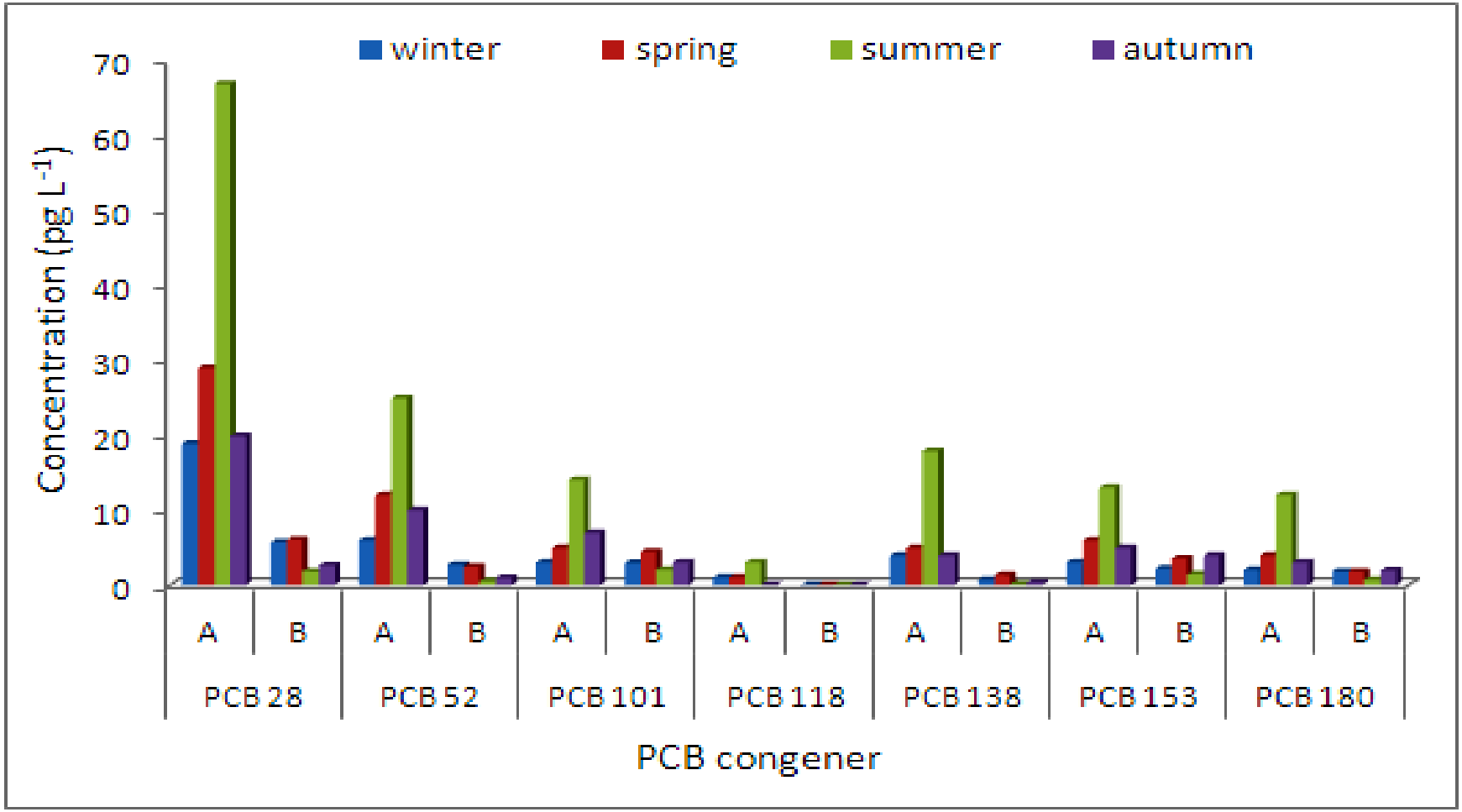


Figure 5.13: PCB concentrations recorded in the (A) present study (B) reported by Vrana et al. (Submitted for publication)

Levels of PCBs obtained during the summer season were significantly higher as compared to those recorded in all the other seasons of the year. The following explanation may justify this observation. As mentioned previously, the bulk of South Africa's rainfall is received in summer and insignificant amounts during the other seasons of the year. Most PCB congeners are highly hydrophobic compounds which preferentially adsorb strongly onto soil particles and sediments. Therefore, heavy rain events disrupt these strong interactions thereby remobilising them into the water phase. Moreover, a good portion of the water that eventually ends up in the sample site can be traced to the surroundings of the industrially endowed city of Johannesburg (Figure 4.2). Surface runoff from the urban areas may also transport PCBs associated with spills and leakages from e.g. dumpsites.

5.2.3.3 OCPs

The estimated freely dissolved water phase OCP concentrations are shown in Table 5.21. Seasonal ranking from lowest to highest followed the trend: summer, autumn, spring and winter. The water-borne OCP levels were up to one order of magnitude higher than PCBs but slightly less than those of PAHs. OCPs mainly comprised HCHs and DDX. Among the two, HCHs contributed over 78% of the quantified amount and their water dissolved concentrations ranged from about 9.2 ng L^{-1} in summer to 10.4 ng L^{-1} in winter (Table 5.21). Overall seasonal trend of total HCH concentrations in water is shown in Figure 5.14, while Figure 5.15 presents dissolved concentrations of selected HCH isomers.

Particularly high levels of β-HCH were detected in the sample site in all the 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 the other isomers, which then favours partitioning from air to water. As compared to the γ- and α-HCH, β-HCH is the most recalcitrant (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) that gave significantly lower concentrations. For instance, Wang et al. (2009) reported concentrations that ranged from 0.10 to 0.63 ng L^{-1} in a Chinese river. These researchers attributed the observation to the usage of lindane, which contains γ-HCH as its main component. It appears the technical-grade HCH mixture, which contain considerably high β-HCH (5 – 12%) was the most used formulation. However, the generally low concentrations of γ-HCH witnessed in this study suggest no recent major application of the pesticide in or around the sampled areas.

Table 5.21: Estimated OCP water concentrations (ng L^{-1}) (n = 3) in the different seasons

	Season			
Compound	Winter	Spring	Summer	Autumn
HCHs				
α-HCH	2.320	2.212	0.666	2.921
β-HCH	6.780	6.661	8.102	6.151
γ-HCH	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
o,p'-DDD	0.033	0.052	0.088	0.062
p,p'-DDD	0.065	0.104	0.176	0.124
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**

ND: not detected

Because of its relative volatility, this globally-banned pesticide can easily find its way into water systems via atmospheric deposition. Since the overall seasonal trends of HCHs generally mirrored those of PAHs (with the exception of values

obtained in spring), we conclude that the similar factors may have affected them. However, the decrease in HCH concentrations from winter to spring was insignificant. Losses through volatilisation as a result of increasing temperatures during spring may not have played a major role.

Interestingly, DDT and its metabolites showed seasonal patterns similar to those of PCBs, albeit, with higher water dissolved concentrations. Estimated water soluble concentrations of ΣDDX ranged from about 0.31 ng L^{-1} in winter to 0.83 ng L^{-1} in summer (Table 5.21). The seasonal ranking order of ΣDDX concentrations is shown in Figure 5.14. Temporal trends of water-borne DDX concentrations of some individual HCH isomers are presented in Figure 5.15. Except for β-HCH, the trends of all the other isomers reflected the overall ΣDDX pattern.

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 (ATSDR, 2002). Findings from this study suggests that wet deposition of DDT and its metabolites may be playing an important role in re-introducing them into the sample site as higher water concentrations coincide with high precipitation (summer).

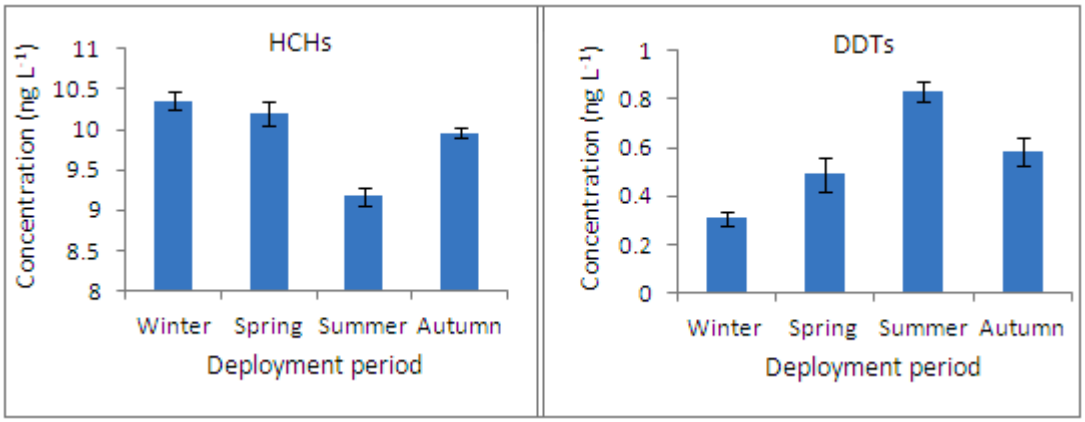


Figure 5.14: Estimated water dissolved total concentrations of HCHs and DDTs as influenced by seasonal changes

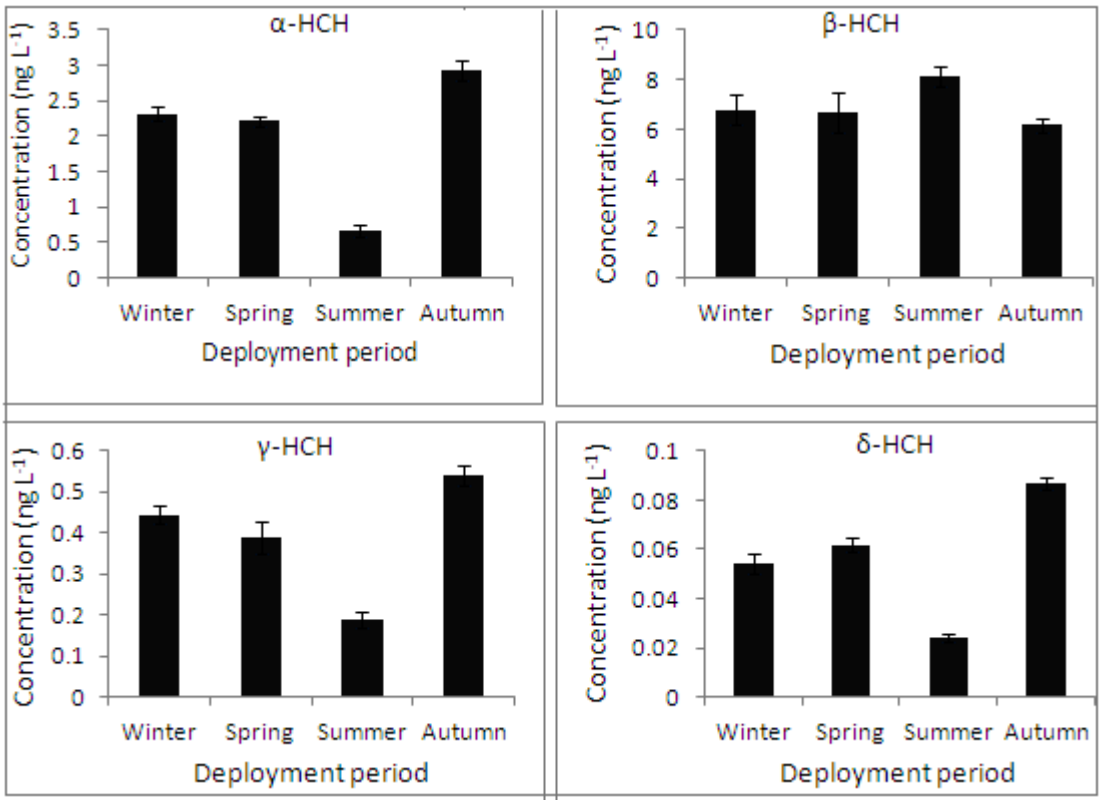


Fig 5.15: Water dissolved concentrations of individual HCHs as affected by seasonal change

Additionally, considering the relatively high octanol-water partition coefficients associated with DDX (log K_{ow} between 5.8 and 6.79), remobilisation of the particle/sediment-bound fraction as a consequence of heavy rainfall is possible. Moreover, contributions resulting from surface runoff cannot be ignored. Put together, all these factors may explain the observed temporal trends of DDX in the sampling site.

5.2.4 Source identification of PAHs in the Hartbeespoort dam

Figure 5.14 shows the diagnostic ratios of PAHs measured using SPMD-derived data in the sampling site during the four seasons of the year. As discussed in section 5.1.5, ratios of certain PAHs can be used to apportion probable sources to the contaminants. In addition to the Flt/(Flt + Pyr) ratio denoting a petrogenic source and Ant/(Ant + Phe) ratio indicating a pyrogenic source, ratios of indeno[1 ,2,3-cd]Pyrene/(indeno[1,2,3-cd]Pyrene + benzo[g,h,i]perylene) in the range of

0.3 to 0.4 tend to support fossil fuel combustion or pyrogenic sources (Brandli et al., 2008). As Figure 5.16 clearly shows, with the exception of concentrations obtained 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 observed during this season may be explained as follows. Firstly, as Harding et al., (2004) reported, a huge proportion (>50%) of the water entering the dam is of treated wastewater nature emanating from Johannesburg city. These effluents may be loaded with PAHs of domestic and industrial origins that were not adequately degraded in the WWTPs. In addition, the season is associated with very low temperatures which generally encourage atmospheric deposition of the compounds as opposed to loss through volatilisation. It is thus, possible that vehicular emissions from the roads and urban centres nearby may be finding their way into the dam. A steep increase in the Flt/Flt + Pyr ratio was observed from winter to spring before decreasing slightly during summer. A further drop in the ratio, although to a smaller extent, occurred between summer and autumn.

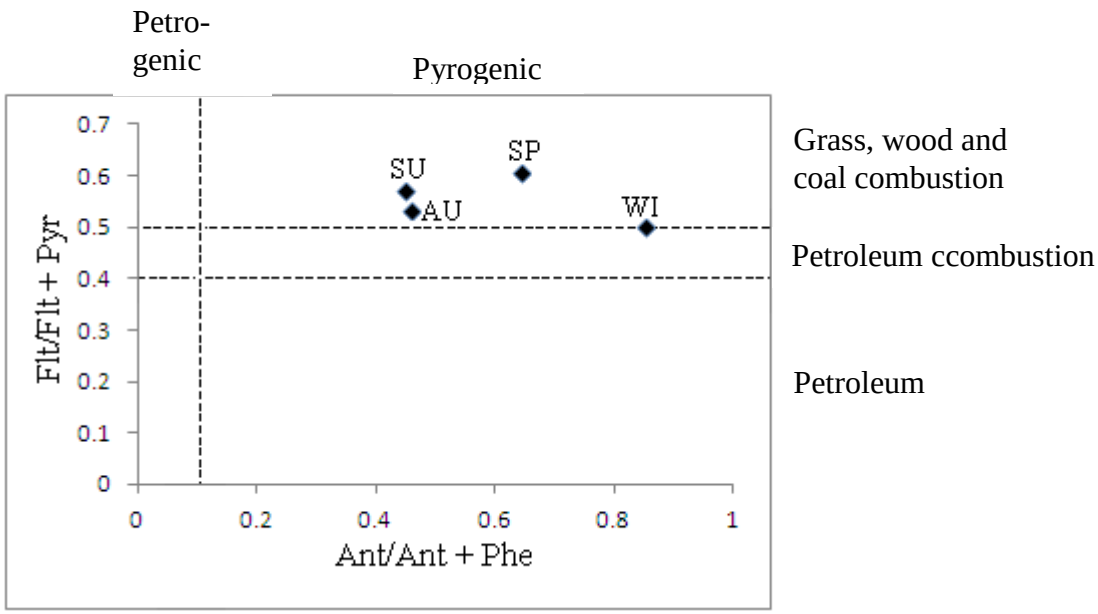


Fig. 5.16: Diagnostic ratios of PAH concentrations measured with SPMDs in the Hartbeespoort dam. WI: Winter; SP: Spring, SU: Summer, AU: Autumn, AV: average;FLT: Fluoranthene; PYR: Pyrene; ANT: Anthracene; PHE: Phenanthrene

Summer conditions are characterised by hot temperatures and heavy precipitation. Such conditions facilitate volatilisation of soil-bound PAHs into the atmosphere where they get washed back into water systems through rain events. Remobilisation of soil-sorbed PAHs and runoff from urban areas add to the pollutant load.

5.2.5 Conclusions

In this study, SPMDs were used to monitor the water-borne concentrations of POPs in the Hartbeespoort dam, South Africa. Generally, total contaminant concentrations in the dam increased in the order: summer < spring < autumn < winter. Water dissolved PAH concentrations ranged from a low of 30.2 ng L^{-1} in summer to a high of 60.8 ng L^{-1} in winter. Concentrations of the PAHs and HCH isomers decreased with increasing water temperature, which likely reflects the seasonality in atmospheric deposition. Low water-borne PCB concentrations (38 to 150 ng L^{-1}) were detected in the various seasons of the year whereas dissolved concentrations of OCPs (HCHs and DDX) were in the range of 10.0 to 10.7 ng L^{-1}. Dissolved concentrations of PCBs and DDT isomers showed a similar temporal trend with highest levels recorded in summer. This observation was most likely related to desorption of the analytes from suspended particles due to heavy rainfall. Diagnostic ratios of PAHs measured in SPMDs indicated that the analytes found in the dam during spring, summer and autumn were mainly of pyrogenic origin while the winter levels comprised both pyrogenic and petrogenic sources.

5.2.6 Monitoring of temporal changes in PAH water concentrations using solid phase extraction

Excised water samples from the sampling site taken at the time of deployment and retrieval of the SPMDs in all the four seasons were extracted using solid phase extraction (SPE). The extracts were analysed for presence of five small molecular weight PAHs: naphthalene, Acenaphthene, phenanthrene, fluoranthene and Pyrene. Changes with seasonality of these compounds are shown in Figure 5.17.

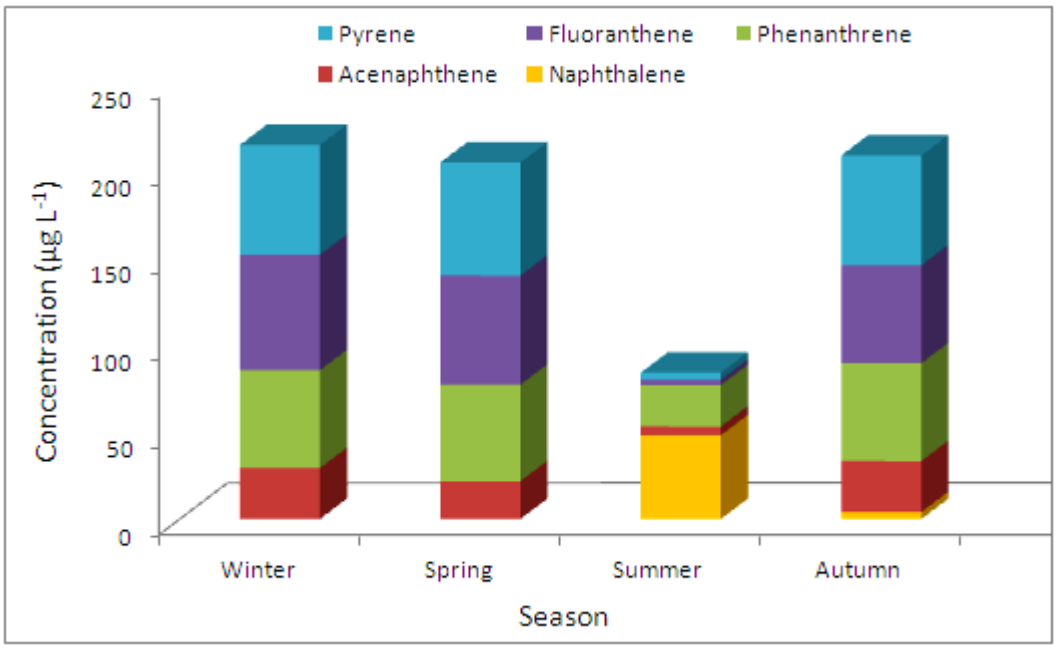


Figure 5.17: Water concentrations of selected PAHs extracted using SPE

Total concentrations of water soluble PAHs ranged from 39.2 µg L^{-1} in summer to 214.1 µg L^{-1} in winter. SPE is non-selective extraction method in which the truly dissolved analytes, as well as those sorbed to particulates and colloids are all extracted. This goes to explain why higher concentrations of the PAHs were detected using this approach than in SPMDs.

In spite of analyte concentrations being generally higher, this sample preparation technique produced results that exhibited a similar temporal pattern as was shown by SPMDs deployed in the same site. As explained previously, the increased sources of PAH emission in winter in combination with decreased water temperatures tend to favour atmospheric deposition of the contaminants to water phase. In summer, water volumes in the dam increase significantly leading to dilution effects on the total PAH concentrations in the water phase. Moreover, higher temperatures associated with this season encourage volatilisation of the water soluble analytes.

Interestingly, naphthalene was not detected in the water samples during all the seasons except in summer (92%) and autumn (8%). The main reason for this

observation lies in naphthalene's comparatively higher volatility and water solubility. Being the most volatile PAH, elevated temperatures experienced during this season encourages increased losses through volatilisation of soil-bound naphthalene. Higher rainfall then makes it possible for the compound to be introduced to the water body through atmospheric deposition. It is also possible that remobilisation of sediment-bound naphthalene caused by increased water volumes and flow velocities in the rivers feeding the dam, or in the dam itself may have happened. Surface runoff from polluted areas is yet another possible contributor.

The SPE-derived PAH concentrations from the summer season sampling exercise were compared with both the concentrations found in fish (Oduntan et al, unpublished) obtained from the same site at the time of sampling and SPMD estimated water concentrations. These values are shown in Table 5.22. Clearly, the SPE and fish PAH values were higher than the SPMD concentrations. As mentioned earlier, passive samplers sequesters the truly dissolved/bioavailable analytes in water phase.

Table 5.22: Comparison of PAH concentrations in water using SPE, fish extracts and SPMDs

	Concentration		
Compound	SPMD (ng L^{-1})	SPE (µg L^{-1})	Fish (µg kg^{-1})
Naphthalene	43.2	52.0	ND
Acenaphthene	1.1	26.7	50.0
Phenanthrene	0.8	47.7	63.3
Fluoranthene	1.2	49.5	59.5
Pyrene	0.1	48.1	73.4

ND: not detected

Although fish also targets this same fraction, and based on the SPMD estimated concentrations, it appears considerable bioaccumulation (over 79 times) occurred in the organisms. As the norm, bioaccumulation was generally more pronounced

for the higher molecular weight PAHs. Higher organisms, such as fish, are usually able to degrade most PAHs as opposed to bioaccumulation. Save for naphthalene, all the other 4 PAHs were not fully metabolised by the fish in this study. It is suggested that the rate of PAH uptake by the fish may have been faster than the degradation rate.

5.3: Laboratory calibration and field application of the polar organic chemical integrated sampler (POCIS) for naproxen, ibuprofen and triclosan in wastewater

5.3.1 Analytical performance and quality assurance

In the POCIS calibration experiments, target analytes were not detected in aliquots of water or in POCIS extracts from the negative blank control. Likewise, POCIS extracts from laboratory procedural and the field blanks yielded no detectable amounts of target analytes. Positive controls did not show any observable dissipation of the target compounds. Thus, there was no need for blank corrections to be made in these data.

Solid phase extraction (SPE) of the analytes yielded recoveries that ranged from 75% to 108%. Table 5.23 presents the analytical figures of merit that include instrumental detection limit (LODs), quantification limits (LOQs) and linearity. LOD and LOQ values for target compounds were defined as the analyte concentration that produced a peak with a signal-to-noise ratio of 3 and 10, respectively. The lowest calibration standard solution for each target analyte was used. Calculated LODs and LOQs for the analytes ranged from 0.2 to 4.1 μg L^{-1}, and from 0.7 to 17 μg L^{-1}, respectively. All the compounds exhibited good linearity with coefficients of determinations (r^2) being higher than 0.9982 (Figure 5.18). Figure 5.19 shows a typical chromatogram of 0.1 ppm naproxen and ibuprofen.

Table 5.23: LODs, LOQs and linearity of POCIS for the extraction of naproxen, ibuprofen and triclosan (n = 3)

Compound	LOD (μg L^{-1})	LOQ (μg L^{-1})	r^2	Recovery (%)
Naproxen	0.2	0.7	0.9989	92 ± 9
Ibuprofen	0.7	3.1	0.9983	108 ± 5
Triclosan	4.1	17.0	0.9979	75 ± 8

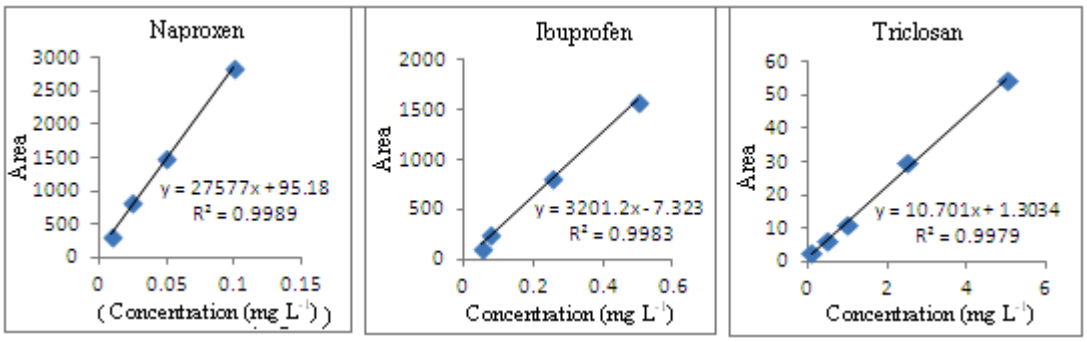


Figure 5.18: Typical calibration curves for naproxen, ibuprofen and triclosan

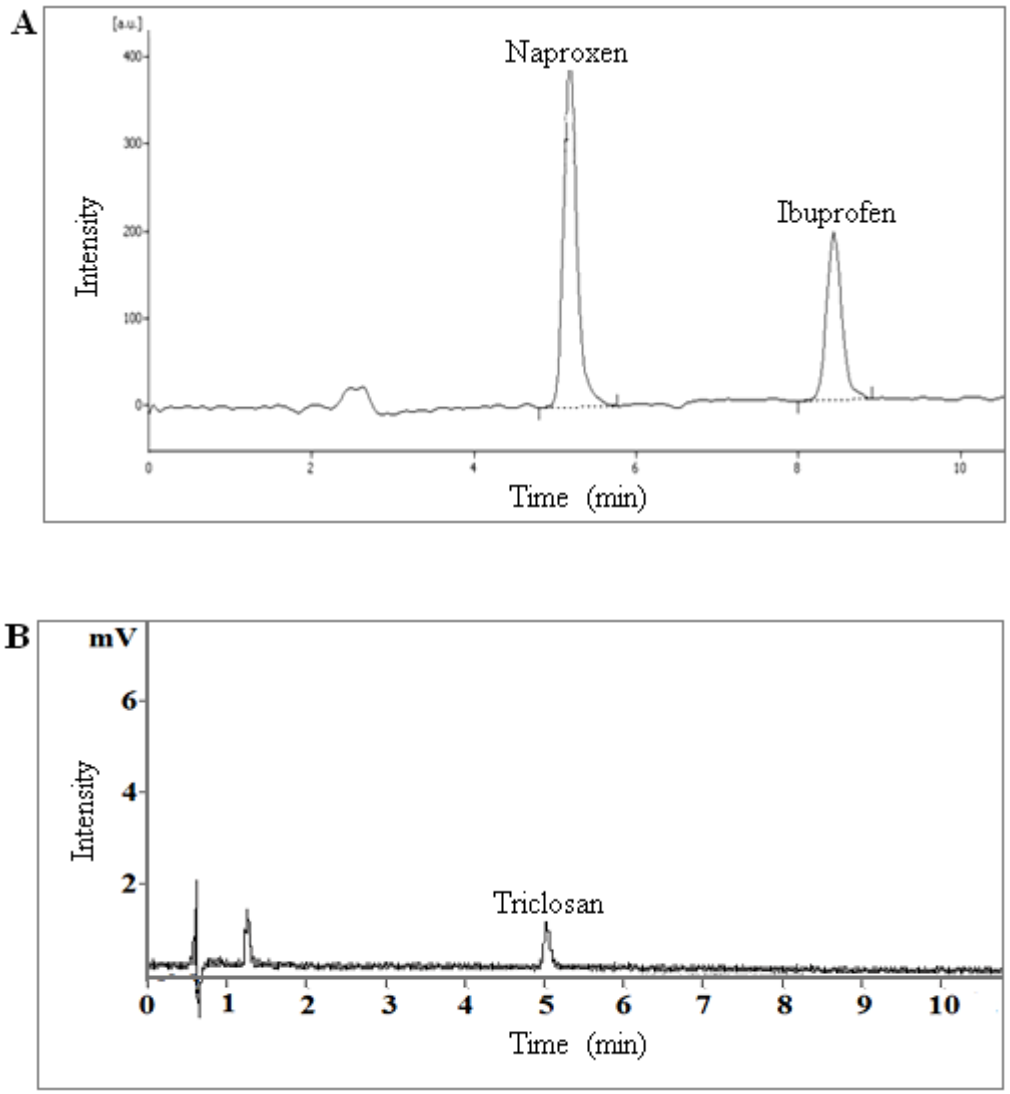


Figure 5.19: Typical chromatograms of standards containing (A) 0.05 mg L^{-1} naproxen and ibuprofen (B) 0.1 mg L^{-1} triclosan

5.3.2 Mass balance

In this study, mass balances (MB) for target compounds were determined. Equation 5.5 was used in this calculation.

$$MB = 100 \times \frac{M_A}{M_D} \qquad 5.5$$

Where M_A = [the amount extracted by POCIS + the mass in water at the end of the uptake experiment + the mass dissipated as measured from the control tank]; M_D = Initial mass of analyte prior to POCIS extraction.

The calculated mass balances for the PPCPs were as listed: naproxen (89%), ibuprofen (97%), and triclosan (64%). These values were comparable to those reported by Li et al. (2010). It was observed that triclosan gave a relatively lower mass balance than the pharmaceuticals. This may have been due to degradation of the compound after sequestration by the sorbent or thereafter. Indeed, Macleod et al. (2007) also reported a low mass balance for triclosan and they attributed it to the instability of the compound and/or poor recovery during POCIS extraction.

5.3.3 Uptake kinetics of the PPCPs and Sampling rate

As observed by Li et al. (2010), determination of PPCP uptake by POCIS can be based on the decline in water concentrations over time, or the amounts of analytes sequestered by the sorbent in POCIS over the exposure period (Mazzella et al., 2007; Togola and Budzinski, 2007). In the present study, R_s of target compounds were calculated using the decrease in analyte water concentrations over time i.e. $\mathrm{Ln}[C_w(t)/C_w(0)]$ (equation 5.2). Loss of all the three analytes from the fortified water was linear over the entire 7-day extraction period. Figure 5.20 (A - C) presents a plot of $\mathrm{Ln}C_w(t)/C_w(0)$ against exposure time used to determine the loss of the PPCPs as a result of POCIS uptake over 7 days at 25^0C.

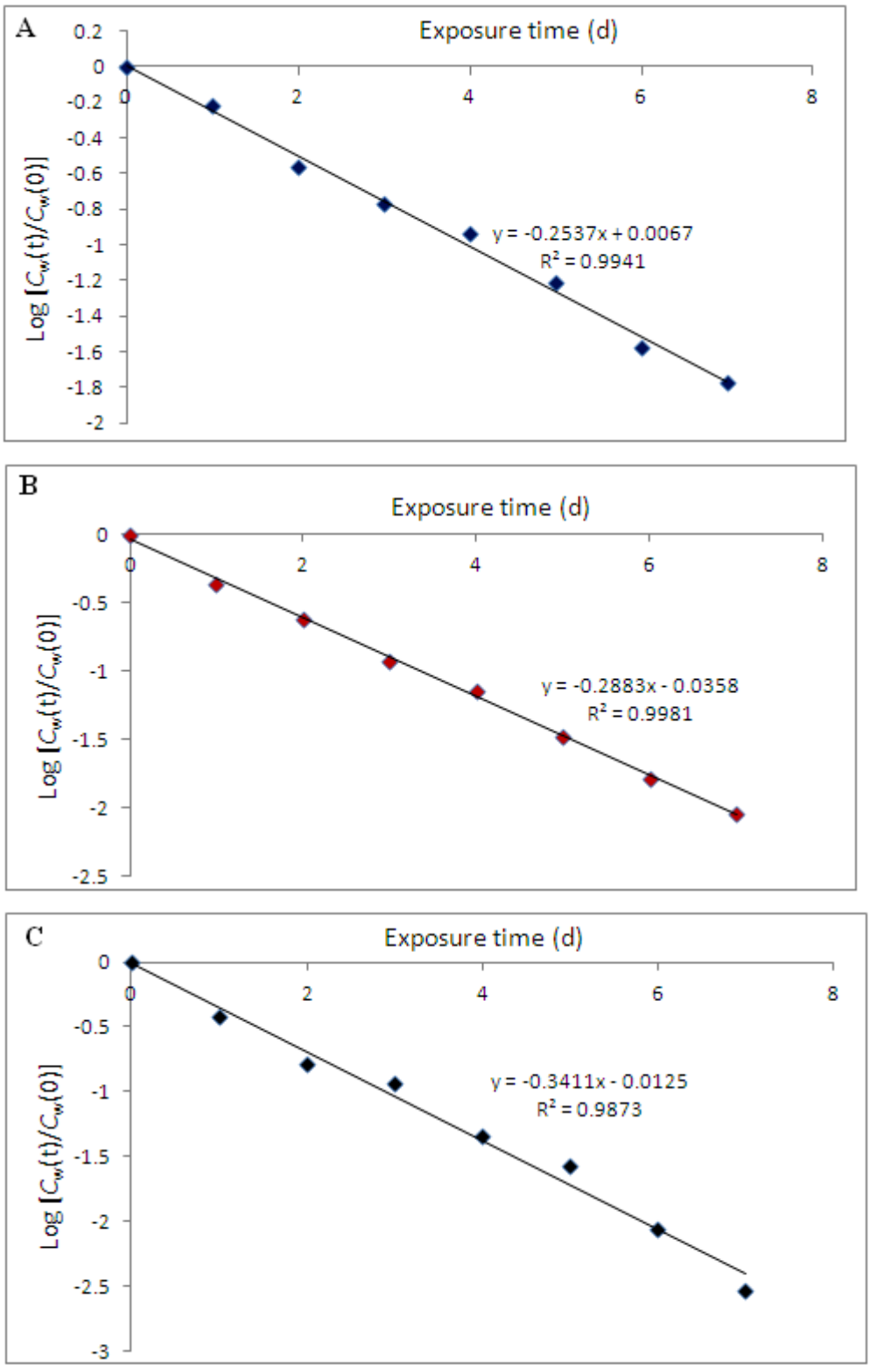


Figure 5.20: Plots of LnC_w(t)/C_w(0) vs exposure time for experiments used to determine the loss of naproxen (A), ibuprofen (B) and triclosan (C) as a result of POCIS uptake over 7 days at 25^0C

Good correlation coefficients of the linear regressions were obtained with r^2 for individual compounds being 0.994 for naproxen, 0.998 for ibuprofen and 0.987 for triclosan.

Estimated uptake rate constants obtained from the accumulation of the analytes in POCIS over time had good precisions as shown by their relative standard deviations from triplicate determinations (all < 10%). Analyte R_s values determined at 25^0C under quiescent and stirred conditions are presented in Table 5.24. Quiescent conditions produced R_s values for individual PPCPs that were in the range of 0.087 to 0.383 L d^{-1}, whereas, stirred conditions gave values that were between 0.125 and 0.936 L d^{-1}. This study yielded R_s values that were consistent with those obtained from similar calibration set-ups elsewhere.

Table 5.24: Sampling rates (R_s) determined from quiescent and stirred Polar organic chemical integrative samplers (POCIS)

	Sampling rates (L d^{-1})			
Compound	Quiescent	Stirred	MB	Literature
Naproxen	0.087 ± 0.014	0.125 ± 0.048	89	0.166 (±0.053)[a]; 0.392 (±0.024)[b]; 0.298 (±0.016)[b] 0.170 (±0.038), 0.11[c]
Ibuprofen	0.102 ± 0.019	0.182 ± 0.037	97	0.348 (± 0.052)[b]; 0.254 (±0.019)[b]; 0.17[c]
Triclosan	0.383 ± 0.115	0.936 ± 0.116	64	1.929 (±0.232)[b]; 1.442 (±0.105)[b]; 1.920 (±0.620)[a]

(MB: mass balance (%); [a]Macleod et al., 2007; [b]Li et al., 2010; [c]Togola and Budzinski, 2007).

Except for triclosan, the results for naproxen and ibuprofen are in agreement with those reported by Macleod et al (2007), and Togola and Budzinski (2007).

However, R_s values for all the three compounds were significantly lower than those obtained by Li et al. (2010). These differences may have arisen because the authors utilised more vigorous stirring rates (800-900 rpm) in their experiments.

The influence of hydrodynamics on R_s was visible when values derived from quiescent and agitated conditions were compared. For all compounds, stirred extraction conditions gave significantly higher R_s values at 25^0C than quiescent water ($p<0.05$, paired t test). A less than three-fold increase in the R_s was observed between these conditions. This may indicate the influence of water boundary layer control in analyte mass transfer into POCIS (Alvarez et al., 2007; Mazzela et al., 2007; Togola and Budzinski, 2007). The influence of flow velocities on accumulation kinetics of hydrophobic compounds by SPMDs was been reported by Vrana and Schuurmann, (2002). SPMD sampling rates are affected by environmental exposure conditions by as high as ten-fold for flow effects and four-fold for temperature effects (Li et al., 2010). Comparatively, it seems the hydrodynamic effects on R_s are not as pronounced in POCIS as in SPMDs.

Two aliquots of 20 mL water excised from the test solution for analysis each day of the 8-day exposure period led to 11.6% reduction in the initial water volume. However, this did not significantly influence the calculated R_s for the compounds when compared to data obtained from a parallel experiment involving 5 days of exposure.

5.3.4 Correlation between R_s and physicochemical properties

Results from this study indicated an increase in the PPCP R_s with increasing hydrophobicity of the compound (as shown by its log K_{ow} value). Thus, triclosan for instance, characterised by the least polarity among the analytes of interest, exhibited the highest R_s value. A plot of the R_s obtained from naproxen, ibuprofen and triclosan at 25^0C under stirred conditions against their log K_{ow} (R_s vs log K_{ow}) values, generally gave a linear relationship between the two parameters for the

two groups of test compounds (Figure 5.21). However, this argument may not be conclusive as only two acidic pharmaceuticals and one personal care product was used in the present study. For a better understanding, more compounds from each group need to be used.

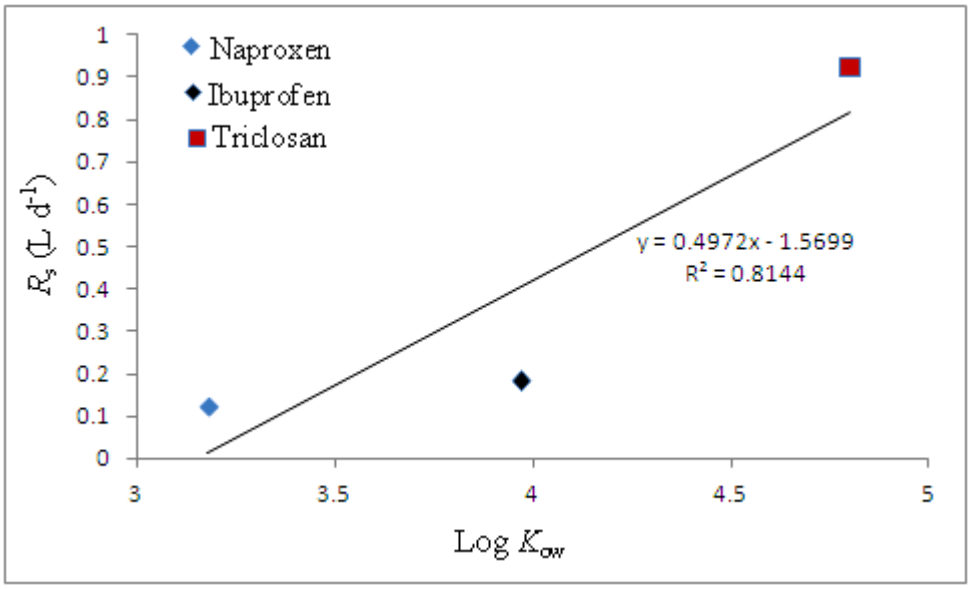


Figure 5.21: Relationship between the compounds polarity and sampling rate in PPCPs as sampled using POCIS

As Li et al. (2010) also observed, the increase in R_s values with increasing log K_{ow} was apparently small for naproxen and ibuprofen. The prevailing pH conditions in the sample medium may have had an influence on R_s of the acidic drugs. Typically, low pH values (< 3) favour their existence molecular forms but at higher pHs (> 7), they get ionised. The difference in uptake of neutral and ionic species by POCIS may arise from the diffusion processes through the membrane and the properties of the mixed phase (HLB) sorbent that is used in POCIS (Li et al., 2010). This polymeric sorbent exhibit both hydrophilic and lipophilic retention characteristics and retention is improved when analytes exist in neutral states. Thus, adsorption of acidic compounds is enhanced after adjusting the water samples to low pH, and for basic analytes, to high pH (Waters Oasis HLB disks Care and Use Manual, 2012).

The R_s value for triclosan (0.936) obtained under stirred conditions was about 5-fold that of ibuprofen although their log K_{ow} values differ by by a small margin (0.83 units). This log K_{ow} difference is comparable to the one observed between ibuprofen and naproxen (0.79) and yet their R_s values are almost similar. It is therefore not clear why triclosan was sampled at rates higher than would be predicted from log K_{ow} (Figure 5.16).

Relationships between R_s and log K_{ow} in hydrophobic organic compounds have also been observed in other passive samplers. Huckins and co-workers (1999) in a study of PAH uptake by SPMDs reported the presence of a linear relationship between R_s of the compounds and their log K_{ow}. Similar observations have also been reported for hydrophobic compounds with log K_{ow} values ranging between 3.5 and 5 while using SPMDs (Vrana et al., 2006).

5.3.5 Field deployment of pharmaceutical POCIS

5.3.5.1 Occurrence of PPCPs in POCIS extracts

The laboratory-derived R_s values were applied in the estimating TWA concentrations of analytes based on amounts sequestered by POCIS. The samplers were deployed for 14 days at two WWTPs located around Johannesburg city. The deployment exercise was undertaken in September 2012 and average water temperatures at both treatment plants remained relatively stable (20 ± 2^0C) over the entire deployment period. Mean pH values at Goudkoppies and Northern WWTPs were between 7.9 to 8.2 and 8.1 to 8.4, respectively during exposure. Insofar as no analytes were detected in the field blank extracts, corrections were unnecessary. Estimated concentrations ($\mu g\ L^{-1}$) of the target analytes in both the treated effluent and influent in the sampling sites from the deployment exercise are presented in Table 5.25.

Table 5.25: Estimated mean concentrations of naproxen, ibuprofen and triclosan in wastewater (μg L^{-1}) from POCIS deployed in Goudkoppies and Northern WWTPs (n = 3)

Compound	Sampling site			
	Goudkoppies WWTP		Northern WWTP	
	Influent	Effluent	Influent	Effluent
Naproxen	55.02 ± 5.57	13.52 ± 0.79	52.33 ± 3.43	20.42 ± 2.89
Ibuprofen	39.77 ± 3.69	12.55 ± 2.87	111.89 ± 0.45	24.58 ± 2.03
Triclosan	78.41 ± 6.23	10.65 ± 0.48	127.65 ± 21.52	22.93 ± 4.04

Estimated concentrations of the PPCPs at Goudkoppies WWTP ranged from 39.8 to 78.4 μg L^{-1} in the influent and 10.6 to 13.5 μg L^{-1} in the treated effluent. On the other hand, Northern WWTP yielded target analytes which ranged in concentration from 52.33 to 127.65 μg L^{-1} (influent) and 20.42 to 24.58 μg L^{-1} (effluent). As expected, lower contaminant levels were found in the effluent than in the influent, courtesy of degradation and removal activities occurring during the treatment process.

A comparison of analyte levels in the influents of both treatment plants showed that Northern waste works consistently gave higher levels than Goudkoppies WWTP. A similar trend was also evident in the effluent. While the differences in influent analyte concentrations may be ascribed to the nature of the population served by the WWTP, levels in the treated effluent can be explained by the treatment processes applied at the individual facility.

PPCP levels in the influent of Northern WWPT may be explained as follows: In addition to collecting sewage from the upmarket residential estates such as Sandton, Randburg, Bedfordview, Edenvale, Germiston and the northern areas of Johannesburg, this plant also receives and treats domestic sewage from Alexandra, one of the biggest townships in the country. In essence, the plant handles mainly domestic sewage from a population of close to one million people.

Moreover, other diffuse sources that include discharges from several hotels and restaurants, hospitals and clinics, and some industries may be adding to the contaminant load.

On the other hand, Goudkoppies WWTP serves the city centre and the south eastern areas of Johannesburg. A significant portion of its sewage is of industrial origin with household and hotel sources accounting for a smaller percentage. Its catchment area is generally smaller than for the Northern treatment plant and the human population involves is likewise smaller.

5.3.5.2 SPE extraction versus POCIS estimates

A comparative evaluation was made between the POCIS-derived water concentrations and average values from SPE extraction of grab samples. Data from triplicate sets of analyses obtained from spot samples at the times of deployment and retrieval were averaged (n = 6) and compared with TWA concentrations from POCIS. Figure 5.22 presents the estimated TWA PPCP concentrations from POCIS compared with the mean concentrations obtained from grab samples at Goudkoppies WWTP, while a similar presentation for the analytes at Northern WWTP is shown in Figure 5.23. Sample chromatograms for the compounds are shown in Figure 5.24. The estimated water concentrations of the PPCPs were comparable to those obtained from spot samples, although the latter, generally, gave higher levels than the former. Based on the relative agreement in analyte concentrations between these two techniques, it can be inferred that the laboratory-derived R_s values were within reasonable limits and, hence, appropriate for determination of TWA concentrations.

Although complete characterisation of temporal trends in analyte concentrations is not possible with grab sampling, the approach, however, provides a general picture of the concentration ranges at the sampling location.

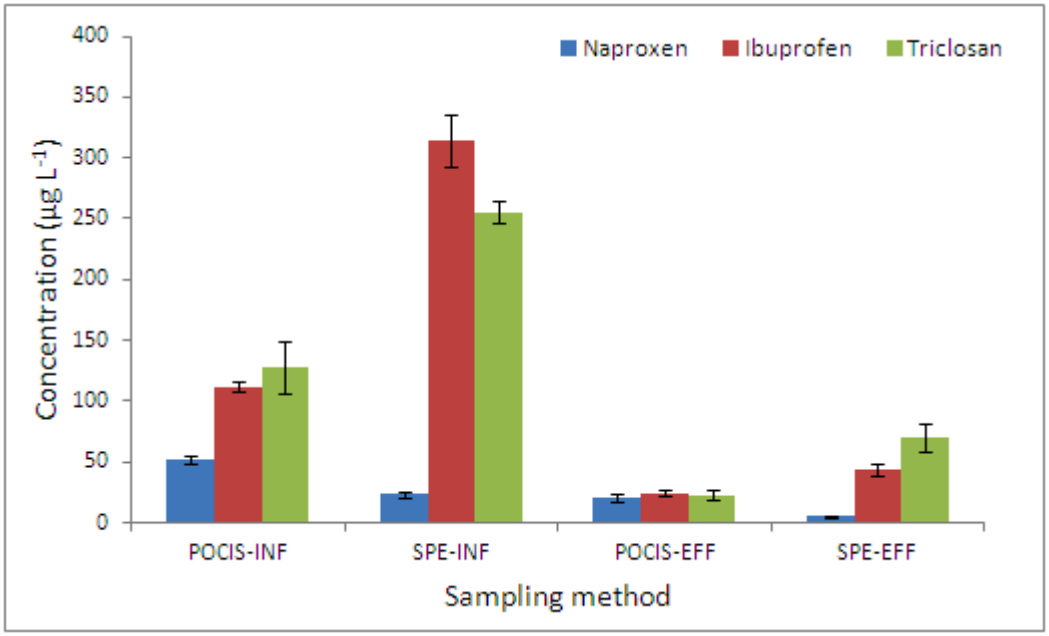


Figure 5.22: Estimated PPCP concentrations in wastewater from POCIS data compared with the mean concentrations obtained from grab samples at Goudkoppies WWTP

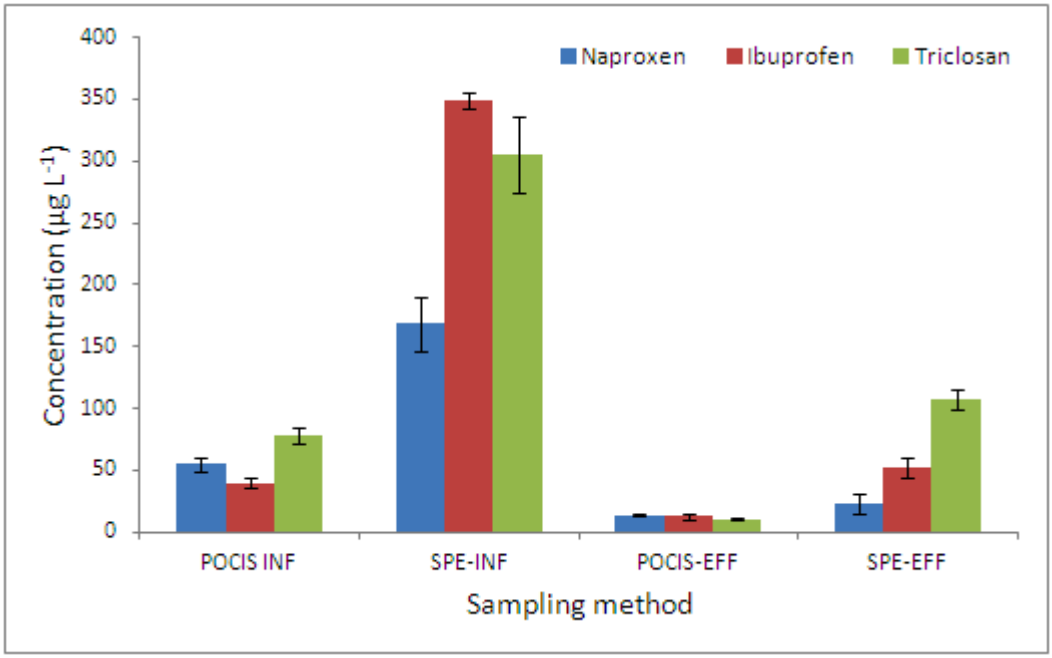


Figure 5.23: Estimated PPCP concentrations in wastewater from POCIS data compared with the mean concentrations obtained from grab samples at Northern WWTP

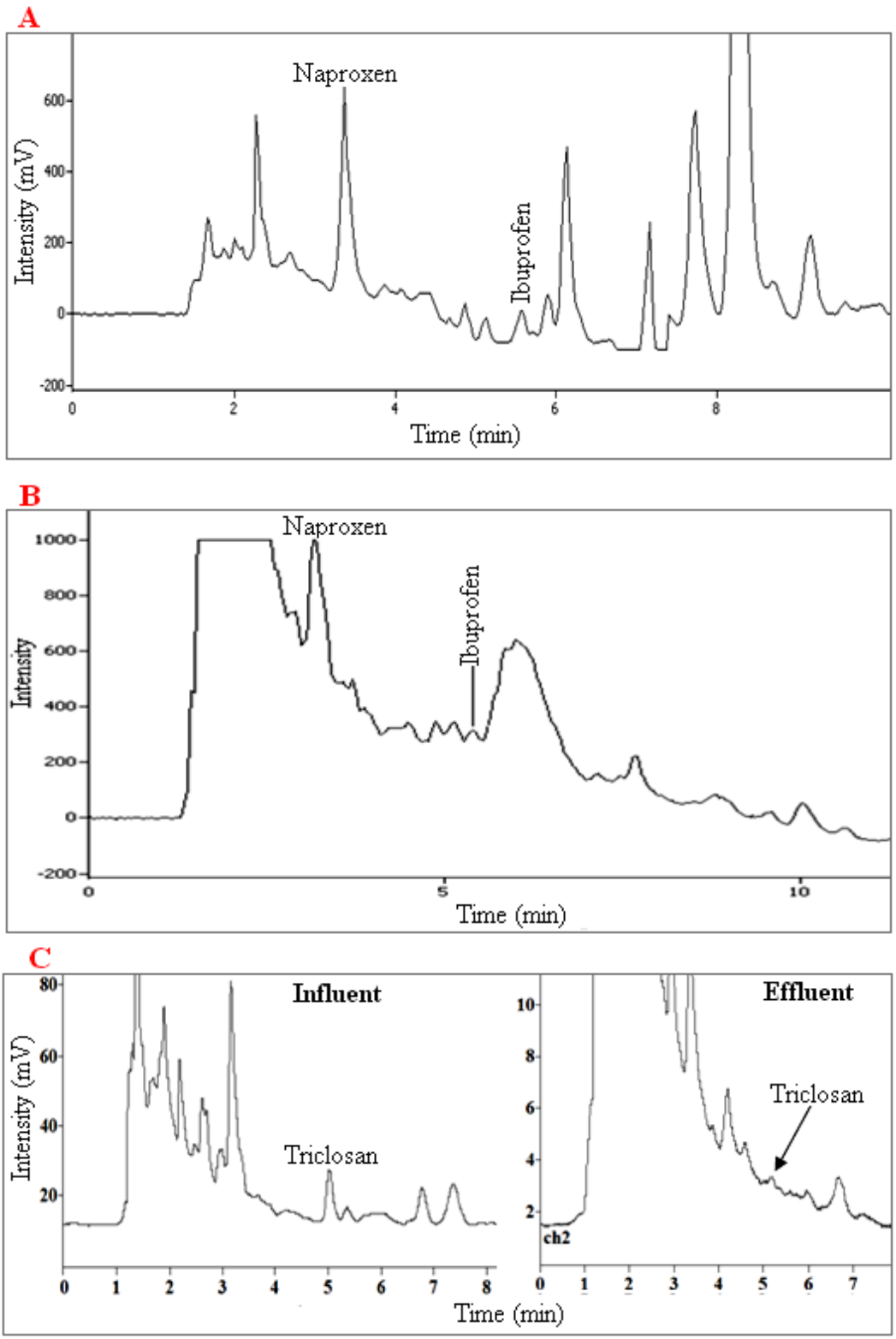


Figure 5.24: Sample chromatograms of extracts from POCIS deployed in Northern WWTP: (A) and (B) naproxen and ibuprofen in influent and effluent, respectively, and (C) triclosan in influent and effluent.

Obtaining TWA concentrations of analytes over the deployment period are not a practical possibility from spot samples. The majority of TWA concentrations estimated using POCIS were lower than for spot samples. Apart from SPE's ability to extract both the freely dissolved and particle bound analyte fractions, a host of several extraneous environmental factors such as temperature changes, biofouling and sample turbulence not adequately accounted for in the laboratory calibration may have affected analyte levels as determined by POCIS.

Estimates of aqueous diffusion coefficients (D_w) based on Hayduk and Laudie model, suggest a 30% increase in diffusivity and, hence, R_s for small molecule PPCPs from 10 to 20^0C and 75% from 10 to 30^0C (Macleod et al., 2007; Alvarez et al., 2005). During deployment, field temperatures were found to be generally close to laboratory temperatures, and serious fluctuations were not witnessed. Therefore, it is suggested that, influence of temperature on field R_s may not have been a major factor in the present study.

Biofouling of the field deployed samplers can reduce the R_s values and hence, uptake of analytes by POCIS. It does this by enhancing resistance to mass transfer of the compounds into passive samplers (Vrana et al., 2005; Huckins et al., 2002; Alvarez, 1999). As the fouling layer is largely composed of organic material, the effect will be more pronounced in less polar analytes (Harman et al., 2009). However, all the target compounds studied had log K_{ow} values less than 6 (Table 2.10), and as proposed by Huckins et al. (2002), this figure is the lower limit at which fouling by microorganisms is expected to significantly affect R_s of compounds. Furthermore, the PES membrane used in POCIS is known to resist fouling (Morin et al., 2012; Alvarez et al., 1999).

The retrieved POCIS samplers did not show extensive biofouling, but the deployment cages had considerable deposits of biotic and inorganic material on its surface to varying degrees by site. Samplers deployed at Northern WWTP were found to be more fouled than their Goudkoppies WWTP counterparts. Being the

most hydrophobic compound among the target analytes, triclosan was expected to suffer from the effects of biofouling most. Although lower analyte levels were obtained from POCIS in comparison with spot samples, there was no evidence linking increased hydrophobicity of the analyte with lower R_s. Thus, it appears that the influence of biofouling on the results in this study may not have been severe. Nonetheless, a greater understanding of the influence of membrane fouling on the uptake and hence, R_s, of polar compounds by POCIS is required.

The flow velocity prevailing at the sample site is known to profoundly influence R_s (Booij et al., 2007) and, actual field conditions encountered during deployment are not exactly identical to laboratory conditions. The observed discrepancies between TWA and spot sample concentrations in this study may be associated with differences in flow rates between laboratory calibration and field conditions. An overestimated R_s value is obtained if the laboratory calibrated sampling rate is too low (Macleod et al., 2007) and is underestimated if the calibrated R_s is too high. TWA concentrations for the PPCPs from Goudkoppies and Northern WWTPs effluents based on the laboratory-derived R_s resulted in TWA concentrations that on average ranged between 40 and 65% lower than the concentrations determined from the grab samples. It is therefore possible that during deployment of POCIS, the hydrodynamics in the field may have been different from laboratory calibration values. To overcome challenges associated with biofouling and flow velocities, the ideal approach is to incorporate performance reference compounds (PRCs) as has been done in other passive samplers such as SPMDs (Vrana et al., 2005; Huckins et al., 2002). Unfortunately, suitable pharmaceutical PRCs that will significantly desorb from the POCIS sorbent are yet to be found (Morin et al., 2012; Alvarez et al., 2004).

SPE technique targets the truly dissolved, particle-bound and colloidal-sorbed fractions of the analytes. Conversely, the POCIS method samples only the water-borne fraction of the compounds. Typically, higher analyte concentrations are obtained in SPE due to their exhaustive extraction capability. The observation was

clearly demonstrated in this study where SPE estimated water concentrations were up to two-fold the POCIS estimates.

5.3.6 Conclusions

In this work the applicability of POCIS for determining two acidic drugs (naproxen and ibuprofen) and one personal care product (triclosan) in wastewater was assessed. Laboratory calibration of POCIS under the optimised conditions produced sampling rates (R_s) for target compounds that ranged between 0.087 to 0.383 L d^{-1}, and 0.125 to 0.936 L d^{-1} in quiescent and stirred conditions, respectively.

Field performance of the POCIS in wastewater effluent yielded estimated concentrations of the PPCPs that ranged from 10.7 to 13.5 μg L^{-1} and 20.4 to 24.6 μg L^{-1} in Goudkoppies and Northern WWTPs, respectively. Influent PPCP concentrations in both treatment plants did not exceed 127.7 μg L^{-1}. It was also apparent that Northern WWTP had higher analyte levels than Goudkoppies WWTP. It was thought that the bigger human population that releases its sewage to the treatment plant may have been the influencing factor.

Comparison of POCIS-estimated analyte concentrations with grab samples showed that values from the latter approach were up to two times higher than the former. Temperatures during laboratory calibration and in the actual field, as well as biofouling were not seen as significant contributors to the difference. However, flow rates in the sampling site may have been different from laboratory conditions. Differences in analyte concentrations were also attributed to the exhaustive nature of SPE technique. In general, these results showed POCIS' potentiality as a tool for assessing TWA concentrations of PPCPs in wastewater and especially, the freely dissolved fraction. Flow rate issues in the actual field environment can be dealt with by performing *in situ* calibration of the devices since, as of now, no PRCs for pharmaceuticals have been developed.

5.4 Development of a hollow fibre-based extraction method in combination with HPLC-UV and HPLC-FLD for determination of naproxen, ibuprofen and triclosan in wastewater

5.4.1 Analytical performance and quality assurance

Chromatographic analysis of the PPCPs was achieved by HPLC-UV/FLD and assessment of linearity was done using standard solutions in ACN. Standards whose concentrations ranged from 0.01 to 0.1 μg mL^{-1} for naproxen, 0.05 to 0.5 μg mL^{-1} for ibuprofen, and 0.1 to 5 μg mL^{-1} for triclosan were used. A calibration curve for each compound was constructed and all compounds exhibited a correlation coefficient (r^2) value greater than 0.996.

The instrumental limits of detection (ILOD) and quantification (ILOQ) were calculated as the analyte concentration that produced a signal to noise ratio (S/N) of 3 and 10, respectively. Together with the intra-day and inter-day precision, ILODs, ILOQs for each target compound are presented in Table 5.26. A chromatogram of the reagent water spiked with 0.1 mg L^{-1} standard analyte mixture is shown in Figures 5.25 A and B.

Table 5.26: Instrumental detection and quantification limits, linearity, and intra- and inter-day precision of HPLC-Fl method for the determination of naproxen and ibuprofen, and HPLC-UV for triclosan.

Compound	ILOD (μg L^{-1})	ILOQ (μg L^{-1})	r^2	Intra-day precision (%)	Inter-day precision (%)
Naproxen	0.8	3.0	0.998	4.4	6.8
Ibuprofen	2.2	5.3	0.999	3.7	4.6
Triclosan	5.0	16	0.996	3.9	5.5

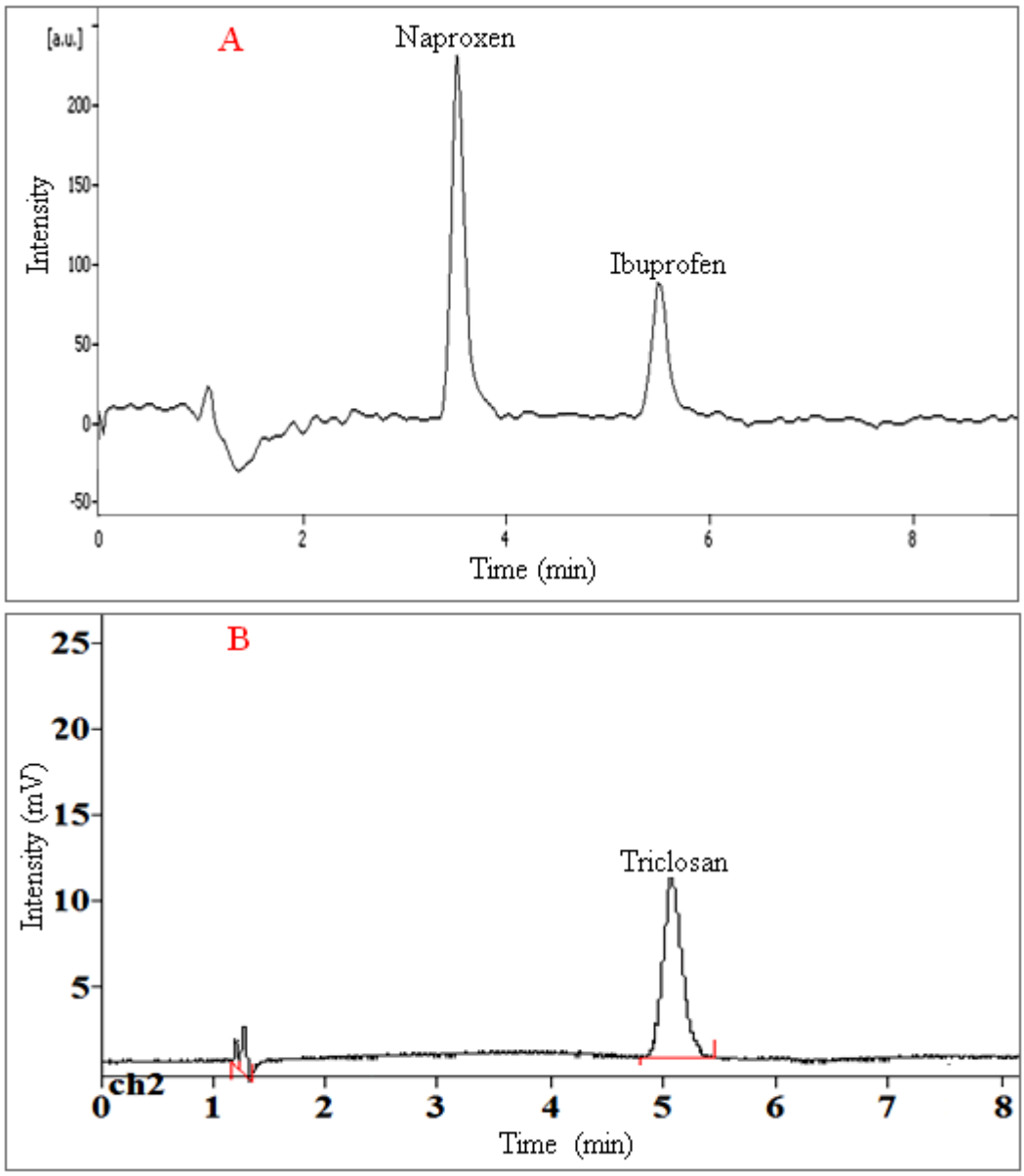


Figure 5.25: A chromatograms of (A) naproxen and ibuprofen in 0.05 mg L^{-1}, and (B) triclosan in 1 mg L^{-1} standard solutions.

5.4.2 Optimisation of the hollow fibre extraction method

In order to achieve the best extraction conditions by the hollow fibre, several parameters were optimised. Each of them is discussed in the following section.

5.4.2.1 Type of buffer used as acceptor phase

Two types of acceptor solutions i.e. ammonium carbonate [$(NH4)_2CO_3$] and disodium hydrogen phosphate [$(Na)_2HPO_4$] were compared based on their ability to trap naproxen, ibuprofen and triclosan from spiked reagent water. As shown in Figure 5.26, of the two, Na_2HPO_4 exhibited better trapping capability with the concentrations of the 3 PPCPs ranging from 0.19 to 5.09 mg L^{-1} over the exposure period in a 0.05 mg L^{-1} solution. These amounts were significantly higher than those accumulated in $(NH4)_2CO_3$ (0.16 to 1.43 mg L^{-1}). Both extractions were carried out under identical conditions.

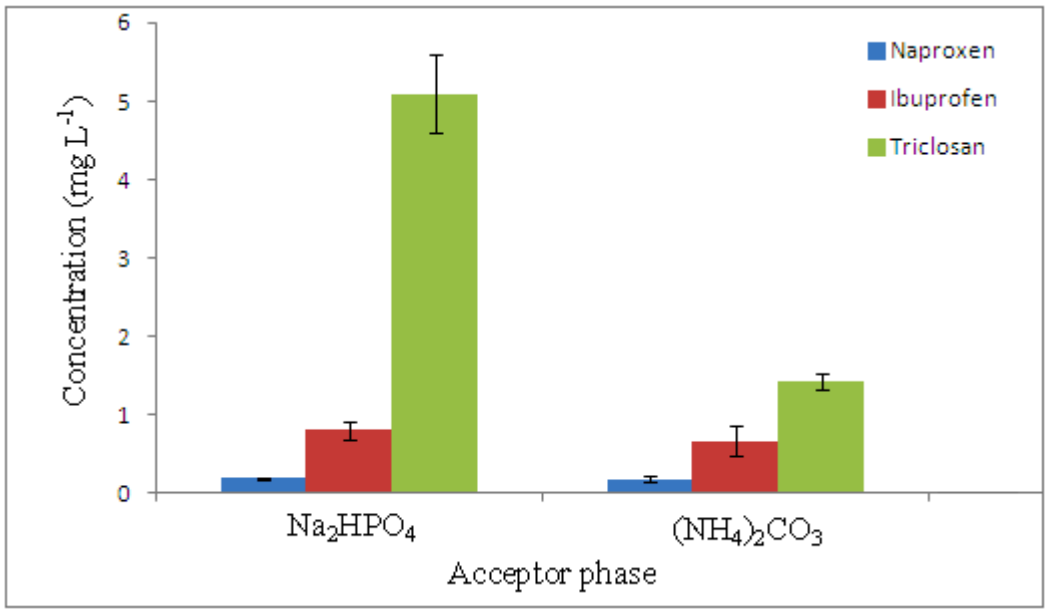


Figure 5.26: Effect of acceptor phase type on uptake of PPCPs by hollow fibre membrane. Each buffer had a concentration of 0.05 M.

In hollow fibre membrane techniques, the type of buffer chosen as the acceptor solution is critical. After diffusing through the membrane into the acceptor phase, stripping of the analyte occurs. Successful trapping occurs if all the analytes are completely ionised and retained on entering the acceptor phase. The concentration of the non-ionised compounds in this phase is therefore kept at zero, hence, maintaining a concentration gradient between the donor and acceptor phase (Nyoni et al., 2011). The difference in the extraction efficiencies of the two

buffers may be attributed to their buffering capacity. It seems that Na_2HPO_4 is able to maintain its buffering strength (given by its pH) for a longer period as compared to $(NH_4)_2CO_3$. Henceforth, experiments were conducted using Na_2HPO_4 as the acceptor phase.

5.4.2.2 Concentration of Na_2HPO_4 acceptor phase

Figure 5.27 shows the influence of acceptor phase concentration on uptake of the 3 PPCPs in a hollow fibre membrane system. In terms of the PPCP amounts accumulated by acceptor phases, ranking was as follows: 0.1 M Na_2HPO_4 < 0.25 M Na_2HPO_4 ~ 0.5 M Na_2HPO_4. Contrary to expectation, lower amounts of triclosan concentration were obtained in the 0.5 M acceptor solution as compared to the 0.25 M solution but the concentrations of naproxen and ibuprofen were not significantly different.

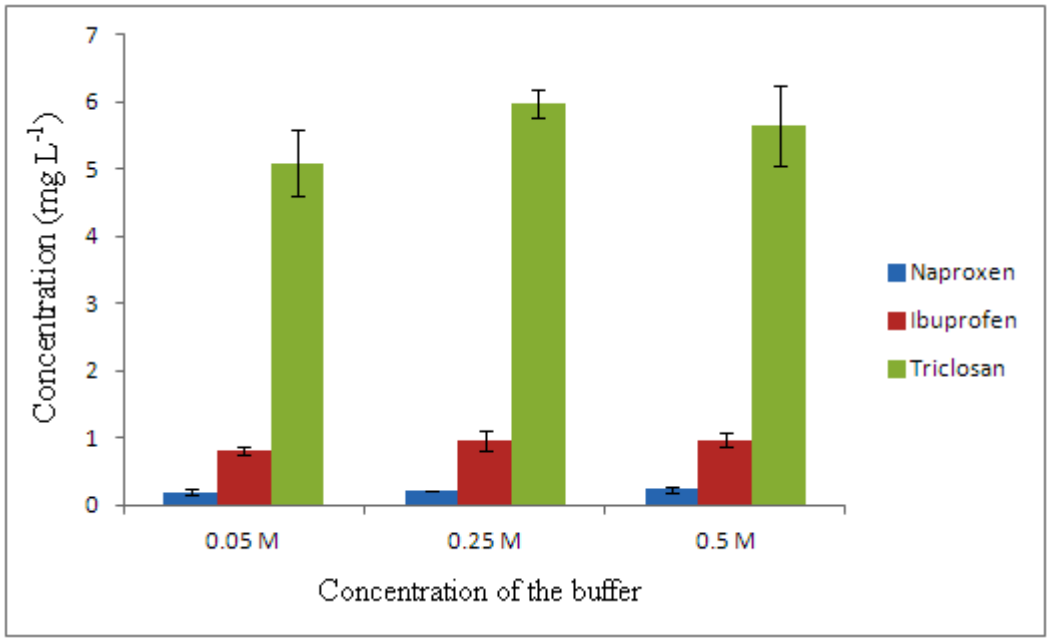


Figure 5.27: Effect of buffer concentration (Na_2HPO_4) on PPCP uptake by hollow fibre system exposed to 0.1 mg L^{-1} analyte solution (pH 7.2) for 24 hours.

Extraction of analytes in large sample volumes typically needs a more concentrated buffer (that has more hydroxyl groups, in this case). As Chimuka et

al. (1998) observed, such strongly concentrated buffers may be attractive in the context of long-term extraction processes or even in field sampling. With respect to triclosan extraction, it is suggested that the more concentrated 0.5 M Na_2HPO_4 solution may have encouraged degradation of the already sequestered analyte, thus, leading to the smaller amounts detected.

However, this observation requires further investigation in order to arrive at a more conclusive reason. Based on these findings, further experiments on PPCP extraction using the hollow fibre were conducted using 0.25 M Na_2HPO_4 as the acceptor solution.

5.4.2.3 Use of dihexyl ether (DHE) as an organic solvent

Figure 5.28 (A) presents concentrations of analytes extracted over time where the hollow fibre pores were impregnated with either dihexyl ether (DHE) or reagent water prior to application as described in section 4.3.5.1. Here, extraction of the analytes in both set-ups was monitored over a six-hour period. Figure 5.28 (B) shows the effect of prolonged extraction period (24 hours) on the effectiveness of DHE solvent as a membrane as compared to water. It was observed that in the first 4 hours of exposure, mass transfer of the analytes was significantly enhanced by use of DHE membrane. Thereafter, analyte uptake by the water-based hollow fibre membrane was superior. All extractions were done under stirred conditions at about 20 ± 2^0C. Extraction of the compounds for 24 hours under similar conditions indicated that fibre with DHE did not show any clear advantage over the water impregnated hollow fibre.

In conventional three-phase supported liquid membrane (SLM) technique, the organic solvent plays an important role in analyte extraction. The analyte is initially partitioned into the organic membrane before it is stripped into the aqueous acceptor phase.

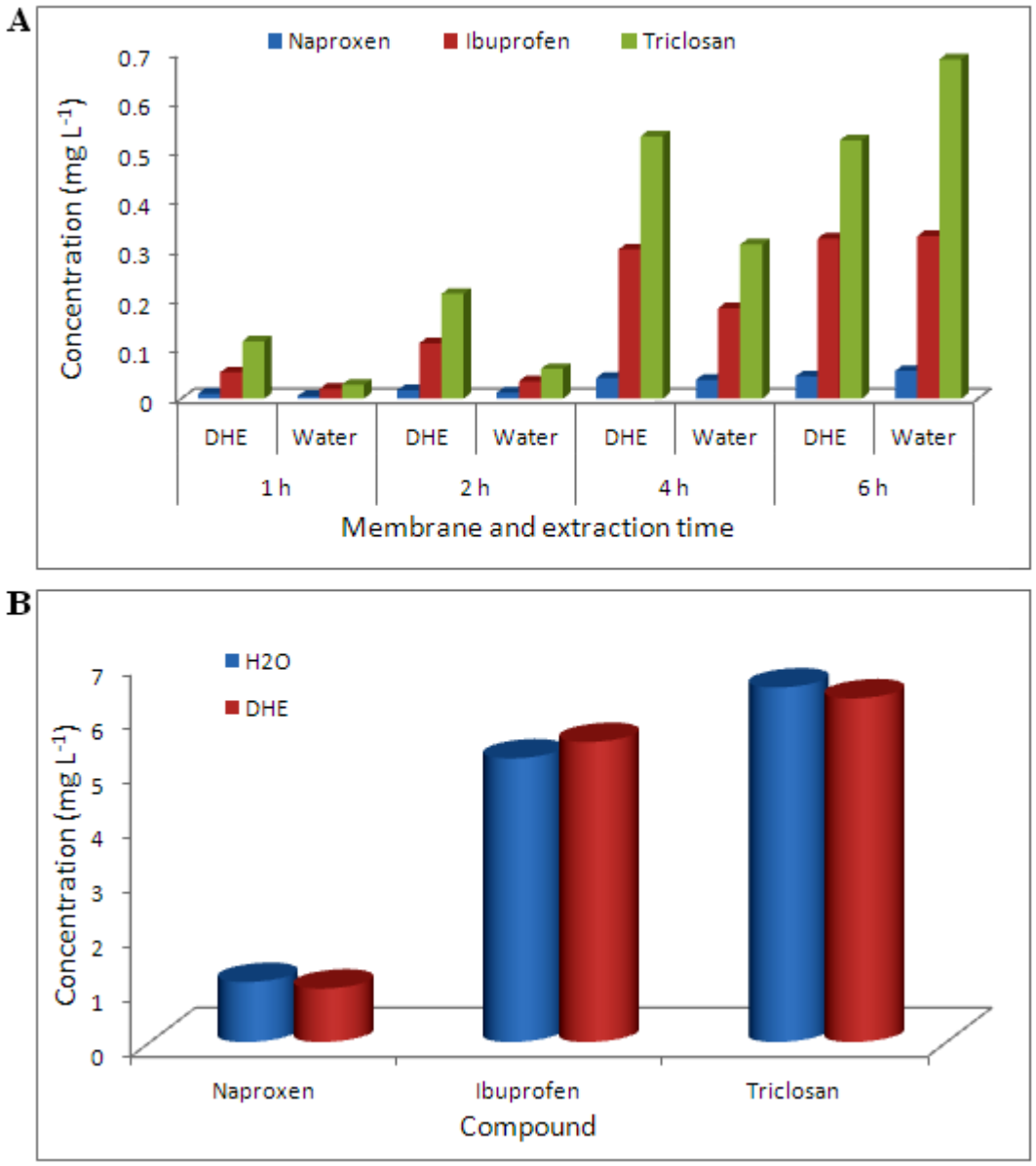


Figure 5.28: Effect of DHE on PPCP uptake by silicone hollow fibre in 0.1 mg L^{-1} analyte solution (pH 7.2) under stirred conditions (A) exposure over 6 hours (B) 24-hour extraction period.

Choice of the membrane solvent is guided by the physico-chemical properties of the analytes and sample matrix, as well as water solubility of the solvent (Chimuka, 2001; Jonsson et al., 1993). In addition, the volatility and the viscosity of the solvent are factors that can modify its extraction efficiency (Sagrista, 2012).

In real environmental application of this technique, large quantities of aqueous

samples interact with the thin layer of organic solvent in the hollow fibre pores. Such large water volumes slowly, wash out the membrane over time. This process is speeded up if extraction is carried out in turbulent conditions and over extended periods.

In the present study, analyte extraction was done under stirred conditions and over long durations (24 hours). A combination of the effects of both factors appears to have contributed to the deterioration of the organic membrane, especially, after about 4 hours of extraction. It is predicted that after wearing out and exiting the hollow fibre pores, the DHE was mostly replaced by water molecules and extraction, albeit, using the aqueous solvent membrane continued. This justified carrying out further experiments using hollow fibres with water as the membrane, especially, after considering the cost implications associated with DHE.

5.4.2.4 Agitation of sample solution

The effect of donor phase agitation on analyte extraction was studied under quiescent and stirred conditions. Magnetic stirring of the sample was done at 400 rpm and all other extraction conditions were identical. Figure 5.29 presents the enrichment factors (E_e) of the analytes obtained under these two conditions. As expected, higher enrichment factors for all the target compounds were achieved under turbulent conditions. Sample stirring gave mean increases of 72%, 85% and 67% for naproxen, ibuprofen and triclosan, respectively.

In 3-phase SLM, agitation of the sample solution is supposed to improve mass transfer of analytes through the organic membrane and, ultimately, into the acceptor solution. For polar organic compounds that are sufficiently hydrophobic ($\log K_{ow} \geq 2.0$), the use of high sample flow rates yields higher enrichment factors and reduces the extraction time. However, for more polar compounds ($\log K_{ow} < 2.0$), the effect may not positive.

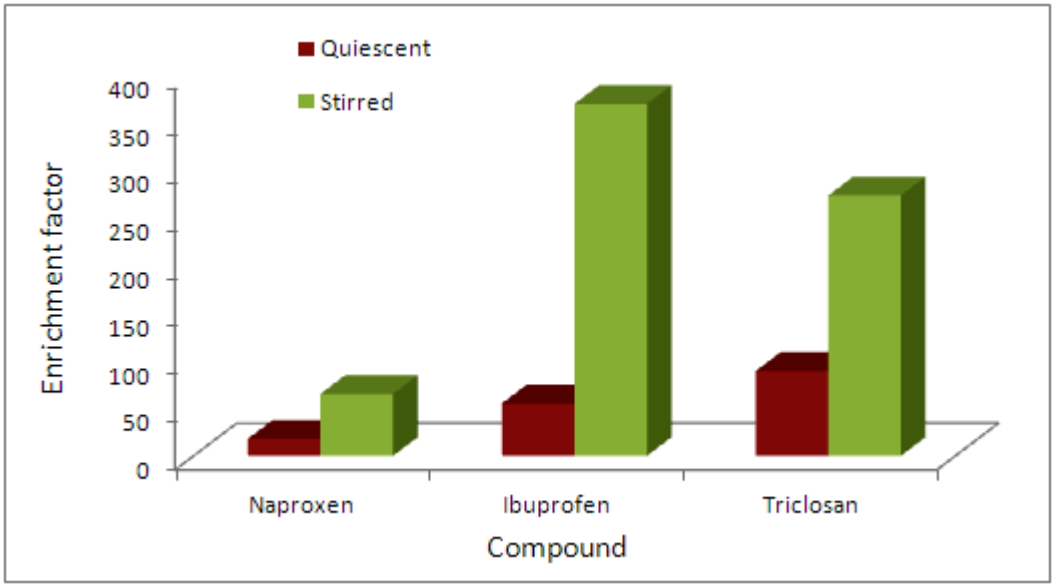


Figure 5.29: Effect of sample agitation on extraction of naproxen, ibuprofen and triclosan in spiked reagent water (pH 4) at a concentration of 0.1 mg L^{-1}.

Extraction efficiency of such analytes characterised by very low log K_{ow} values is controlled by their dissolution into the membrane (Jönsson et al., 1993). Increased contact time should be allowed for the compounds to dissolve into the membrane which may result into longer extraction periods since each degree of enrichment takes more time (Chimuka, 2001). In the current case, all the target compounds had Log K_{ow} values greater than 2 (Table 2.10) and an aqueous membrane was used. Thus, just like in other passive samplers (e.g. SPMDs), it can be inferred that diffusion through the water boundary layer is the limiting factor. Sample agitation thins this layer and therefore facilitates faster analyte diffusion into the membrane.

5.4.2.5 Donor and acceptor phase pH

In membrane extraction systems with pH gradient, the donor and acceptor phase pHs should be adjusted depending on the acidity or basicity of target compounds (Jönsson et al., 1993). Typically, for acidic compounds, the pH of the acceptor phase should be maintained at least 3.3 units higher than the pKa of the least acidic analyte, and vice versa for basic compounds (Chimuka et al., 2001). In essence, all analytes must be kept in their ionic form in the acceptor phase so as to

avoid re-extraction to the donor solution. For the purposes of this study, a pH of 11.0 was chosen calculated from 3.3 units above the pKa of triclosan (7.9).

On the other hand, the pH of the sample (donor) solution in the extraction of acidic analytes must be adjusted to at least 2 units below the pKa of the most acidic compound and at least 2 units above the pKa of the most basic compound. This is done to ensure that all the analytes are kept in their non-ionised state. For this reason, two pHs (2 and 4) were assessed. When the pKa values of the target compounds were considered (naproxen, 4.15; ibuprofen, 4.91; triclosan, 7.90), pH of the sample solution ideally ought to be adjusted close to 2.15.

However, contrary to expectation, the extraction efficiencies of the compounds in sample solutions adjusted to pH 2 were significantly lower than at pH 4 (Table 5.27). Results obtained showed up to a four-fold increment in enrichment factors of analytes when the donor solution was kept at pH 4 in comparison to pH 2. As mentioned previously, these observations may be resulting from analyte losses due to acid-mediated degradation processes. However, further studies on the degradation pathways and products of these analytes under the studied conditions need to be carried out.

Table 5.27: Effect of donor pH on extraction of naproxen, ibuprofen and triclosan in a 0.1 mg L^{-1} PPCP solution under stirred conditions (n = 3).

	Concentration (mg L^{-1})	
Compound	pH 2	pH 4
Naproxen	0.4	1.1
Ibuprofen	7.9	15.7
Triclosan	3.3	4.9

5.4.2.6 Extraction time

In order to study the influence of extraction time on uptake of analytes, reagent

water spiked at 5 and 50 µg L^{-1} constituting the 3 PPCPs was extracted for different durations ranging from 6 to 336 hours. Extraction was done in sample solutions at pH 7.2 (natural water) and another one whose pH had been adjusted to 4 (as described in section 5.4.2.4).

Extraction of sample solution at pH 7.2

Figure 5.30 shows the effect of the extraction time on the enrichment factors of the PPCP compounds where the pH of the donor phase was not adjusted (pH 7.2).

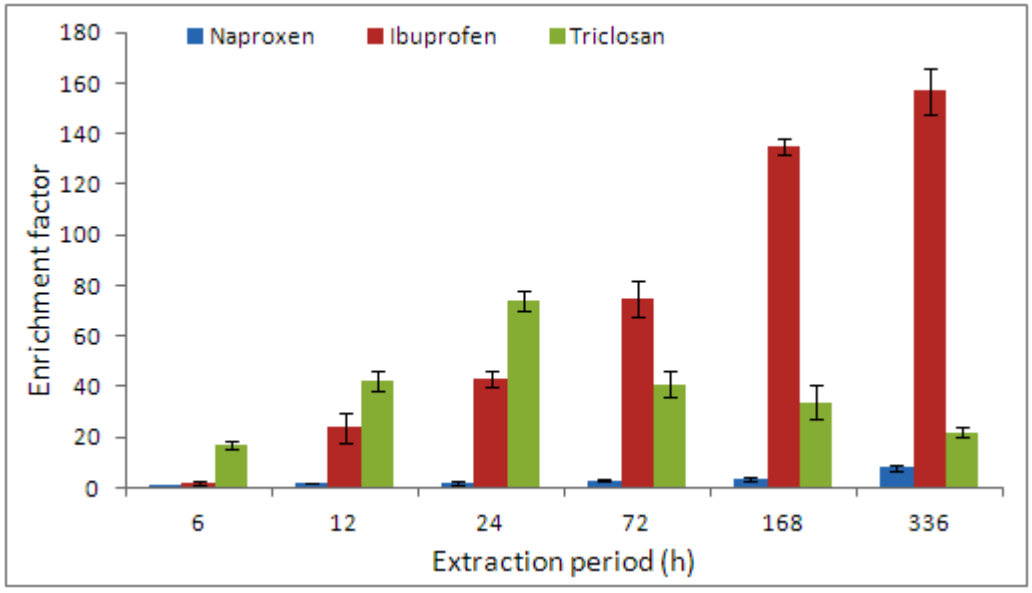


Figure 5.30: Extraction time profiles for naproxen, ibuprofen and triclosan in spiked reagent water (pH 7.2) at a concentration of 0.05 mg L^{-1}

Enrichment factors for naproxen and ibuprofen increased over the entire exposure period. However, triclosan's enrichment increased steadily up to 24 hours of extraction and thereafter started decreasing. This strange observation was attributed to either, loss of the sequestered analyte through degradation or/and decreasing buffering capacity of the acceptor phase due to protonation. Average enrichment factors for the PPCPs obtained after the 24-hour extraction were 2.1, 43 and 74 for naproxen, ibuprofen and triclosan, respectively.

These values were lower than those derived from an acidified (pH 4) sample solution. These findings indicate that the sorption capacity of the acceptor solution appears not to have been exhausted even after 336 hours of analyte extraction.

Extraction of sample solution at pH 4.0

The effect of extraction time on the enrichment factors of PPCPs when the sample solution was adjusted to pH 4 is presented in Figure 5.31. Enrichment factors for naproxen and ibuprofen increased linearly over the entire extraction period, indicating that no equilibrium condition had been attained by the end of the extraction.

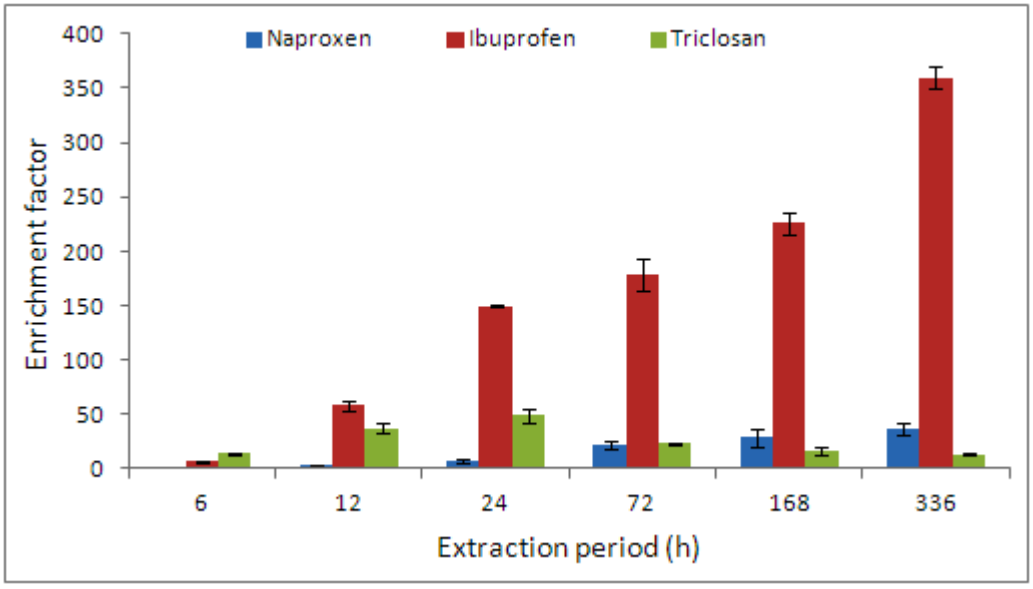


Figure 5.31: Extraction time profiles for naproxen, ibuprofen and triclosan in spiked reagent water (pH 4.0) at a concentration of 0.05 mg L^{-1}

Except for triclosan, average enrichment factors at this pH were generally higher by up to three times than was observed at non-acidified (pH 7.2) donor phase conditions. This clearly demonstrated that at a lower sample pH, the analytes are kept in their non-ionised forms which encourage their mass transfer across the membrane and into the acceptor phase.

Just like in the case where the donor phase pH was maintained at 7.2, maximum enrichment factors for triclosan peaked after 24 hours and thereafter decreased. The values obtained after the one day extraction period were 7 (naproxen), 157 (ibuprofen) and 65 (triclosan). Hence, further extractions were done for 24 hours at pH 4 for the sample solution.

Extraction of 5 and 50 µg L^{-1} PPCP solution at pH 4

Reproducibility of enrichment factors was tested by extracting reagent water containing 5 and 50 µg L^{-1} of the analyte mixture adjusted to pH 4 for 24 hours using the hollow fibre membranes. Findings of these experiments are presented in Table 5.28.

Table 5.28: 24-hour extraction of reagent water spiked with 5 and 50 µg L^{-1} PPCP mixture and adjusted to pH 4 (n = 3).

	Enrichment factor	
Compound	5 µg L^{-1}	50 µg L^{-1}
Naproxen	7 ± 0.3	11 ± 1
Ibuprofen	150 ± 23	157 ± 11
Triclosan	37 ± 4	49 ± 6

Expectedly, analyte concentrations extracted in the 5 µg L^{-1} sample were lower than in the 50 µg L^{-1} solution, but their enrichment factors were comparable. Average enrichment factors that ranged from 7 to 150 and 11 to 157 in the 5 and 50 µg L^{-1} donor phases, respectively, were observed. Differences in the enrichment factors of individual compounds between the two extractions did not exceed 25%. These laboratory-derived enrichment factors were then used to estimate water soluble concentrations of the analytes in actual field samples.

5.4.3 Field application

5.4.3.1 Occurrence of naproxen, ibuprofen and triclosan in the WWTPs

Samples were collected from similar WWTPs as investigated using POCIS (section 5.3). The wastewater treatment processes in the plants were previously described in sections 4.2.4.1 and 4.2.4.2. Upon completion of the treatment processes, effluent from Goudkoppies and Northern treatment plants are discharged to Klip and Juskei Rivers, respectively.

Influent and effluent wastewaters were analysed using the optimised hollow fibre extraction method. Grab samples from the WWTPs were collected in August and October 2012. Mean concentrations of the three PPCPs in the raw influent and treated effluent from both WWTPs are summarised in Table 5.29. Figures 5.32 and 5.33 displays sample chromatograms of the PPCPs in the wastewater samples of Goudkoppies and Northern treatment plants, respectively.

The highest concentrations in the influent correspond to triclosan followed by ibuprofen and eventually, naproxen.

Table 5.29: Estimated mean concentrations of naproxen, ibuprofen and triclosan in wastewater (μg L^{-1}) from Goudkoppies and Northern WWTPs (n = 3)

	Sampling site			
Compound	Goudkoppies WWTP		Northern WWTP	
	Influent	***Effluent***	***Influent***	***Effluent***
Naproxen	1.1 ± 0.16	0.4 ± 0.01	2.3 ± 0.11	0.8 ± 0.01
Ibuprofen	5.2 ± 0.49	1.1 ± 0.02	7.2 ± 0.59	1.6 ± 0.22
Triclosan	18.4 ± 1.37	2.7 ± 0.29	22.5 ± 1.08	6.1 ± 0.49

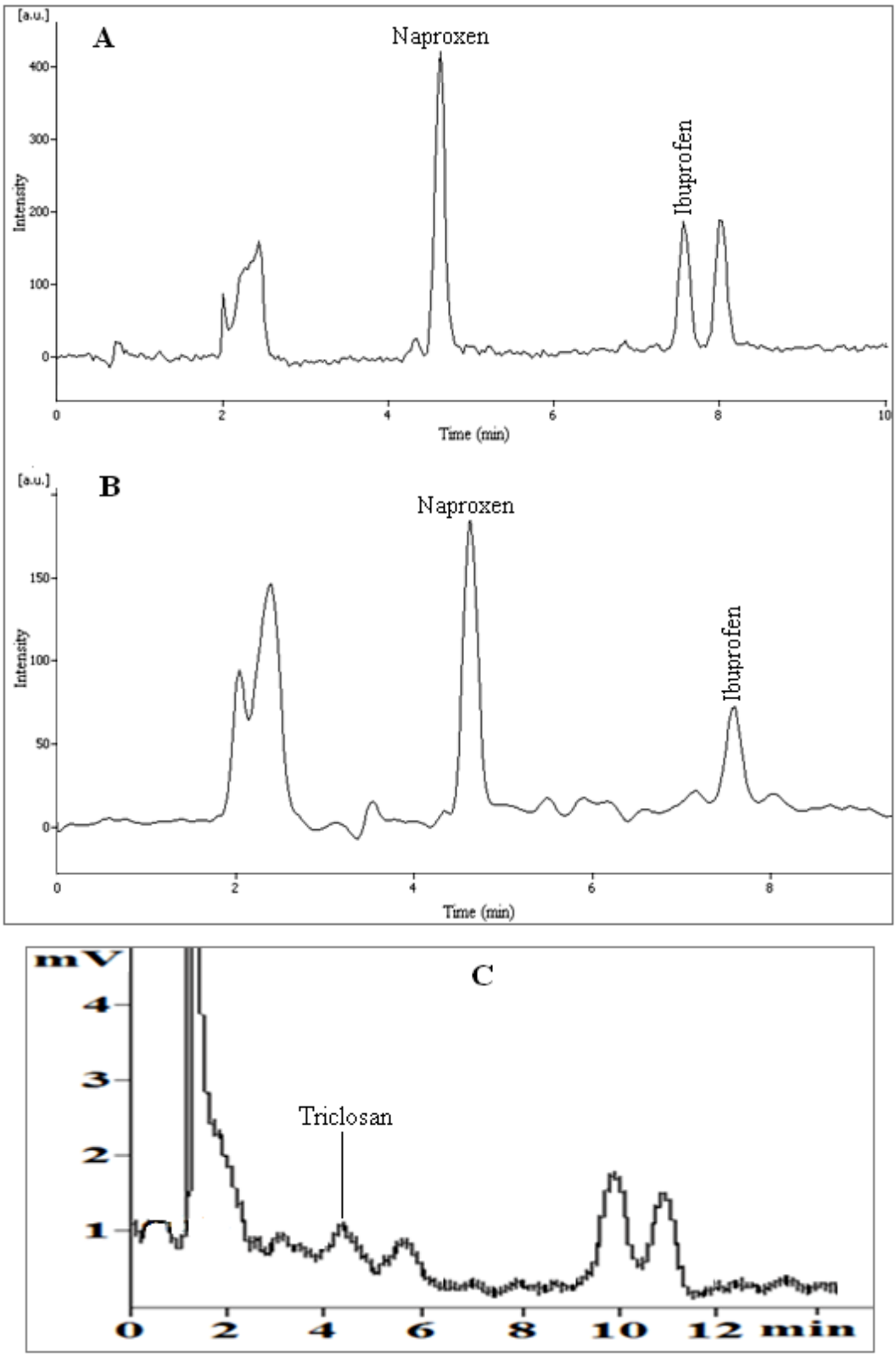


Figure 5.32: Chromatograms of naproxen and ibuprofen in (A) influent and (B) effluent, and (C) triclosan in effluent from Goudkoppies wastewater samples

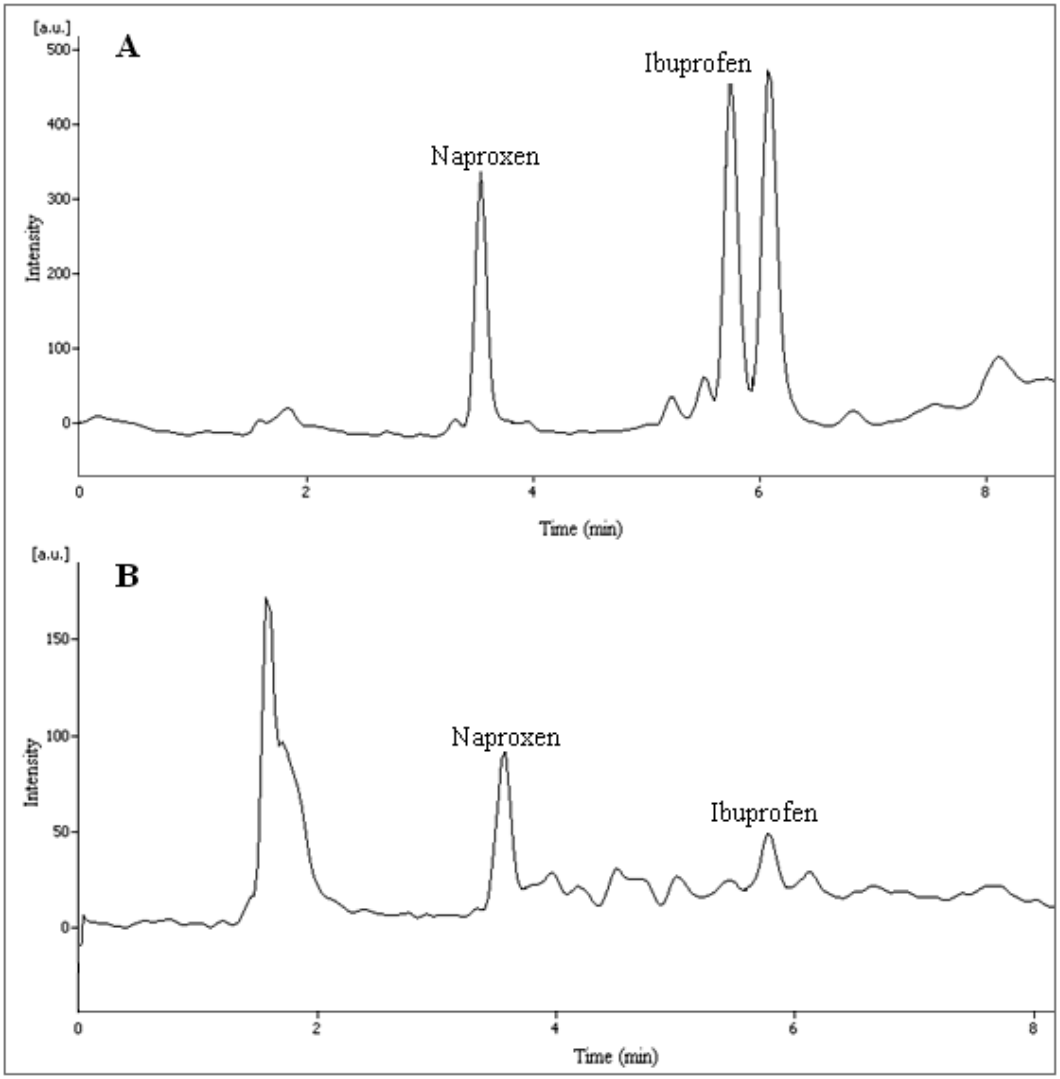


Figure 5.33: Chromatograms of naproxen and ibuprofen from Northern wastewater samples (A) influent (B) effluent

Average concentrations of the compounds in the influent of the two treatment plants were 1.7, 6.2 and 20.5 μg L^{-1} for naproxen, ibuprofen and triclosan, respectively. Mean analyte concentrations in the effluent of the two treatment plants were 0.6 μg L^{-1} (naproxen), 1.4 μg L^{-1} (ibuprofen) and 4.4 μg L^{-1} (triclosan). As previously seen in POCIS estimated concentrations, analyte levels in the influent of Northern waste works were higher than in Goudkoppies WWTP. A similar trend is also evident in the effluent. The concentrations obtained from the sampling sites were generally comparable to reported levels in the literature and are summarised in Table 5.30.

Table 5.30: Comparison of average PPCP concentrations from the current study with those reported in the literature.

Analyte	Present study *(S. Africa)*		Sagrista et al., 2013 *(Spain)*		Hordern et al., 2009 *(Netherlands)*		Heidler and Halden, 2009 *(Sweden)*	
	INF	EFF	INF	EFF	INF	EFF	INF	EFF
Naproxen	1.7	0.6	2.1	0.3	2.1	0.3	-	-
Ibuprofen	6.2	1.4	3.5	0.5	2.0	0.5	-	-
Triclosan	20.5	4.4	0.9	0.3	168.7	47.5	23.9	0.8

INF: influent, EFF: effluent

The higher PPCP concentrations in the influent of Northern WWTP were expected because, in addition to collecting sewage from the upmarket residential estates like Sandton, Randburg, Bedfordview, Edenvale, Germiston and the northern areas of Johannesburg, this plant also receives and treats domestic sewage from Alexandra, one of the biggest townships in the country. In essence, the plant handles domestic sewage from a population of close to one million people. On the other hand, the Goudkoppies WWTP serves the city centre and the south eastern areas of Johannesburg. A good portion of its sewage is of industrial origin and household sources account for a smaller percentage.

Among the target compounds, concentrations of triclosan were the highest in the influent and effluent of both treatment plants. As previously elaborated, this broad-based biocide is an important ingredient in many personal care and consumer products.

Their widespread application has made it one of the most ubiquitous contaminant found in virtually every domestic, industrial and hospital effluent. Its presence has also been detected in surface water (Hua et al. 2005) and biosolids (Sagrista et al., 2011; Ying and Kookana, 2007).

5.4.3.2 Temporal trends of PPCPs in Northern WWTP

A study was undertaken to investigate variations in PPCP concentrations in the influent of Northern WWTP during the day. Figure 5.34 presents the temporal trends of the average PPCP concentrations in the influent of the treatment plant sampled in the same day.

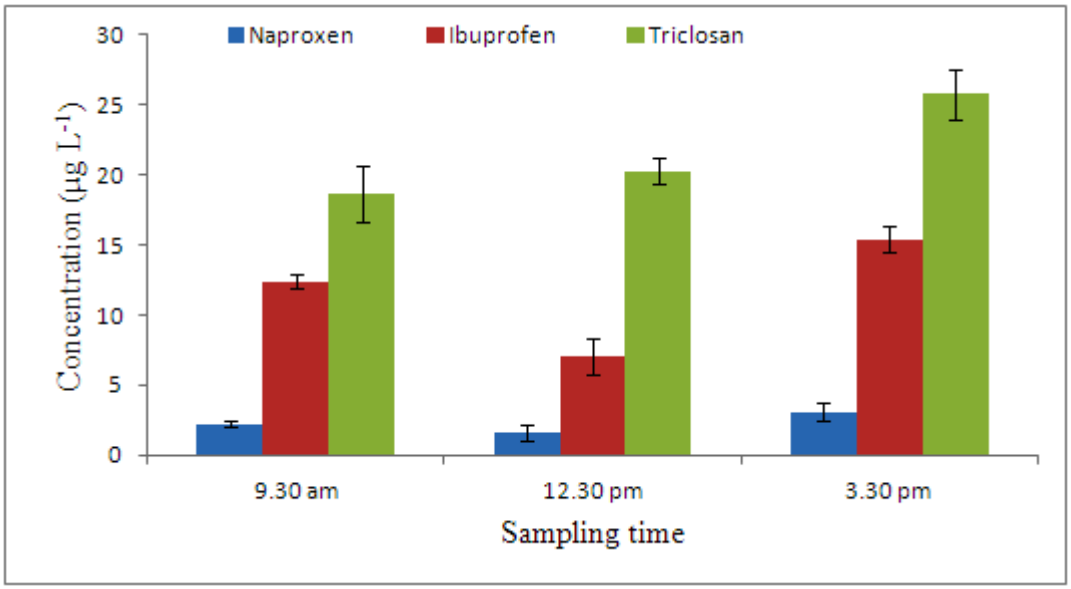


Figure 5.34: Temporal evolution during the same day of the average concentrations of the PPCPs detected in the influent of Northern WWTP

Mean analyte concentrations were found to range from 1.6 to 3.1 µg L^{-1} (naproxen), 7.1 to 15.4 µg L^{-1} (ibuprofen) and 18.6 to 25.8 µg L^{-1} (triclosan). Ranking of these concentrations with respect to their temporal evolution was in the order 12.30 pm < 9.30 am < 3.30 pm. A significant increase in the levels of each analyte was witnessed from 12.30 to 3.30 pm: naproxen (48%), ibuprofen (54%) and triclosan (28%).

Although the 3.30 pm wastewater samples gave the highest triclosan concentrations, the overall order slightly differed from that of the acidic drugs. Ranking of triclosan's average concentrations with time followed the trend: 9.30

< 12.30 < 3.30. Generally, higher concentrations of triclosan were recorded in the wastewater samples irrespective of the sampling time.

A similar study in a Spanish WWTP done by Sagrista et al. (2013) found out that the lowest and highest concentrations of naproxen and ibuprofen were detected at 9 am and 12 noon, respectively. However, triclosan was not included in the investigation.

As discussed previously, triclosan is a compound found in many consumer and personal care products and its availability at high concentrations in the wastewater samples is an indication of its widespread application. It also seems that, ibuprofen being a non-prescriptive drug, is widely consumed by the populace. It has been reported that, in the South African public sector alone, over 5 million prescriptions of this NSAID are made annually (WRC, 2013).

Considering the time lag between release of the PPCPs and discharge at the WWTP (situated close to 40 km from Johannesburg), it can only be speculated that most releases of the pharmaceuticals occur at around 1 to 2 pm. In most cases these drugs are taken in the morning, around lunch hour and in the evening. The relatively high concentrations detected at 9.30 am may be attributed to the morning time consumption of the drugs. The high triclosan levels registered at 3.30 pm may be linked to releases occurring in late morning to early afternoon, associated with, say, heavy utilisation of soaps and detergents containing the disinfectant in households, restaurants, hotels, and other general laundry activities.

This temporal study shows that fluctuations in analyte concentrations do occur and grab sampling may miss such episodic events. The problem could be remediated by using passive samplers that give TWA analyte concentrations over the exposure period.

5.4.3.3 Comparison of SPE and the hollow fibre method

Figure 5.35 shows the estimated analyte concentrations in wastewater by the hollow fibre extraction method compared with the mean SPE concentrations obtained from grab samples at the WWTPs. For all the compounds studied, the SPE method gave higher concentrations. However, as shown in Figure 5.36, cleaner chromatograms were obtained by the hollow fibre method, suggesting that this approach is suitable for determining the PPCPs in wastewaters. In general, lower analyte concentrations were detected using the developed method as compared to SPE. On average, SPE-derived influent PPCP concentrations ranged from 24 to 215 µg L^{-1} at Northern WWTP and 87 to 198 µg L^{-1} at Goudkoppies WWTP.

The effluent had analyte levels ranging from 5 to 70 µg L^{-1} and 22 to 76 µg L^{-1} in Northern and Goudkoppies WWTPs, respectively. As previously discussed, differences in SPE and hollow fibre extracted concentrations is linked to the fraction of analytes targeted by each technique. Hollow fibre method extracts only the truly dissolved fraction of the analytes while SPE extracts both the particle bound and truly dissolved fractions.

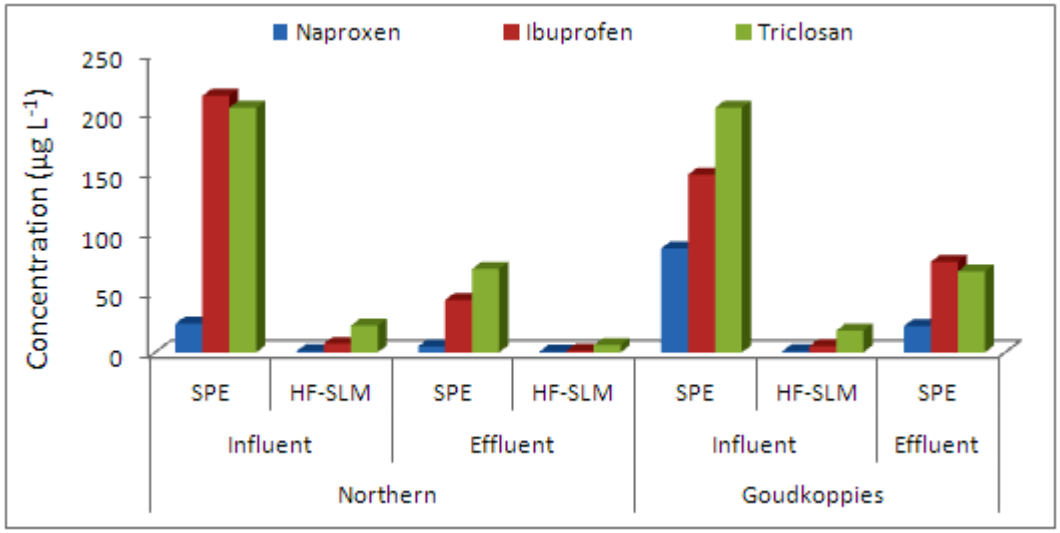


Figure 5.35: Comparison of PPCP concentrations in wastewater derived from solid phase extraction (SPE) and the developed hollow fibre extraction methods.

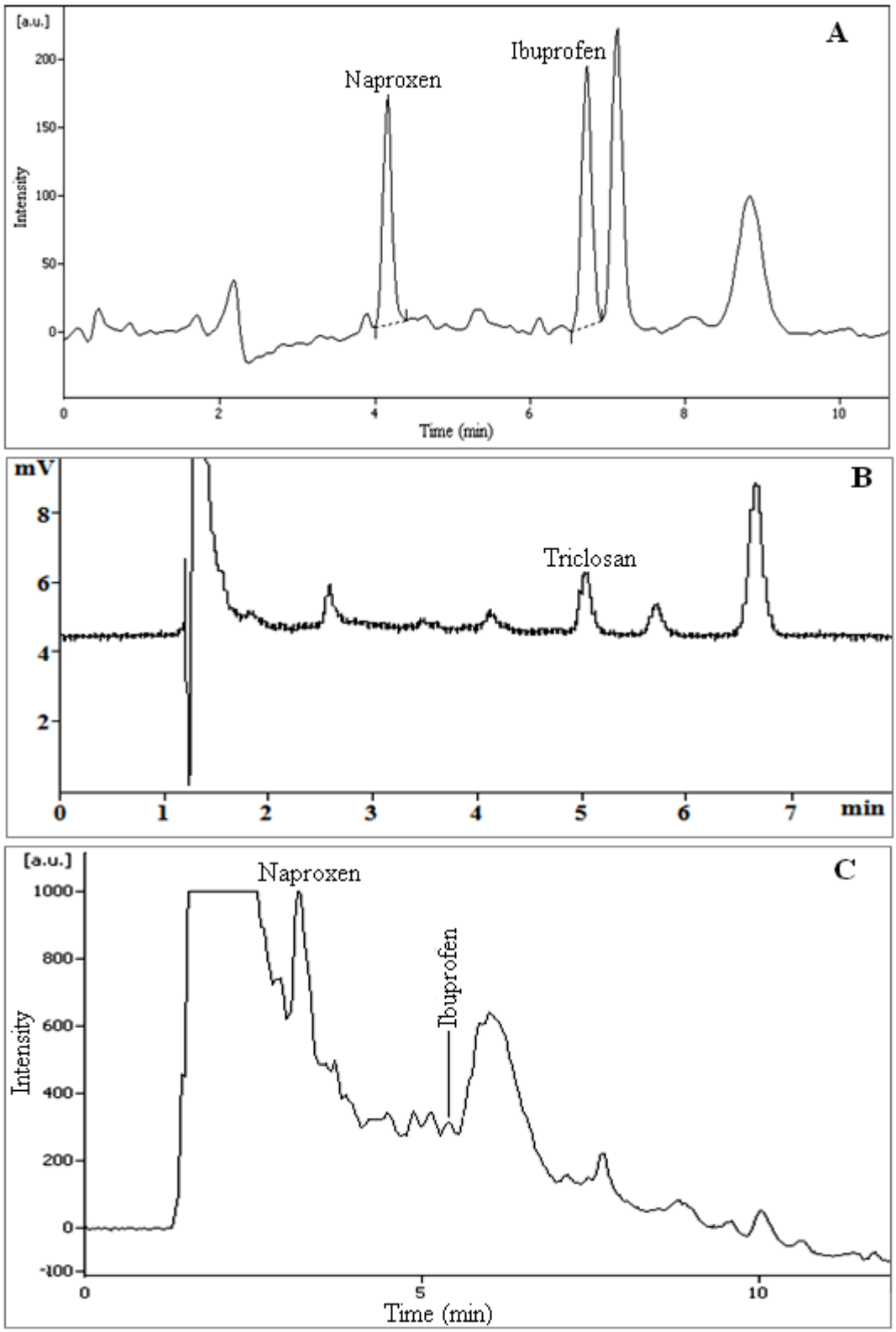


Figure 5.36: Chromatograms of naproxen and ibuprofen (A) and (B) triclosan obtained from the hollow fibre extraction method, and naproxen and ibuprofen (C) using SPE method. Influent samples from Northern WWTP were used.

5.4.4 Membrane assisted passive sample (MAPS)

The hollow fibre extraction system was applied as a passive sampler (herein, referred to as MAPS) to determine TWA concentrations of the three compounds in the influent and effluent of both WWTPs. The samplers were deployed together with POCIS devices in the same steel cages and exposed in the wastewater for 14 days. Concentrations of the PPCPs in the sample sites were estimated from the accumulated amounts of the analytes in the MAPS. Table 5.31 presents estimated concentrations of the target compounds in the influent and effluent wastewater of the Goudkoppies WWTP.

Table 5.31: Estimated mean concentrations of PPCPs by MAPS in wastewater (μg L^{-1}) from Goudkoppies and Northern WWTPs (n = 3)

	Sampling site			
Compound	Goudkoppies WWTP		Northern WWTP	
	Influent	Effluent	Influent	Effluent
Naproxen	0.7 ± 0.11	0.1 ± 0.01	0.9 ± 0.11	0.2 ± 0.01
Ibuprofen	1.1 ± 0.25	0.4 ± 0.13	1.2 ± 0.57	0.5 ± 0.02
Triclosan	1.5 ± 2.03	0.3 ± 0.32	1.9 ± 0.18	0.8 ± 0.01

In comparison to laboratory extracted samples, generally, lower analyte concentrations that ranged from 0.7 to 1.5 μg L^{-1} were estimated in the influent of Goudkoppies WWTP, whereas the effluent of the same site showed average levels that varied from 0.1 to 0.4 μg L^{-1}. On the other hand, Northern WWTP yielded contaminant residues whose levels were in the ranges of 0.9 to 1.9 μg L^{-1} and 0.2 to 0.8 μg L^{-1} in the influent and effluent, respectively.

As previously discussed, successful extraction of these ionisable compounds is pH dependent. In this case, the pH of the influent and effluent during deployment in both sampling sites ranged between 7.9 and 8.4. Clearly, these values are way above the ideal pH conditions (pH 2 to 4) suitable for extraction of these

compounds. It is, thus, possible that high pH levels prevalent in the sites rendered most of the analytes unavailable due to their existence in ionised forms.

The acceptor phase pH, and hence, the buffering capacity, may also have been compromised through interactions with organic acids during the long exposure period. Organic acids such as humic acids can diffuse through the membrane into the acceptor phase where they get deprotonated. As more of these compounds find their way into the acceptor phase, (facilitated by the elongated extraction time) more H^+ are released into the acceptor phase. The net effect of these reactions is lowering of acceptor phase pH and decreased buffering capacity. Bergstrom et al. (2007) observed such a pH drop when processing large volumes of landfill leachates using supported liquid membrane extraction technique. As the acceptor phase pH drops, loss of the already trapped analytes may also occur via back extraction into the donor phase. Based on these findings, MAPS may be a promising passive sampling device, only, where the pH conditions of the bulk solutions are suitable for the target compounds.

5.4.5 Removal efficiency of the PPCPs in the WWTPs

The overall removal efficiency of the PPCPs in WWTPs was determined by considering the mean concentrations of each analyte in the raw influent and treated effluent. Figure 5.37 presents the removal rates (%) of the PPCPs in the studied WWTPs. Average removal rates of the compounds ranged from 68 to 86% at Goudkoppies WWTP and 65 to 82% at Northern WWTP.

The findings of the current study are generally comparable to those reported by several researchers (Sagrista, 2013; Al-Rifai, 20012; Gros, 2010; Zorita et al., 2009; Lindqvist et al., 2005). Table 5.32 presents the removal efficiencies (%) of the target PPCPs obtained in the current study as compared to findings reported elsewhere.

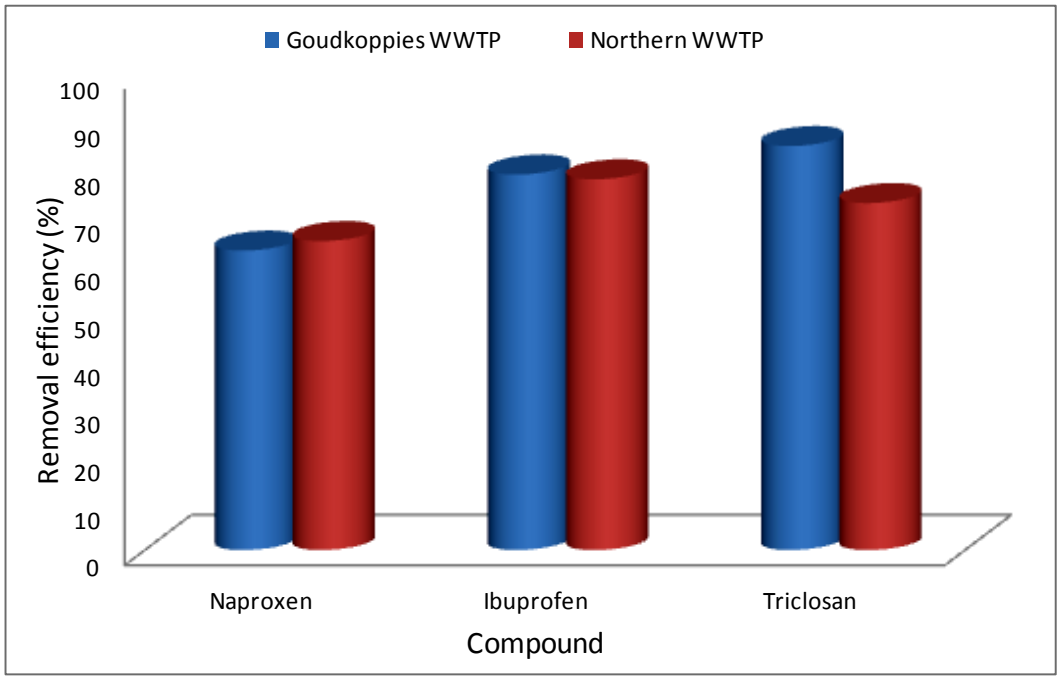


Figure 5.37: Removal efficiency of naproxen, ibuprofen and triclosan in Goudkoppies and Northern WWTPs

5.4.6 Conclusions

A method based on hollow silicon membrane was successfully developed and applied in the extraction and clean-up of 2 pharmaceuticals and one personal care product. Significantly high enrichment factors which ranged from 65 to 369 were obtained for the analytes in spiked reagent water and using the optimised method (sample pH 4, acceptor phase pH 11 and 24 hours extraction period). The developed method was then applied to the determination of the PPCPs in wastewater influent and effluent in two WWTPs. The method was found to be very selective and produced clean chromatograms even in the presence of complex sample matrix. Analyte concentrations in the influent wastewater at Goudkoppies WWTP ranged from 1.1 to 18.4 μg L^{-1} and those in Northern WWTP samples ranged from 2.3 to 22.5 μg L^{-1}. On the other hand, treated effluent in both treatment plants did not exceed 6.1 μg L^{-1}. Overall, concentrations of the compounds were generally higher in Northern WWTP samples than in Goudkoppies WWTP. This was attributed to the relatively bigger population served by the treatment plant.

Table 5.32: Removal rates (%) of investigated PPCPs in the present study as compared to literature values

Compound	Removal rate (%)	Sample	Country	Reference
Naproxen	67	Wastewater	South Africa	Current study
Naproxen	79	Wastewater	Spain	Sagrista et al. (2013)
Naproxen	81	Wastewater	Sweden	Zorita et al. (2007)
naproxen,	> 90	Wastewater	Australia	Al-Rifai (2012)
Naproxen	81	Wastewater	Finland	Lindqvist et al., 2007
Naproxen	60-100	wastewater	Spain	Gros (2010)
Ibprofen	78	Wastewater	South Africa	Current study
Ibprofen	90	Wastewater	Spain	Sagrista et al. (2013)
Ibprofen	94	Wastewater	Sweden	Zorita et al. (2007)
Ibprofen	> 90	Raw WW	Australia	Al-Rifai (2012)
Ibprofen	91	Wastewater	Finland	Lindqvist et al., 2007
Ibprofen	65-100	wastewater	Spain	Gros (2010)
Triclosan	84	Wastewater	South Africa	Current study
Triclosan	77	Wastewater	Spain	Sagrista et al. (2013)
Triclosan	> 22	Wastewater	USA	Hua et al. (2005)

An attempt to use the hollow fibre membrane as a passive sampler targeting the PPCPs in wastewater was made. Comparatively lower estimated analyte concentrations were obtained after the two-week exposure period. Several factors may have contributed to this observation. Firstly, high sample solution pH may have caused ionisation of the analytes rendering them less available for uptake by the sampler. Secondly, loss of acceptor phase buffering capacity due to introduction of protons by organic acids present in the sample solution. Finally, biofouling on the surface MAPS may have slowed down transport of analytes from the bulk solution into the acceptor phase. These factors may have acted individually or collectively to lower the amount of accumulated analytes during the exposure period.

High removal efficiencies were recorded for all the PPCPs in the two WWTPs. Removal efficiencies were between 68 and 86%, and 65 and 82% at Goudkoppies and Northern WWTPs, respectively. These values were in agreement with existing literature values.

5.5 Influence of temperature on mass transfer of an incomplete trapping single hollow fibre membrane assisted extraction of pharmaceuticals and personal care products

5.5.1 Optimisation of the hollow fibre membrane extraction system for mass transfer studies

In this technique, overall mass transfer of the target analytes resulting from their diffusion through the membrane is given by the extraction efficiency (*E*). Several parameters that include pH of the donor and acceptor phases, agitation of the sample solution and composition of the membrane are known to control extraction efficiency (Jönsson et al., 1993). Information on the physical characteristics of the compounds can be utilised in the determination of some of these parameters. As mention previously, it is critical to maintain the pH of the acceptor solution at least 3.3 units above the pKa of the least acidic analyte. This implies that ideally, the optimum pH for the acceptor solution should be 7.45, 8.21 and 11.20 for naproxen, ibuprofen and triclosan, respectively. In this study, a compromise acceptor pH of 11.0 was used consisting 0.25 M disodium hydrogen phosphate (Na_2HPO_4) buffer. Although at this pH a little portion of triclosan may have been excluded, but generally, all the three compounds were successfully trapped in the acceptor phase. This observation was based on optimisation experiments done where acceptor phase pH was 7, 9 and 11.

The success of this technique is also heavily reliant on the pH of donor phase. Sample solution pH need to be adjusted in such a way that all the compounds are in their molecular (non-ionised) form in order to promote diffusion through the membrane. Therefore, the pH of the sample solution is ideally kept at least 2.2 units below the pKa of the most acidic analyte (Jönsson et al., 1993). In an ideal case, the pH of the donor phase should be 1.95 for naproxen, 2.71 for ibuprofen and 5.70 for triclosan. Based on optimisation experiments carried out as described in section (5.4.2.6), the donor solution was adjusted to pH 4.0.

In a typical SLM technique, partitioning of the compounds from the donor to the membrane is determined by both physical properties of the analytes and the membrane composition (Michel et al., 2009). However, in the current SLM-like set-up, no organic solvent was used as the membrane. As previously elaborated, sample agitation (stirring at 400 rpm) coupled with long extraction times (24 hours) led to organic membrane instability and eventual loss. Therefore, the pores of the hollow fibre were instead impregnated with water molecules to form an aqueous membrane. Analytes are thus, expected to diffuse through the water boundary layer (WBL) and the aqueous membrane before being stripped into the acceptor phase.

5.5.2 Determination of mass transfer parameters

Mass transfer parameters were determined using the principles developed by Chimuka et al. (1998) and Larner and Seen. (2005). Since a positive correlation exists between concentrations of the analyte in a stagnant acceptor phase with exposure time, it holds that the mass of analytes sequestered in the acceptor solution is related to the extraction period as shown in Equation 5.5.

$$M = \frac{DCtA}{\Delta g} \qquad 5.5$$

where M is the amount (mg) of the analyte trapped in the acceptor phase, D is the diffusion coefficient (cm^2s^{-1}) of the analyte in the membrane, C is the dissolved concentration (mg cm^{-3}) of the analyte in the donor phase, t is the duration of extraction (s), A is the surface area (cm^2) of the hollow fibre, and Δg is the hollow fibre thickness (cm). The external surface area (A) of the hollow fibre was ca. 39.0 cm^2 determined from the dimensions shown in Table 4.2, while the acceptor phase volume was approximated to about 1 cm^3. The thickness of the hollow fibre was 0.04 cm.

It was observed that at higher temperatures (313 K and 333K), plots of the amount, M, of analyte accumulated in the acceptor phase versus extraction time, t,

deviated from linearity. In a bid to restore linearity of the plots Equation 5.5 was amended to Equation 5.6. Calculation of *D* using Equation 5.6 was, thus, possible. Plotting M/t^2 against $1/t$ was found to be linear at all temperature ranges studied.

$$\frac{M}{t^2} = \frac{DCA}{\Delta g t} \qquad 5.6$$

D is obtained from the slope of the plot of M/t^2 against $1/t$ as per the relationship in Equation 5.7.

$$Slope = \frac{DCA}{\Delta g} \qquad 5.7$$

Using Fick's first law, the flux can be determined from the change in analyte concentration (ΔC) between the donor and acceptor phases, and the thickness of the membrane, Δg (cm). Equation 5.8 gives this relationship.

$$-J = \frac{D\Delta C}{\Delta g} \qquad 5.8$$

Where *D* is the diffusion coefficient ($cm^2\ s^{-1}$), and *J* is the flux ($mol\ cm^{-2}\ s^{-1}$).

With the approximation that ΔC is very close to C_0, Equation 5.9 was then used to calculate the flux.

$$-J = \frac{DC_0}{\Delta g} \qquad 5.9$$

Where C_0 is the analyte concentration in the donor solution before commencement of extraction.

Equation 5.10 (Stokes Equation) was used to calculate the apparent change of viscosity (η) with temperature.

$$D = \frac{K_\beta T}{6\pi a \eta} \qquad 5.10$$

where η, K_β, T and a are the apparent viscosity (kg m^{-1} s^{-1}), Boltzmann distribution coefficient, absolute temperature (K) and molecular radius, respectively.

5.5.3 Influence of temperature on mass transfer

Figures 5.38 (A) to (C) presents plots of analyte concentration measured in the acceptor phase versus extraction time at the various temperatures used. A positive relationship was observed between the concentrations of PPCPs in the acceptor phase and increase in extraction time, especially at 298 K (Figure 5.38 A). A deviation from this relationship was, however, seen at higher extraction temperatures (313 K and 333 K; Figures 5.38 B and 5.38 C) and longer extraction periods ($\geq$ 22000 s) where the transport appeared to reach equilibrium. Similar observations were reported by Michel et al. (2009) in an extraction study of triazoles fungicides using SLM technique.

Analyte concentrations found in the bulk donor phase plotted against extraction time at the different extraction temperatures are presented in Figure 5.39. Concentrations of the analytes decreased steadily with increase in extraction time. This clearly indicates continuous depletion of the compounds from the bulk solution due to uptake by the hollow fibres. Rate of loss of these compounds from the sample solution was temperature dependent. Extraction at higher temperature encouraged faster mass transfer and hence, more pronounced losses of the analytes from the donor phase within any given time period.

Before analytes are extracted into the acceptor phase, several resistances must be overcome. These resistances include diffusion of analytes from the bulk water phase into the WBL, transport analytes from the WBL through the membrane, and finally, compound stripping into the acceptor solution.

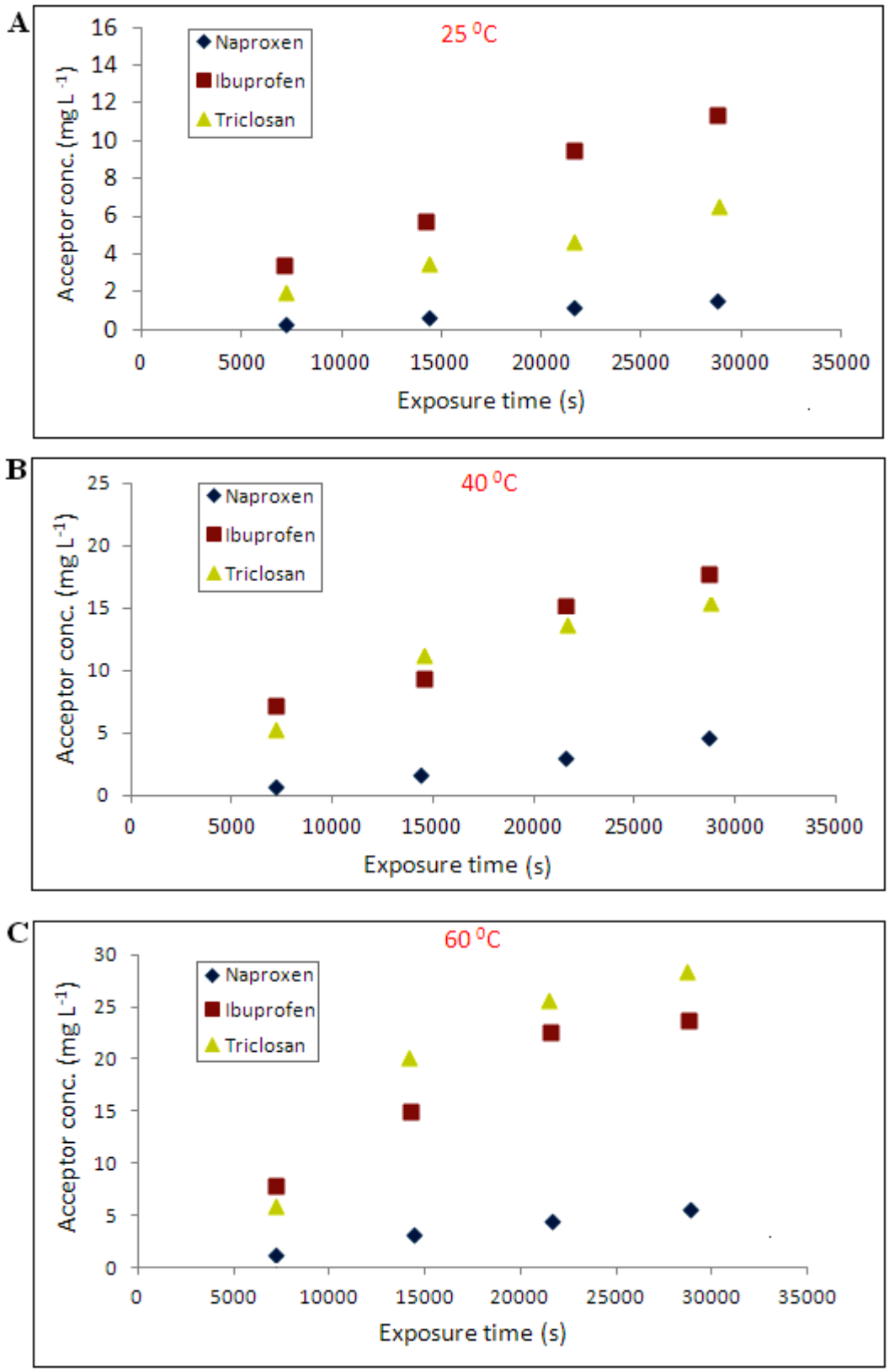


Figure 5.38: Plots of determined concentration in acceptor phase vs extraction time at various temperatures for (A) naproxen, (B) ibuprofen and (C) triclosan.

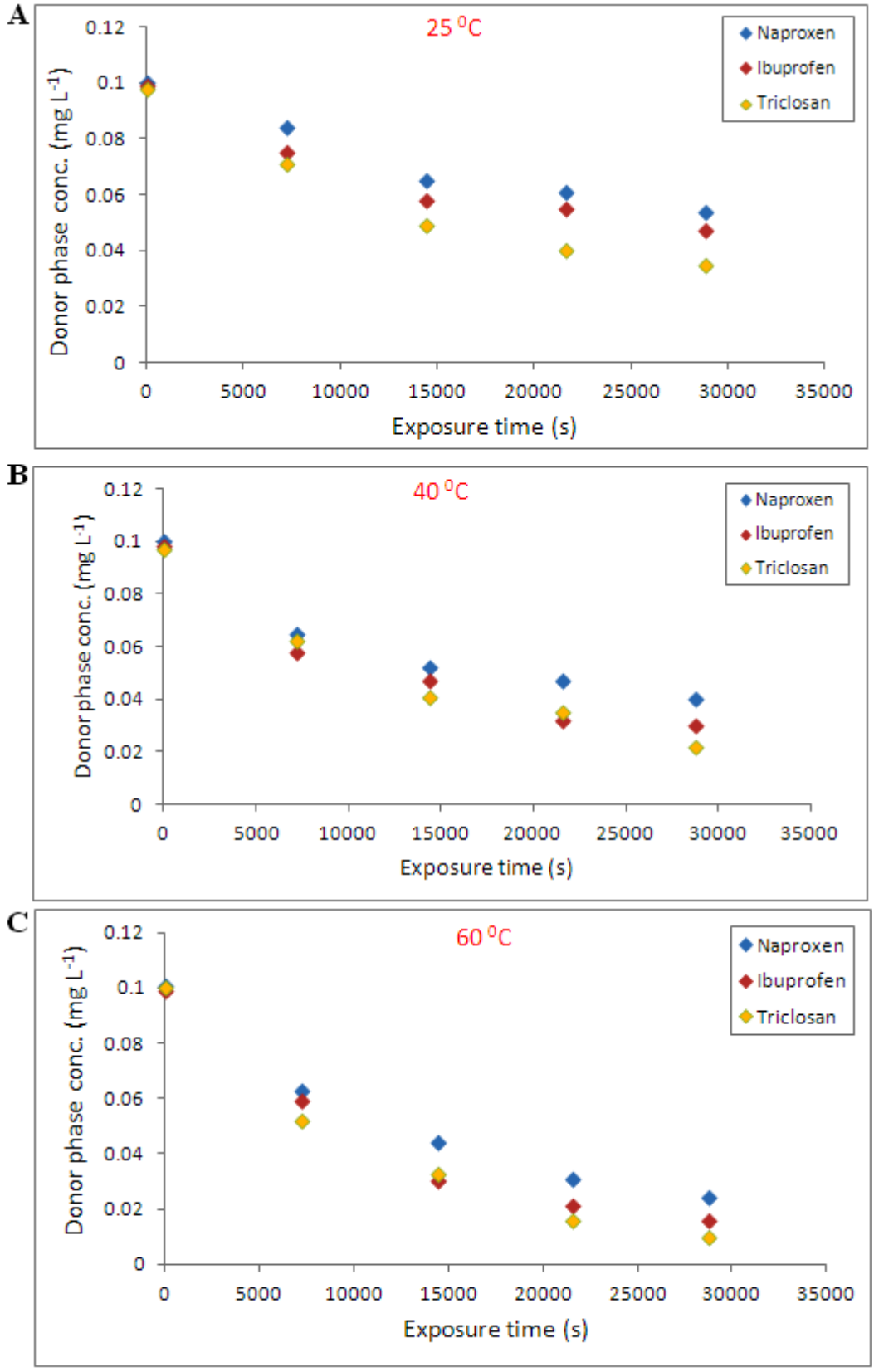


Figure 5.39: Plots of determined concentration in donor phase vs extraction time at different temperatures for (A) naproxen, (B) ibuprofen and (C) triclosan.

Enhanced rates of mass transfer is, thus, possible under conditions where the analytes diffuse rapidly into the WBL, then through WBL-liquid membrane interphase, and eventually fast stripping into the acceptor phase. Usually, rapid stripping of the compounds is enhanced by complete trapping of analytes in the acceptor phase (i.e. where no re-extraction of analytes from the acceptor phase into the liquid membrane occurs). These experiments suggest that at lower temperatures (Figure 5.38 A), mass transfer is constrained by analyte diffusion from the bulk sample solution through the donor-membrane interphase and across the liquid membrane.

However, at high temperatures (Figures 5.38 B and 5.38 C), the rate of mass transfer is limited by stripping of the compounds into the acceptor solution from the membrane. Agitation of the bulk donor phase influences analyte extraction through reducing the width of the WBL (Vrana et al., 2005). Since the experiments were carried out under stirred conditions at the same rate (400 rpm), the influence of WBL on mass transfer was, therefore, expected to be uniform in all extractions.

The diffusion coefficient and flux are important parameters that can be determined from permeation curves obtained by plotting the t^{-1} against mt^{-2}. Such typical plots for naproxen, ibuprofen and triclosan are displayed in Figure 5.40. Equation 5.7 was used to calculate the diffusion coefficients of the compounds at different temperatures, whereas flux was calculated using Equation 5.9. The mass transfer parameters determined at various temperatures are summarised in Table 5.33.

As shown by the plots in Figure 5.41 and Table 5.33, an increase in temperature resulted in enhanced diffusion coefficient and flux for each compound. The increase was highest with triclosan because it has the smallest α_A (analytes in unionised form) value (1.20×10^{-4}) and is therefore, trapped more in the acceptor phase. On the other hand, naproxen showed the lowest increase in *D* value with temperature.

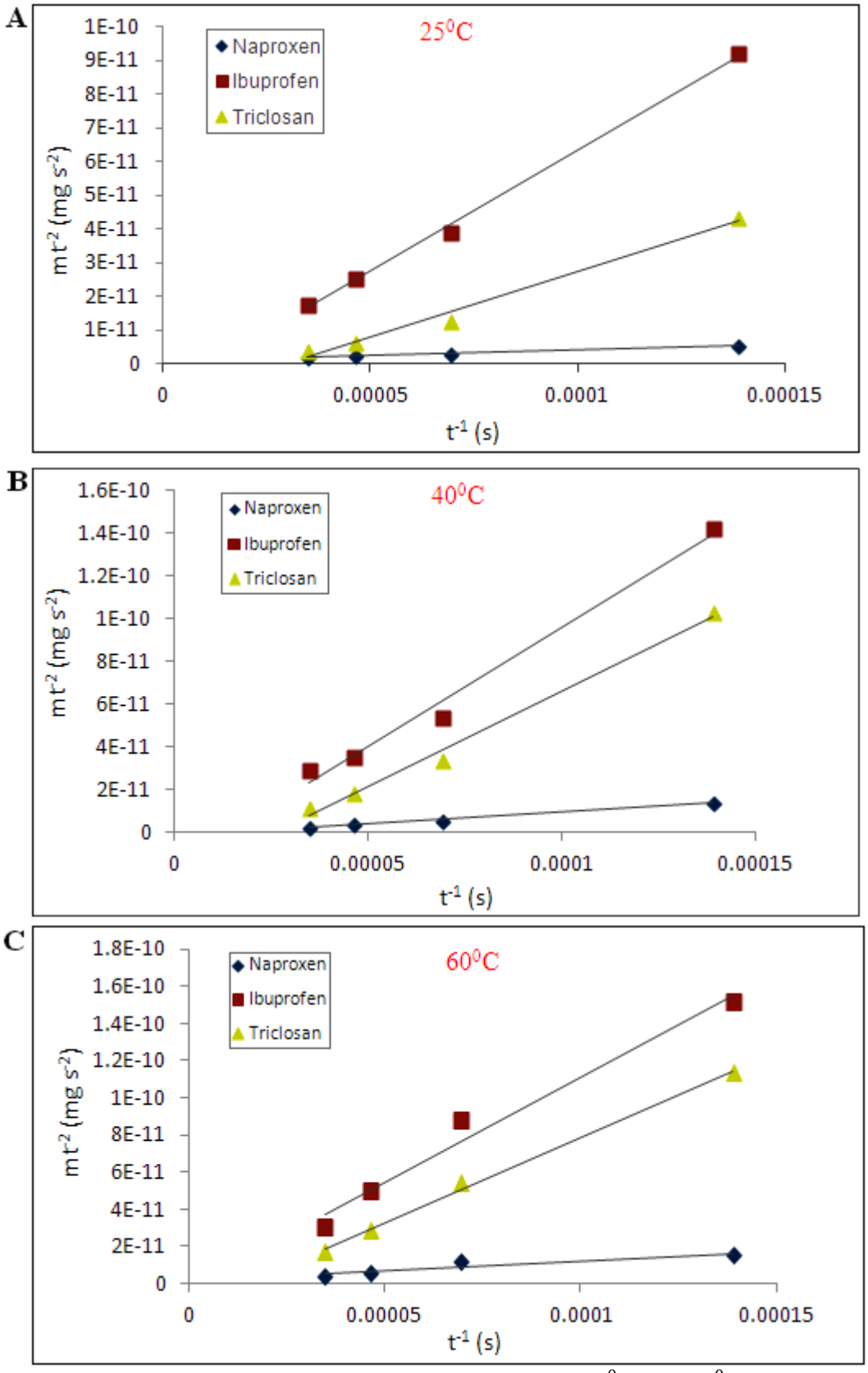


Figure 5.40: Typical permeation plots obtained at (A) 25^{0}C, (B) 40^{0}C and (C) 60^{0}C

Table 5.33: Summary of the diffusion coefficients and flux of the compounds at various extraction temperatures

Temperature (^{0}C)	Naproxen	Ibuprofen	Triclosan
		D (cm^2 s^{-1})	
25	1.50E-06	1.65E-05	6.30E-06
40	4.20E-06	3.03E-05	2.09E-05
60	1.25E-05	3.92E-05	3.26E-05
		J (mol cm^{-2} s^{-1})	
25	3.27E-14	4.00E-13	1.09E-13
40	9.13E-14	7.35E-13	3.61E-13
60	2.72E-13	9.51E-13	5.63E-13

D; diffusion coefficient, *J*; flux

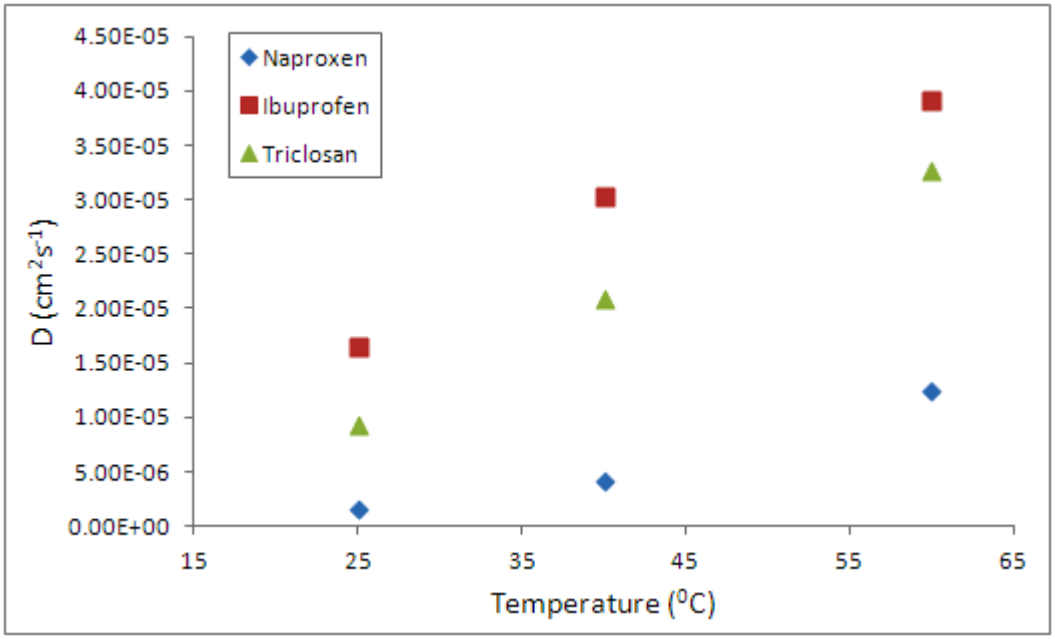


Figure 5.41: Plot of the calculated diffusion coefficients against extraction temperature

A similar argument as for triclosan could be advanced for naproxen. The acidic pharmaceuticals were characterised by α_A values of 4.14 x 10^{-1} (naproxen) and 1.10 x 10^{-1} (ibuprofen), respectively, and the rise in diffusion coefficient was not

as steep at higher temperatures. It seems that the overall mass transfer for triclosan is controlled by diffusion of the compound through the aqueous membrane at lower temperatures. It is therefore, proposed that at higher temperatures, the rate of mass transfer for the acidic pharmaceuticals is limited by their stripping into the acceptor phase.

Plots of the determined analyte concentrations in the acceptor phase against extraction temperature at 4 and 8 hours are shown in Figure 5.42. It is evident in these plots that the amount of the compounds extracted into the acceptor phase increased with increased temperature. The results indicate that any analytical application with this method is to a great extent temperature dependent. Proper choice of extraction temperature is therefore, important to improve mass transfer of analytes and hence reduce extraction time. As such, proper optimisation of the temperature prior to its application in real samples is crucial.

Extractions of analytes in aqueous solutions done under quiescent conditions and/or in cases where analytes are completely trapped call for very careful control of operating temperatures. This is because diffusion coefficient is the limiting factor in such processes and any changes in temperature could affect the transport rate and therefore calculated extraction efficiency (Michel et al., 2009). It can be concluded that the influence of extraction temperature on the overall mass transfer is more visible in membrane or donor controlled extractions. In a study involving extraction of triazole compounds using hollow fibre supported liquid membrane, Michel et al. (2009) also observed a trend where increased temperature led to an increase in the diffusion coefficients of the compounds. Another study by Groβ and Heintz (2000) reported similar findings in an experiment involving extraction of various aromatic compounds at different temperatures. In their study, which was carried out under stirred conditions, these authors observed that trapping of the analytes in the acceptor phase was not the limiting step. They, however, concluded that the rate of mass transfer was controlled by the analyte diffusion through the non-porous membrane used in the extraction process. This may have resulted from their use of an organic membrane unlike in the present study.

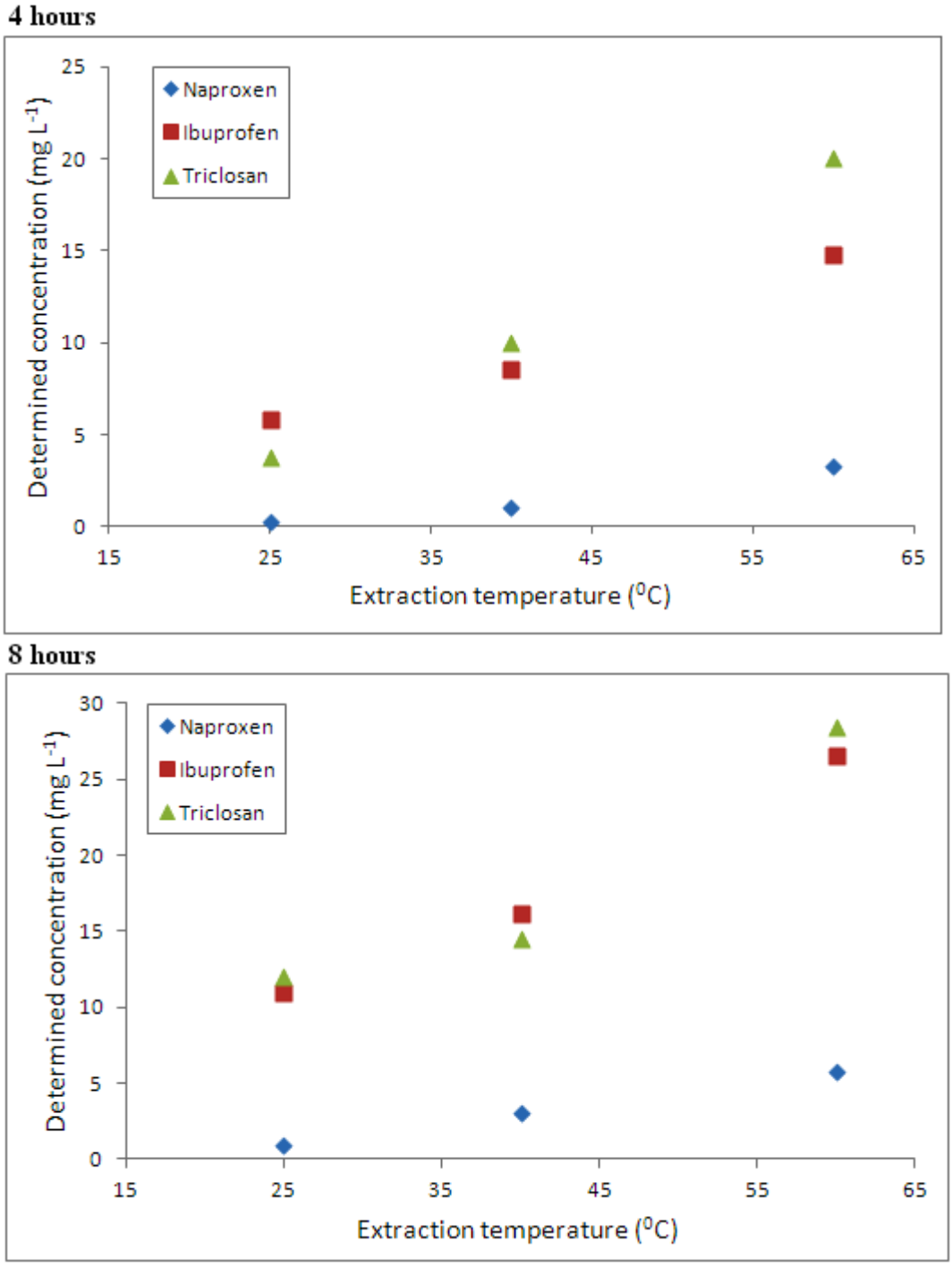


Figure 5.42: Plots of determined concentration in the acceptor phase versus extraction temperature at 4 and 8 hours.

Saf et al. (2006) also studied the transport kinetics of chromium (VI) ions through a bulk liquid membrane containing p-tert-buthycalix[4]arene dioxaoactylamide with sample stirring at extraction temperatures between 293 K and 308 K. They

found out that the rate determining step was not the trapping of the analytes in the acceptor solution but rather the diffusion of chromate ions through the membrane. The extraction was thus deemed as membrane controlled process.

5.5.4 Matrix effect as affected by temperature in the extraction of wastewater samples using the hollow fibre method

In order to investigate the influence of temperature on extraction of environmental samples, the PPCPs wastewater were extracted using hollow fibre under the optimised conditions described earlier. Examples of typical chromatograms obtained from the extractions are shown in Figure 5.43. It was evident that an increase in temperature (from 25^0C to 60^0C) resulted in elevated extraction of the sample matrix into the acceptor phase. Not only does an elevated temperature favour increased mass transfer of the compounds of interest (as shown by increases in analyte concentrations accumulated in the acceptor phase), it also boosts transport of contaminants across the membrane. However, it was found that the sequestered matrix was not too large (Figure 5.43) to subdue or compromise resolution of the target analytes. This illustrates the suitability of the technique in terms of selectivity even in extractions involving complex samples such as wastewater.

5.5.5 Conclusions

The influence of temperature on mass transfer in a SLM-like hollow fibre membrane system was studied in order to understand the factors that limit transport of analytes. Unlike the conventional SLM technique where the hollow fibre pores are filled with an organic solvent, water molecules are instead used in the current system. Prior to stripping into the acceptor phase, analytes must, first diffuse through the aqueous membrane.

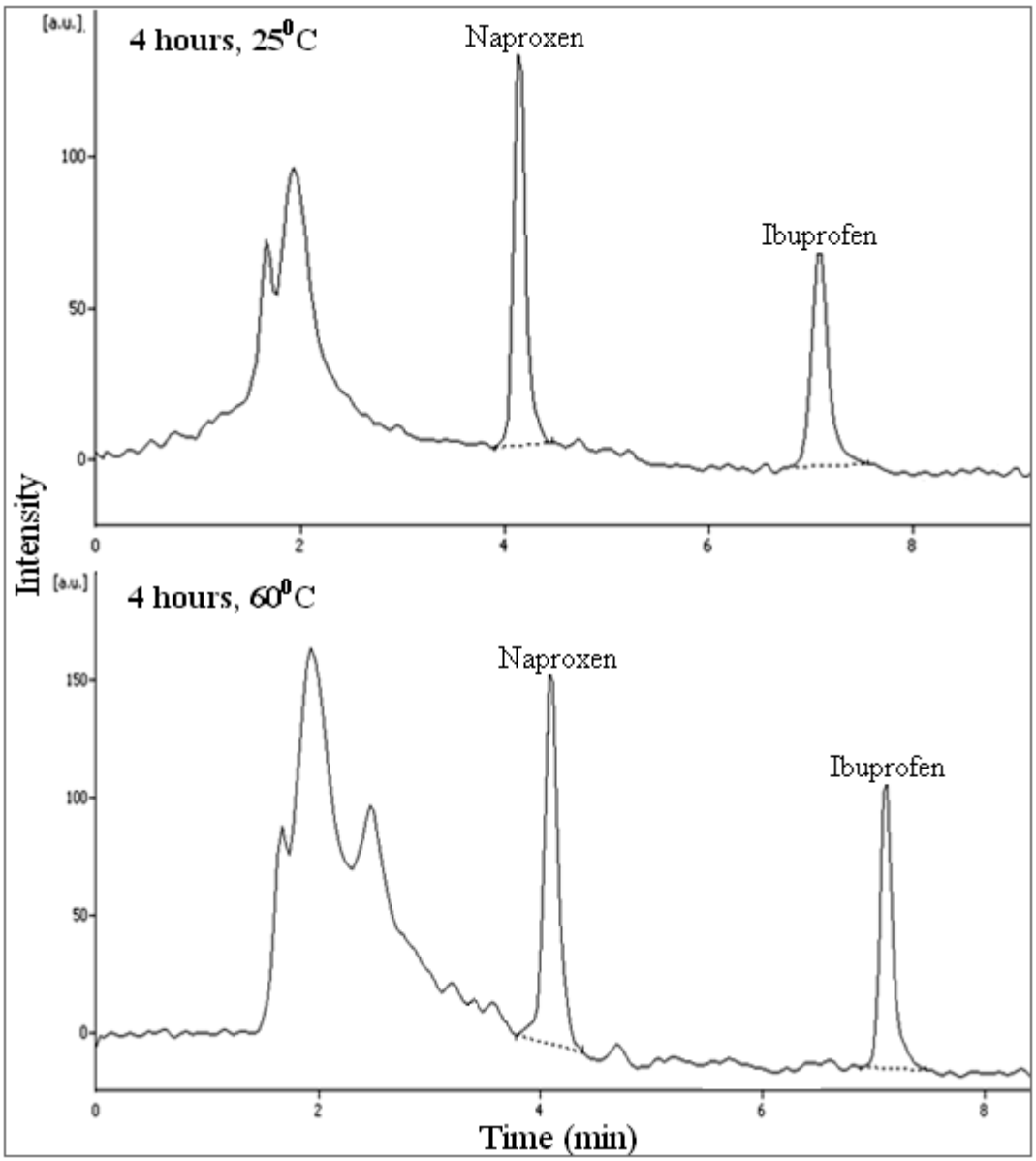


Figure 5.43: Chromatograms of wastewater extracts obtained at 25 and 40^{0}C.

Rate of mass transfer of analytes in this system can be controlled by the donor solution, the aqueous membrane and/or the stripping process of the analytes into the acceptor phase. It was observed that an increase in temperature led to increased uptake of target analytes into the acceptor phase for all the target analytes. However, longer extraction periods at higher temperatures (313 K and 333 K) showed signs of the transport reaching a plateau. Findings of this study therefore, indicate that mass transfer is controlled by diffusion through the donor phase and the membrane. At higher temperatures, transport of analytes is

constrained by their stripping into the acceptor phase from the membrane. It was also evident that at all temperatures, the aqueous boundary layer input to limiting analyte transport may not have been significantly different since all extractions were done under similar conditions of agitation.

The calculated diffusion coefficient and flux for each compound showed an increase with increased extraction temperature. The rise was more pronounced in triclosan and least in naproxen. These differences were attributed to their α_A values and, hence, potential trapping in the acceptor phase. In real samples, higher temperatures encouraged mass transfer elevation in both target analytes and sample matrix. Although this was the case, the accumulated amounts of contaminants did not seem to interfere with the signals of the target compounds.

Chapter 6:

Conclusions & Recommendations

6.1 General conclusions

This work was mainly based on the utilisation of passive sampling techniques in analyte extraction and preconcentration of organic micropollutants in aquatic systems. Depending on the characteristics of target compounds, extracts were analysed using either GC-MS or LC-UV/FLD instrumental techniques.

Successful preparation and field application of the semipermeable membrane devices (SPMDs) targeting PAHs, PCBs and OCPs was demonstrated. Performance reference compounds (PRCs) were incorporated in the triolein lipid receiving phase during sampler fabrication. The dissipation rates of these compounds were used to determine sampling rates and ultimately, the analyte concentrations in the water bodies. These passive samplers were able to sequester quantifiable amounts of the compounds in all sampling sites. Accumulated residues in the SPMDs were then used to estimate the freely dissolved water concentrations of the contaminants.

Total PAH, PCB and OCP amounts accumulated in each SPMD ranged from 1223 to 4766, 6.5 to 76.1 and 4.5 to 921.6 ng sampler^{-1}, respectively. Estimated water soluble total PAH concentrations ranged from a low of 33.5 ng L^{-1} at site CR to a high of 126.8 ng L^{-1} at HSL. On the other hand, freely dissolved PCB residues were in the pg L^{-1} region and close to the limit of quantification. Total freely dissolved OCP concentrations varied between 0.17 ng L^{-1} at AUP and 37.14 ng L^{-1} at JR 2. These levels were found to be comparable to those reported by other researchers (Karacik et al., 2013; Röllin et al., 2009; Wang et al., 2009; Vrana et al., unpublished, 2001). OCPs were principally composed of HCHs and DDX with the former yielding significantly higher concentrations than the latter. In all sampling sites, the predominance of the smaller molecular weight analytes was visible. This was attributed to their higher water solubilities.

It was proposed that the analytes detected in the sampling sites were mainly of anthropogenic origins. Depending on the season, major entry routes of these

contaminants to the water bodies were likely to be through atmospheric deposition, remobilisation of adsorbed compounds in soils and sediments due to heavy rain events, and surface runoff from polluted urban areas and effluent discharge.

A one year assessment of the temporal trends in water-borne analyte concentrations at IFA revealed that levels of PAHs and HCHs were most elevated in winter but subdued in summer. This observation was attributed to increased atmospheric deposition due to lower ambient temperatures experienced in winter. However, PCB and DDX amounts showed an exactly opposite pattern as PAHs and HCHs. In this case, increased summer concentrations were most probably related to desorption of the analytes from soils, sediments and suspended particles due to heavy wet precipitation, and increase in sources (e.g. domestic fires) in winter.

PAH diagnostic ratios were used to identify possible sources of these compounds in the sampling sites and in the various seasons of the year at IFA. The ratios clearly showed an inclination towards pyrogenic origins in most of the water bodies studied, except at sampling sites AUP and CL, which indicated petroleum combustion sources. On the other hand, analytes sampled at IFA during spring, summer and autumn were mainly of pyrogenic origin, while PAHs detected in the winter season had a mixture of both pyrogenic and petrogenic sources.

The polar organic chemical integrated sampler (POCIS) was also successfully fabricated, calibrated and applied in the field for the determination of naproxen, ibuprofen and triclosan in wastewater. Analysis of POCIS extracts was achieved using HPLC in combination with ultraviolet and fluorescence detection. The laboratory calibration of POCIS yielded reasonably good sampling rates (as compared to literature values) for the analytes that ranged from 0.087 to 0.383 L d^{-1} and 0.125 to 0.936 L d^{-1} in quiescent and stirred conditions, respectively. From the POCIS-sequestered amounts, estimated mean PPCP concentrations in the two WWTPs were found to be in the range of 39.8 to 127.7 μg L^{-1} in the effluent.

Influent residue levels in both treatment plants did not exceed 127.7 μg L^{-1}. Estimated wastewater concentrations of PPCPs as derived from POCIS exposure were generally lower by up to two-folds than those obtained from grab samples using SPE method. This was expected because POCIS targets only the freely dissolved analyte fraction while SPE technique targets both the truly dissolved and particle-sorbed fractions. All in all, these findings indicated POCIS' ability to accumulate polar organic contaminants in complex samples and its subsequent potential in estimating the TWA concentrations of the compounds in wastewater.

A sample preparation method based on silicone hollow fibre was developed and calibrated for the extraction and clean-up of naproxen, ibuprofen and triclosan. In the current method, the fibre pores were impregnated with water molecules instead of the traditional organic solvent used in supported liquid membrane (SLM) approaches. Use of larger sample volumes, longer extraction periods and sample agitation, all known to reduce organic membrane stability in SLM, necessitated the exclusion of the organic membrane in this set-up. Several parameters that are known to affect extraction efficiency of analytes when applying this technique were optimised. Determination of the PPCPs was achieved using the developed method in conjunction with HPLC-UV/FLD analysis.

High enrichment factors that varied between 65 for naproxen and 369 for ibuprofen were realised in analyte-fortified water at optimised conditions. The method showed good sensitivity and selectivity with limits of detection ranging from 0.8 to 5 μg L^{-1}. All the three compounds showed good recoveries that did not drop below 78% in both influent and effluent samples.

Average analyte concentrations in influent wastewater were between 1.1 to 22.5 μg L^{-1}, while effluent concentrations ranged from 0.4 to 6.1 μg L^{-1}. Overall, concentrations of the compounds were generally higher in Northern WWTP samples than in Goudkoppies WWTP. This was attributed to the relatively bigger human population served by the treatment plant.

Generally, lower estimated concentrations of all the analytes were obtained in both the influent (0.7 to 1.5 μg L^{-1}) and effluent (0.1 to 0.8 1.5 μg L^{-1}) when the developed extraction system was deployed in the wastewater for 14 days as a passive sampler. This drop was attributed to three factors: ionisation of the analytes in the bulk wastewater solution at ambient pH conditions, protonation and hence lowering of acceptor phase pH, and biofouling of the hollow fibre. Elimination rates of the analytes in the WWTPs ranged from 68 to 86% in Goudkoppies WWTP and 65 to 82% in Northern WWTP. These removal efficiencies were comparable to those reported in other parts of the world. The developed method is however applicable only to ionisable organic compounds. More studies are also needed to validate the method's applicability as a passive sampler for the said compounds.

Evaluation of temperature effect on mass transfer in the developed hollow fibre extraction system showed that temperature elevation favoured faster transport of compounds from the bulk donor solution to the acceptor phase. This was an indication that mass transfer of analytes is controlled by diffusion through the donor phase and the aqueous membrane. At higher temperatures, transport of analytes is constrained by their stripping into the acceptor phase from the membrane. It is also assumed that the influence of aqueous boundary layer on mass transfer may not have been a significant factor since all extractions were carried out under identical agitation conditions.

For each compound studied, the calculated diffusion coefficient and flux were found to increase with increased extraction temperature. Such increases were more pronounced in triclosan but diminished in naproxen. These differences were attributed to their α_A values and, hence, potential trapping in the acceptor phase. In wastewater samples, higher temperatures encouraged increased mass transfer of both, target analytes, and sample matrix. However, even at the highest extraction temperature (60^0C) tested, matrix effects did not seem to seriously interfere with

the analyte signals. However, it is always important to carefully consider the effect of extraction temperature when using this sample preparation technique.

6.2 Recommendations

Arising from the findings of this study, the following recommendations are made for future work.

- Escalation of monitoring activities of POPs using SPMDs in other major water bodies in the country so as to get a better understanding on the extent of pollution. Several other passive samplers such as silicon rubber, low density polyethene and Chemcatcher that have been successfully used in other parts of the world could be incorporated in such studies. It is also important to compare the SPMD-derived water soluble analyte concentrations with levels shown in sentinel organisms (daphnids, worms, frogs, fish e.t.c.) in the water systems as such organisms also target the freely dissolved fraction. Monitoring for other potentially more hazardous classes of POPs, such as, dioxins and furans need to be carried out. Such information is extremely scanty in the South African case.

- An evaluation of a wider range of PPCPs needs to be undertaken in most of the major WWTPs using both POCIS and hollow fibre to gauge their levels in these facilities. More interest should be focussed on pharmaceutical groups that include antibiotics, endocrine disruptors, anti-retroviral drugs, growth promoters and illicit drugs. Comprehensive studies of river waters receiving treated effluent should be done. Biomonitoring organisms resident in such rivers also need to be investigated for uptake and possible adverse effects related to the PPCPs. In these cases, it is recommended that calibration of the devices be done *in situ* since such attempts have shown attainment of more accurate sampling rates as compared to laboratory values.

- Further research on the optimisation of the developed SLM-like hollow fibre extraction system for polar organics should be undertaken. Particularly, its use as a passive sampler targeting specific basic and acidic compounds in wastewater systems needs more attention.

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APPENDIX

Table A1: Recoveries (%), coefficients of correlation (r^2), LODs and LOQs of PAHs, PCBs and OCPs from various sampling sites

Compound	Recoveries (%)								r^2	LODs (ng L^{-1})	LOQs (ng L^{-1})
	IFA	***JR 1***	***JR 2***	***EGL***	***HSL***	***AUP***	***CL***	***CR***			
PAHs	88	90	104	80	115	100	55	85	0.9831 - 0.9986	0.1	0.4
PCBs	76	73	83	57	69	94	88	102	0.9785 - 0.9993	< 0.1	0.1
OCPs											
HCHs	79	98	67	77	74	75	88	92	0.9866 - 0.9988	< 0.1	0.1
DDTs	115	96	75	110	82	112	89	86	0.9892 - 0.9990	< 0.1	0.1

Table A2: Products of regression coefficients (*F*) with SPMD surface area (*A*) for each of the sampling sites

Parameter	Sampling site							
	IFA	***JR 1***	***JR 2***	***EGL***	***HSL***	***AUP***	***CL***	***CR***
FA	170.8	214.0	283.1	224.2	11.1	220.6	118.7	207.5

Table A3: Recoveries of individual analytes

PAHs		PCBs	
Compound	***Recovery (%)***	***Compound***	***Recovery (%)***
Naphthalene	55	PCB 28	57
Acenaphthylene	63	PCB 52	75
Acenaphthene	67	PCB101	72
Fluorene	81	PCB 118	97
Phenanthrene	86	PCB 138	86
Anthracene	77	PCB 153	102
Fluoranthene	115	PCB 180	93
Pyrene	95		
Benz[a]anthracene	70		
Chrysene	81		
Benzo[b]fluoranthene	74		
Benzo[k]fluoranthene	98		
Benzo[a]pyrene	85		
Indeno[1,2,3-cd]pyrene	79		
Dibenz[a,h]anthracene	88		
Benzo[ghi]perylene	100		

OCPs

HCHs		DDX	
Isomer	***Recovery (%)***	***Compound***	***Recovery (%)***
α-HCH	79	o,p'-DDE	72
β-HCH	115	p,p'-DDE	67
γ-HCH	80	o,p'-DDD	83
δ-HCH	99	p,p'-DDD	102
ε-HCH	94	o,p'-DDT	89
		p,p'-DDT	95

Table A4: Molecular weights, log K_{ow}, and compound-specific sampling rates of PAHs

Compound	Mw	Log K_{ow}	Sampling rate, R_s (L d^{-1})							
			IFA	***JR 1***	***JR 2***	***EGL***	***HSL***	***AUP***	***CL***	***CR***
Naphthalene	128	3.37	21.7	21.9	29.0	20.7	1.2	22.6	12.1	21.2
Acenaphthylene	152	4.00	20.0	20.2	26.7	19.1	1.1	20.8	11.1	19.6
Acenaphthene	154	3.92	19.9	20.1	26.6	18.9	1.1	20.7	11.1	19.4
Fluorene	166	4.18	19.2	19.4	26.1	18.3	1.0	20.0	10.7	18.8
Phenanthrene	178	4.57	18.4	18.8	24.8	17.7	1.0	19.4	10.4	18.2
Anthracene	178	4.54	18.4	18.3	24.8	17.7	1.0	19.4	10.4	18.2
Fluoranthene	202	5.22	17.5	17.6	23.4	16.7	0.9	18.2	9.8	17.1
Pyrene	202	5.18	17.5	17.2	22.1	16.7	0.9	18.2	9.8	17.1
Benz[a]anthracene	228	5.86	16.5	16.7	22.1	15.8	0.9	17.2	9.3	16.2
Chrysene	228	5.91	16.5	16.4	21.0	15.8	0.9	17.2	9.3	16.2
Benzo[b]fluoranthene	252	5.90	15.8	15.9	21.0	15.0	0.8	16.4	8.8	15.4
Benzo[k]fluoranthene	252	5.90	15.8	15.9	21.0	15.0	0.8	16.4	8.8	15.4
Benzo[a]pyrene	252	6.04	15.8	15.6	21.0	15.0	0.8	16.4	8.8	15.4
Indeno[1,2,3-cd]pyrene	276	6.50	15.1	15.2	20.7	14.4	0.8	15.8	8.5	14.8
Dibenz[a,h]anthracene	278	6.75	15.1	15.2	20.1	14.4	0.8	15.7	8.4	14.7
Benzo[ghi]perylene	276	6.50	15.1	15.2	20.1	14.4	0.8	15.7	8.5	14.8

Table A5: Molecular weights, log K_{ow}, and compound-specific R_s for PCBs

Compound	Mw	Log K_{ow}	Sampling rates, R_s (L d^{-1})					
			IFA	***JR 1***	***JR 2***	***EGL***	***HSL***	***AUP***
PCB 28	258	5.67	12.6	15.7	20.8	16.5	0.8	16.2
PCB 52	292	5.84	11.8	14.8	19.6	15.6	0.8	15.3
PCB101	327	6.38	11.2	14.1	18.6	14.8	0.7	14.5
PCB 118	327	6.74	11.2	14.1	18.6	14.8	0.7	13.9
PCB 138	361	6.83	10.7	13.4	17.8	14.1	0.7	13.9
PCB 153	361	6.92	10.7	13.4	17.8	14.1	0.7	13.9
PCB 180	396	7.36	10.3	12.9	17.0	13.5	0.7	13.3

Table A6: Molecular weights, log Kow, and compound-specific R_s for OCPs

compound	Mw	Log K_{ow}	Sampling rates, R_s (L d^{-1})					
			IFA	***JR 1***	***JR 2***	***EGL***	***HSL***	***AUP***
HCHs								
α-HCH	290.83	3.80	11.8	14.9	19.7	15.6	0.8	15.3
β-HCH	290.83	3.78	11.8	14.9	19.7	15.6	0.8	15.3
γ-HCH	290.83	3.72	11.8	14.9	19.7	15.6	0.8	15.3
δ-HCH	290.83	4.14	11.8	14.9	19.7	15.6	0.8	15.3
ε-HCH	290.83	3.78	11.8	14.9	19.7	15.6	0.8	15.3
DDTs								
o,p'-DDE	318.05	6.00	11.4	14.3	18.9	14.9	0.7	14.7
p,p'-DDE	318.05	6.51	11.4	14.3	18.9	14.9	0.7	14.7
o,p'-DDD	320.05	5.87	11.4	14.2	18.8	14.9	0.7	14.7
p,p'-DDD	320.05	6.02	11.4	14.2	18.8	14.9	0.7	14.7
o,p'-DDT	349.49	6.79	10.8	13.6	17.9	14.2	0.7	14.0
p,p'-DDT	349.49	6.91	10.8	13.6	17.9	14.2	0.7	14.0

Table A7: Molecular weights, log Kow, and compound-specific R_s for PAHs

Compound	Mw	Log K_{ow}	Sampling rates, R_s (L d^{-1})			
			Winter	**Spring**	**Summer**	**Autumn**
Naphthalene	128	3.37	17.7	13.3	64.7	13.8
Acenaphthylene	152	4.00	16.4	12.3	59.7	12.7
Acenaphthene	154	3.92	16.3	12.2	59.3	12.6
Fluorene	166	4.18	15.7	11.8	57.3	12.2
Phenanthrene	178	4.57	15.2	11.4	55.4	11.8
Anthracene	178	4.54	15.2	11.4	55.4	11.8
Fluoranthene	202	5.22	14.3	10.8	52.2	11.1
Pyrene	202	5.18	14.3	10.8	52.2	11.1
Benz[a]anthracene	228	5.86	13.5	10.2	49.3	10.5
Chrysene	228	5.91	13.5	10.2	49.3	10.5
Benzo[b]fluoranthene	252	5.90	12.9	9.7	47.1	10.0
Benzo[k]fluoranthene	252	5.90	12.9	9.7	47.1	10.0
Benzo[a]pyrene	252	6.04	12.9	9.7	47.1	10.0
Indeno[1,2,3-cd]pyrene	276	6.50	12.4	9.3	45.1	9.6
Dibenz[a,h]anthracene	278	6.75	12.3	9.3	44.9	9.6
Benzo[ghi]perylene	276	6.50	12.4	9.3	45.1	9.6

Table A8: Molecular weights, log Kow, and compound-specific R_s for PCBs

Congener	Mw	Log K_{ow}	Sampling rates, R_s (L d^{-1})			
			Winter	**Spring**	**Summer**	**Autumn**
PCB 28	258	5.67	12.8	9.6	46.5	9.9
PCB 52	292	5.84	12.0	9.1	43.9	9.3
PCB101	327	6.38	11.4	8.6	41.6	8.9
PCB 118	327	6.74	11.4	8.6	41.6	8.9
PCB 138	361	6.83	10.9	8.2	39.7	8.5
PCB 153	361	6.92	10.9	8.2	39.7	8.5
PCB 180	396	7.36	10.4	7.8	38.1	8.1

Table A9: Molecular weights, log Kow, and compound-specific R_s for OCPs

Compound	Mw	Log K_{ow}	Sampling rates, R_s (L d^{-1})			
			Winter	**Spring**	**Summer**	**Autumn**
HCHs						
α-HCH	290.83	3.80	12.1	9.1	44.0	9.3
β-HCH	290.83	3.78	12.1	9.1	44.0	9.3
Lindane	290.83	3.72	12.1	9.1	44.0	9.3
δ-HCH	290.83	4.14	12.1	9.1	44.0	9.3
ε-HCH	290.83	3.78	12.1	9.1	44.0	9.3
DDX						
o,p'-DDE	318.05	6.00	11.6	12.5	42.2	8.7
p,p'-DDE	318.05	6.51	11.6	12.5	42.2	8.7
o,p'-DDD	320.05	5.87	11.5	12.5	42.1	8.7
p,p'-DDD	320.05	6.02	11.5	12.5	42.1	8.7
o,p'-DDT	349.49	6.79	11.0	11.9	40.1	8.3
p,p'DDT	349.49	6.91	11.0	11.9	40.1	8.3

Table A10: A sample spreadsheet detailing how of C_w of individual analytes are calculated

Compound	FA	M	Rs	Log Kow	LogKSPMD	KSPMD	t (dy)	V(L)	Ns	Cw (ng/L)
Naphthalene	202.2	128	20.6725	3.37	3.1577	1437.81	14	0.00495	260	36.5316
Acenaphthylene	202.2	152	19.0684	4	3.92	8317.64	14	0.00495	150	3.6488
Acenaphthene	202.2	154	18.9516	3.92	3.8232	6655.8	14	0.00495	30	0.91087
Fluorene	202.2	166	18.2949	4.18	4.1378	13734.1	14	0.00495	60	0.90344
Phenanthrene	202.2	178	17.7045	4.57	4.6097	40709.9	14	0.00495	118	0.82741
Anthracene	202.2	178	17.7045	4.54	4.5734	37445.5	14	0.00495	112	0.81939
Fluoranthene	202.2	202	16.6827	5.22	5.3962	249000	14	0.00495	142	0.66741
Pyrene	202.2	202	16.6827	5.18	5.3478	222741	14	0.00495	105	0.49886
Benz[a]anthracene	202.2	228	15.7598	5.91	6.2311	1702550	14	0.00495	31	0.14235
Chrysene	202.2	228	15.7598	5.86	6.1706	1481153	14	0.00495	43	0.19784
Benzo[b]fluoranthene	202.2	252	15.0357	5.9	6.219	1655770	14	0.00495	34	0.1636
Benzo[k]fluoranthene	202.2	252	15.0357	5.9	6.219	1655770	14	0.00495	38	0.18285
Benzo[a]pyrene	202.2	252	15.0357	6.04	6.3884	2445682	14	0.00495	79	0.37857
Indeno[1,2,3-cd]pyrene	202.2	276	14.4063	6.5	6.945	8810489	14	0.00495	38	0.18885
Dibenz[a,h]anthracene	202.2	278	14.3575	6.75	7.2475	1.8E+07	14	0.00495	0	0
Benzo[ghi]perylene	202.2	276	14.4063	6.5	6.945	8810489	14	0.00495	36	0.17891

Table A11: The 16 priority pollutant PAHs targeted for chemical analysis

PAH	CAS RN	Retention time (min)	Monitored ions (M/Z)
Naphthalene	91-20-3	5.24	127, 128, 129
Acenaphthylene	208-96-8	7.81	151, 152, 153
Acenaphthene	83-32-9	8.26	152, 153, 154
Fluorene	86-73-7	9.72	165, 166, 167
Phenanthrene	85-01-8	13.57	152, 178, 179
Anthracene	120-12-7	13.79	152, 178, 179
Fluoranthene	20644-0	20.52	200, 202, 203
Pyrene	12900-0	21.89	200, 202, 203
Benz[a]anthracene	56-55-3	28.12	226, 228, 229
Chrysene	218-01-9	28.26	226, 228, 229
Benzo[b]fluoranthene	205-99-2	31.92	126, 250, 252
Benzo[k]fluoranthene	207-08-9	31.98	126, 250, 252
Benzo[a]pyrene	50-32-8	32.91	126, 250, 252
Indeno[1,2,3-cd]pyrene	193-39-5	37.46	138, 276, 277
Dibenz[a,h]anthracene	53-70-3	37.72	139, 278, 279
Benzo[ghi]perylene	191-39-5	38.72	138, 276, 279

Molecular ions are underlined