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.