# Calibration and field application of a molecularly imprinted membrane-passive sampler for the sampling of indicator polychlorinated biphenyls in selected aquatic environments of South Africa

Dennis S. Mkhize, Laura P. Quinn, Hlengilizwe Nyoni, Bhekie B. Mamba and Titus A. M. Msagati

## ABSTRACT

A passive sampling device, based on molecularly imprinted membranes (MIM), was fabricated and optimised for sampling polychlorinated biphenyls (PCBs) in aquatic ecosystems. The newly-developed passive sampler was subjected to *in-situ* calibration studies to determine PCB sampling rates under various conditions of water turbulence and temperature. This was carried out by exposing the passive samplers to water spiked with PCBs in a continuous-flow exposure setup. The samplers were preloaded with known concentrations of performance reference compounds (PRCs) prior to exposure. Sampling rates of seven indicator PCBs' congeners (PCBs 28, 52, 101, 118, 138, 153 and 180) ranged between 15.3 and 95.6 L/d for the different environmental conditions investigated. To determine the field suitability, the samplers were preloaded with PRCs and deployed for 10 days at the Roodeplaat and Hartbeespoort Dams, in South Africa. Water samples were taken at the end of the deployment period to compare the spot-and-grab samples to the developed samplers. PCBs 28, 101 and 138 were detected in the samplers deployed at Hartbeespoort Dam. The samplers deployed at the Roodeplaat Dam had quantifiable amounts of PCBs 28, 52, 101, 138 and 180 (0.047–0.828 ng $mL^{-1}$ $d^{-1}$). The sampler enhanced the detectability of PCB 52 and PCB 180, which were not detected in water samples. The field suitability trials indicated that the developed sampler could successfully be used for PCB monitoring. The sampler enhanced the detection of PCBs that would otherwise be too low to detect in samples collected through the traditional spot-and-grab sampling technique.

**Key words** | molecularly imprinted membranes, passive sampling, performance reference compounds, polychlorinated biphenyls, time-weighted average concentrations

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## INTRODUCTION

Polychlorinated biphenyls (PCBs) are ubiquitous persistent organic pollutants (POPs) that have attracted the attention of scientists and policy makers alike, due to their toxicity and persistence in the environment (Sun *et al.* 2007; Nieuwoudt *et al.* 2009). They are carcinogenic, neurogenic and endocrine disruptors that affect the reproductive and immune system as well as the functioning of the thyroid hormones (Battershill 1994; Lind *et al.* 2000; Lundberg *et al.* 2006). Therefore, their presence in the environment is of great concern. Out of 209 possible congeners, seven PCBs have been identified as indicator PCBs (PCBs 28, 52, 101, 118, 138, 153 and 180) due to their prevalence within the environment (McFarland & Clarke 1989; Hamers *et al.* 2011).

One of the greatest challenges in PCB sampling is obtaining reliable and accurate data. This could be due to the low concentrations of PCBs in aquatic environments and the intrinsic variations of environmental conditions with time (Vrana *et al.* 2006a, 2006b). Traditional sampling techniques such as spot sampling often require the collection of large volumes of samples and a higher sampling frequency (Bopp *et al.* 2005, 2007; Popp *et al.* 2005). This can increase the turnaround time and cost for analysis, as

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multiple concentration steps and more intricate sample clean-up steps are required (Bopp *et al.* 2005, 2007; Popp *et al.* 2005). Alternatively, passive sampling devices, such as semi-permeable membrane devices (SPMDs) and the classical MESCO, can be used to augment the shortcomings of these traditional sampling techniques (Kim *et al.* 2014; Alvarez 2010). However, these passive samplers are designed to sample a variety of non-polar pollutants (Kim *et al.* 2014; Piccardo *et al.* 2010), which can result in poor PCB enrichment occurring in low concentrations. Furthermore, recovery of the sequestered analytes from these samplers, such as the SPMD, can result in complex matrices and increased interferences (Esteve-Turrillas *et al.* 2008; Leonard *et al.* 2002). This can result in more challenges in the detection and analysis of PCBs, which often occur at ultra-trace levels in aquatic environments. Therefore, a sampler with high selectivity is important for accurate and reliable sampling of PCBs. In addition, a sampler that can simplify the extraction, clean-up and the overall analysis of PCBs is required.

To augment the shortcomings of these passive sampling techniques, a novel passive sampling device was designed based on our previously synthesised molecularly imprinted membranes (MIMs) (Mkhize *et al.* 2017). The developed sampler was optimised for sampling PCBs in aquatic environments. The molecular imprinting was aimed at enhancing PCB selectivity and enrichment, and this is crucial as PCBs usually occur at ultra-trace levels in aquatic environments (Sun *et al.* 2007). MIMs were produced from molecularly imprinted polymers (MIPs), which were previously obtained from the polymerisation of a mixture of cross-linkers, porogenic solvent and functional monomers in the presence of a template and radical initiator under heat (Cormack & Elorza 2004; Saad *et al.* 2015; Mkhize *et al.* 2017). In this work, we report the calibration and field application of the newly-developed passive sampler for the sampling of indicator PCBs in selected aquatic environments.

## THEORY OF SAMPLER AND CALCULATIONS

The accumulation of target analytes by passive samplers usually follows linear, curvilinear or equilibrium phases over the deployment period. When uptake occurs over the linear phase, analyte concentrations in water ($C_w$) can be calculated as follows:

$$C_w = \frac{N}{R_s t} \tag{1}$$

where $C_w$ is the TWA concentration (ng/L) of the PCBs in water during the exposure time, $N$ is the PCB concentration (ng) in the sampler accumulated over the exposure or deployment period, $R_s$ is the sampling rate (usually in L/d) and $t$ (days) is the exposure or sampling period.

Regression models to estimate a chemical's site-specific sampling rate and TWA concentrations have been developed, and these are based on octanol-partition coefficients (log $K_{ow}$ values) of the analyte, the desorption rate constant, $k_e$ ($d^{-1}$) of the PRC and the sampler-water partition coefficient ($K_{sw}$). Isotropic exchange takes place when the uptake and offload kinetics are affected by the mass transfer law, and obey first-order kinetics and the half-lives measured during loss and uptake are approximately identical (Huckins *et al.* 2002). This usually takes place between chemicals and their deuterated and/ or $^{13}$C-labelled counterparts (Huckins *et al.* 2002). Therefore, under isotropic exchange conditions, the desorption rate constant $k_e$ of a PRC can be determined according to the following equation (Huckins *et al.* 2002):

$$k_{e-PRC} = \ln \frac{[(N_t|N_0)]}{t} \tag{2}$$

where $t$ is the exposure time for the passive sampler, $N_0$ and $N_t$ are PRC concentrations in the sampler at time 0 and $t$, respectively. According to Equation (3), the log $K_{sw}$ is determined from linear regression models using the PRC's log $K_{ow}$.

$$\log K_{sw} = a_0 + 2.3211 \log K_{ow} - 0.1618 (\log K_{ow})^2 \tag{3}$$

where $a_0$ is the intercept, which is known to be $-2.61$ for PCBs. When the sampler volume, $V$ (mL), is known, the $R_s$-$_{PRC}$ can be determined using $K_{sw}$ and $k_e$ values (already known from the above equations). The equation to calculate $R_s$-$_{PRC}$ is as follows:

$$R_{s-PRC} = V_s K_{sw} k_e \tag{4}$$

TWA concentrations can only be determined once the sampling rates of target analytes are known. The following equation can be used to estimate the sampling rates:

$$R_{s,i} = R_{s,PRC} \frac{\propto_i}{\propto_{PRC}} \tag{5}$$

where $\alpha_i$ is the compound-specific factor on the sampling rate that can be interpolated with a third-order polynomial obtained from the analysis of experimental data on the

PCBs sampling rates:

$$\log \alpha_i = 0.0130\ (\log K_{ow})^3 - 0.3173\ (\log K_{ow})^2 + 2.244\ (\log K_{ow}) \quad (6)$$

Once PRC-derived sampling rates are available, Equation (6) can be used to determine the sampling rates of other analytes, as long as the log $K_{ow}$ values are known. Furthermore, TWA concentrations can be calculated according to Equation (7), once the sampling rates have been determined:

$$C_w = \frac{N}{V_s K_{sw}\left(1 - e^{\left(\frac{-R_s t}{V_s K_{sw}}\right)}\right)} \quad (7)$$

However, it is well-known that sampling rates are affected by a variety of environmental conditions during deployment, and that they are sampling-site specific (Huckins *et al.* 2002). Furthermore, the dissipation rate constants of PRCs are affected by the same factors as sampling rates, under isotropic exchange conditions. Therefore, the effects of environmental factors on sampling rates are corrected by comparing PRC dissipation rates obtained under controlled laboratory conditions ($k_{e\text{-}PRC,cal}$), with those obtained during field deployments ($k_{e-PRC,in\text{-}situ}$). This is demonstrated by Equation (8), as follows:

$$R_{s-corrected} = R_{s-cal}\ x\ \left(\frac{k_{e-PRC,in-situ}}{k_{e-PRC,cal}}\right) \quad (8)$$

The field PRC dissipations rates are determined by comparing the amount of PRCs loaded into the sampler before deployment with the amount remaining after deployment. This mathematical equation (Equation (8)) accounts for environmental conditions and gives a more accurate account for sampling-site specific sampling rates ($R_{s\text{-}corrected}$), thus resulting in a more correct estimation of TWA concentrations.

## EXPERIMENTAL

### Chemicals and materials

Polysulfone (PSf, 97%), ethylene glycol dimethacrylate (EDGMA, 98%), methacrylic acid (MAA, 97%) and 4-phenylphenol were purchased from Sigma Aldrich (St Louis, USA). The radical initiator, azobisisobutyronitrile (AIBN, 97%), was obtained from Fluka Chemicals (St Louis, USA). *N*-methyl-2-pyrrolidone (NMP, 98%) was obtained from DLD Scientific (Johannesburg, South Africa). All reagents were used without further purification. The deuterated polyaromatic hydrocarbons (D-PAHs) – phenanthrene-$D_{10}$ (98%), pyrene-$D_{10}$ (98%) and chrysene-$D_{12}$ (98%) were purchased from Sigma Aldrich (St Louis, USA). The selected native PCBs used in this study represented dioxin-like and the seven indicator PCBs, which are the most toxic and most commonly occurring in the environment, respectively (Faroon *et al.* 2003). The native PCBs: PCB 105 (98.8%), PCB 126 (98.8%), PCB 153 (98.8%) and PCB 183 (98.8%), were purchased from Cerilliant Corporation (Texas, USA). Whilst PCB 28 (98.6%), PCB 52 (98.4%), PCB 101 (98.4%), PCB 118 (98.4%), PCB 138 (98.5%), PCB 180 (98.7%) and the nine multi-congener mix solutions (C-CS-01 to C-CS-09) at 10 μg/mL in iso-octane were obtained from AcuStandard Inc. (Connecticut, USA). The $^{13}C_{12}$-labelled mono-ortho PCB mix, used as internal standard ($^{13}C_{12}$-PCBs 114, 118, 123, 156, 157, 167 and 189), and the PRCs, $^{13}C_{12}$-PCB 28, 101, 105 and 153, were purchased from Cambridge Isotope Laboratories, Inc. (Massachusetts, USA). A summary of the physicochemical properties of the different PCBs used, including the log $K_{ow}$ values was obtained from Mackay and co-workers (Mackay *et al.* 1992a, 1992b). MIMs were prepared as described by Mkhize *et al.* (2017).

### Sampler design and configuration

The newly-fabricated passive sampler was based on a MIM and was optimised to sample PCBs at high sampling rate. The sampler consists of a MIM with an effective area of approximately 30.3 $cm^2$, sandwiched between two metal washers. The passive sampler is based on a single-layer system, where the receiving phase is embedded within the membrane. This sampler eliminates any additional diffusive layers, thus increasing sampling rates through a more direct exposure between PCBs in water and receiving phase.

### Passive sampler preparation and PRC loading

To determine off-load kinetics, MIMs were cut into disks with an effect area of 30.3 $cm^2$ and spiked with PRCs prior to exposure and calibration. $^{13}C_{12}$-PCBs and D-PAHs were used as PRCs. An aqueous solution of PRCs was

prepared by adding 500 μL of methanolic solution (1,000 ng/mL composite containing $^{13}C_{12}$-PCBs 28, 101, 105, 153, phenanthrene-$D_{10}$, pyrene-$D_{10}$ and chrysene–$D_{12}$) to water (50 mL). MIMs were equilibrated overnight in the PRC-enriched water in order to load them with PRCs. The amount of PRCs remaining in the water after equilibration was used to determine the amount loaded into the MIMs. Quantification was done through comprehensive two-dimensional gas chromatography, coupled to time-of-flight mass spectrometry (GC × GC-TOFMS). Samplers were assembled and stored at 4 °C until required. To evaluate the presence of any PRCs in the water used, a negative blank was prepared by exposing MIMs to non-enriched water for 24 hours, followed by GC × GC-TOFMS analysis (see Quantification and instrumental analysis section) of the water after exposure. To determine possible losses during PRC-loading, PRC-enriched water was left to equilibrate for 24 hours in the absence of MIMs.

## Passive sampler calibration

Calibration experiments were carried out in a constant concentration flow-through exposure system, consisting of a 40 L assimilation tank equipped with an overhead stirrer (Figure 1(a) and 1(b)) and an overflow to waste. The flow-through set-up allowed experiments to be carried out

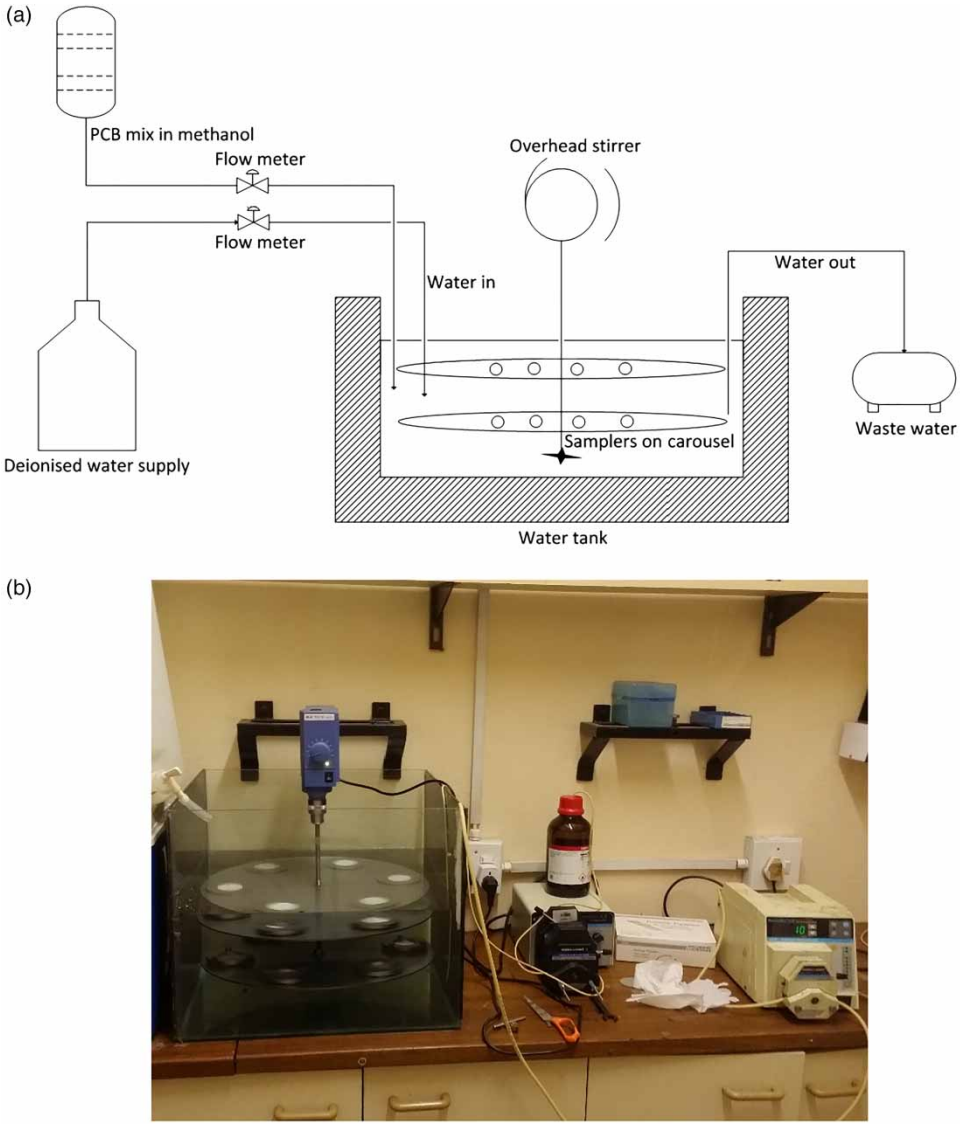


**Figure 1** | (a) A typical set-up showing the calibration of MIM-based passive samplers with a flow-through set-up with an overflow to waste. (b) A typical set-up showing the calibration of MIM-PSD passive samplers using a flow-through set-up with an overflow to waste.

under controlled condition of temperature and PCB concentration, whilst the overhead stirrer was used to investigate effects of water velocity on PCB uptake rates of the sampler.

The experiments were conducted with 24 samplers in a temperature-controlled dark room to minimise photolytic degradation of PRCs. The samplers were mounted on four carousel holders, each capable of housing six passive samplers at a time. Two separate peristaltic pumps were used to introduce water and methanolic solutions of PCBs (PCBs 28, 105, 126, 153 and 183) into the simulation tank at known, controlled flow rates. The feed water was introduced at a flow rate of 2 L/h, whilst the methanol solutions of PCBs were introduced at a flow rate of 100 μL/min (approximately 60 ng/L). The wastewater was pumped out of the simulation tank at the same rate (2 L/h) in order to maintain a constant amount of water. The concentration of PCBs in the simulation tank was maintained in the range of 10–50 ng/L throughout the duration of the experiments. In addition, methanol concentrations in the tank were kept below 1% (v/v) at any given time. PCBs in the simulation tank were allowed to equilibrate for 24 hours prior to exposure of the samplers. The first set of experiments was carried out over a course of 10 days under gentle stirring conditions at room temperature (Table 1).

For statistical purposes, three samplers were removed at set intervals (1, 2, 4, 5, 7, 8, 9 and 10 days) and analysed to determine the uptake and loss of PCBs and PRCs, respectively. The PRC loss data were used to elucidate the sampling rates ($R_s$) of PCBs. Removed samplers were replaced by empty metal washers to maintain hydrodynamic conditions in the water tank. In addition, three water samples (500 mL) were removed and analysed for PCBs each time a sampler was removed. The water samples were analysed using an ultrasonic extraction method.

**Table 1** | A summary of experiments carried out during calibration of the MIM-based passive sampler for different environmental conditions

| Experiments | Temperature (°C) | Stirring speed (cycles/min) | Concentration (ng/mL) | Exposure period (days) |
|---|---|---|---|---|
| 1 | 18 | 40 | 50 | 10 |
| 2 | 21 | 40 | 50 | 10 |
| 3 | 26 | 40 | 50 | 10 |
| 4 | 21 | 0 | 50 | 10 |
| 5 | 21 | 70 | 50 | 10 |

To determine the effects of hydrodynamic conditions on PCB sampling rates, experiments were also carried out under quiescent conditions (no stirring) at room temperature. The contents of the tank were agitated regularly to prevent a concentration gradient from forming. The samplers were removed from the simulation tank and processed to determine the amount of PRCs remaining after exposure and the amounts of PCBs accumulated (Vrana *et al*. 2006b). To investigate the different parameters (hydrodynamic conditions and temperature) on PCB sampling, a total of five experiments (Table 1) were conducted, which were based on fixing one variable whilst altering the other. The effects of hydrodynamic conditions on sampling rates were investigated by conducting two experiments at different speeds (0 and 70 cycles/min), whilst maintaining a constant temperature (21 °C). The nominal PCB concentration was maintained throughout all the investigations.

## Field deployment

For evaluation of the performance for monitoring PCBs under field conditions, PRC-loaded samplers ($n = 3$ at each deployment point) were deployed at the Roodeplaat and Hartbeespoort Dams. The Roodeplaat Dam is located in Pretoria, in the Gauteng province, South Africa (25.62083°S 28.37138°E), whilst Hartbeespoort Dam is located in the North West Province (25.62083°S 28.37138°E), 35 km west of Pretoria. The dams are renowned for poor water quality, resulting from domestic and industrial effluents from surrounding areas (Amdany *et al.* 2014), and were therefore selected as deployment sites for evaluation of the newly-developed MIM-based sampler. Three samplers were deployed at two different harbour points in each dam, denoted Harbour 1 and Harbour 2. Samplers were kept at approximately 4 °C during transportation to the deployment site. Field blanks were taken to each site during deployment and retrieval to account for any possible contamination during transportation and handling (Alvarez 2010). Samplers were immersed approximately 2 m below the surface of the water and secured using a rope. The water temperature during the deployment period ranged between 18 and 21 °C, and no rainfall was recorded over the course of the deployment period. After 10 days of exposure, samplers were retrieved, sealed in foil pre-cleaned with triplicate rinses of acetone and hexane, labelled and stored at approximately 4 °C. In addition, 1 L water samples were collected (glass bottles) in triplicates after deployment

at each harbour point. PRC concentrations at time zero and accumulated PCBs, after deployment were determined.

### Sampler retrieval and processing

After retrieval, MIMs were extracted overnight in hexane *via* Soxhlet extraction. Prior to extraction, internal standard mix was gravimetrically added to the samplers. The resulting extracts were purified using dual layer Florisil/silica SPE cartridges and reconstituted in 100 μL of toluene prior to GC × GC-TOFMS analysis (see Quantification and instrumental analysis section). This was to determine accumulated PCB amounts and PRCs lost during deployment. All three samplers and field blanks from each harbour point were analysed. The final concentration of the extract contained approximately 625 ng/mL of internal standard mix.

### Water sample processing

Water samples from the sampler calibration system were extracted in triplicate using an ultrasonic and liquid-liquid extraction (LLE) with DCM/hexane (3:1%v/v) mixture. The extracts were purified using dual layer Florisil/silica SPE cartridges and reconstituted in 100 μL of toluene prior to GC × GC-TOFMS analysis. Due to larger volumes, field water samples were extracted in an automated extraction system (Horizon™ SPE-DEX 4790 Automated Extractor System) using $C_{18}$ cartridges and eluting with 1:1 ethyl acetate/DCM mixtures. Prior to extraction, internal standard mix was gravimetrically added to the field water samples. The spiked water samples were homogenised and allowed to equilibrate overnight at 4 °C prior to extraction. The final concentration of the extract contained approximately 625 ng/mL of internal standard mix.

### Quantification and instrumental analysis

GC × GC-TOFMS analysis was performed on a LECO Pegasus IV system (LECO Corporation, St Joseph, MI, USA). The autosampler, GC and MS methods were optimised based on the method developed by Focant *et al.* (2004) using a Rxi®-5 Sil MS (30 m, 0.25 mm ID, 0.25 μm df) primary column and an Rxi®-17SilMS (1.5 m, 0.25 mm ID, 0.25 μm df) secondary column. The method used was optimised for all 209 PCB congeners. The multi-ramp temperature program used can be summarised as follows: 80 °C for 2 min, then to 150 °C at 25 °C/min, then to 200 °C at 1.5 °C/min, then to 290 °C at 5 °C/min with a 10 min hold. A 20 °C temperature offset between the primary and secondary oven and a 5 s modulation period. The helium flow through the column was 1.5 mL/min with corrected constant flow via pressure ramps. A 1 μL injection was used with an inlet temperature of 250 °C. Data processing and generation of contour plots was achieved through the Leco ChromaTOF™ software. For each analyte, two mass ions were used, one for confirmation and one for quantification. Quantification was based on a seven-point matrix-matched calibration for both passive samplers and water samples. Absolute recoveries were for both passive samplers and water samples.

### Quality control

Quality control measures included the use of field blanks during deployment and retrieval of samplers. Furthermore, absolute recovery samples for the passive samplers and collected water samples and solvent blanks in-between GC runs were used during quantification. The use of matrix-matched calibrations was also used as a quality control measure.

## RESULTS AND DISCUSSION

### Calibration of passive samplers

Passive samplers were spiked with known concentrations of PRCs and exposed to a constant concentration of PCBs in a continuous-flow simulation tank. Preliminary experiments showed that the sampler reached after 10 days of exposure. The amount of PCBs accumulated and PRCs dissipated from the sampler showed a characteristic and satisfactory (correlation between 0.8 and 1) linear relationship with exposure time. The PRC dissipation curves (Figure 2) show a clear decrease in PRC concentrations as a function of time, which occurs under isotropic conditions (Huckins *et al.* 2002).

A summary of the sampler calibration data (supplementary data, Table S1, available with the online version of this paper) shows that the greatest PRC loss was observed for $^{13}C_{12}$-PCB 28, followed by $^{13}C_{12}$-PCBs 101, 105 and 153.

The labelled PCBs, pyrene and chrysene had dissipation rates between 20 and 80%, and were therefore suitable candidates for estimation of sampling rates for the seven indicator PCBs (Alvarez 2010). Phenanthrene completely dissipated from the MIM-based sampler and thus was not used to estimate sampling rates. To minimise variability associated with the use of a single PRC and to ensure more accurate measurements, sampling rates were estimated from more than one

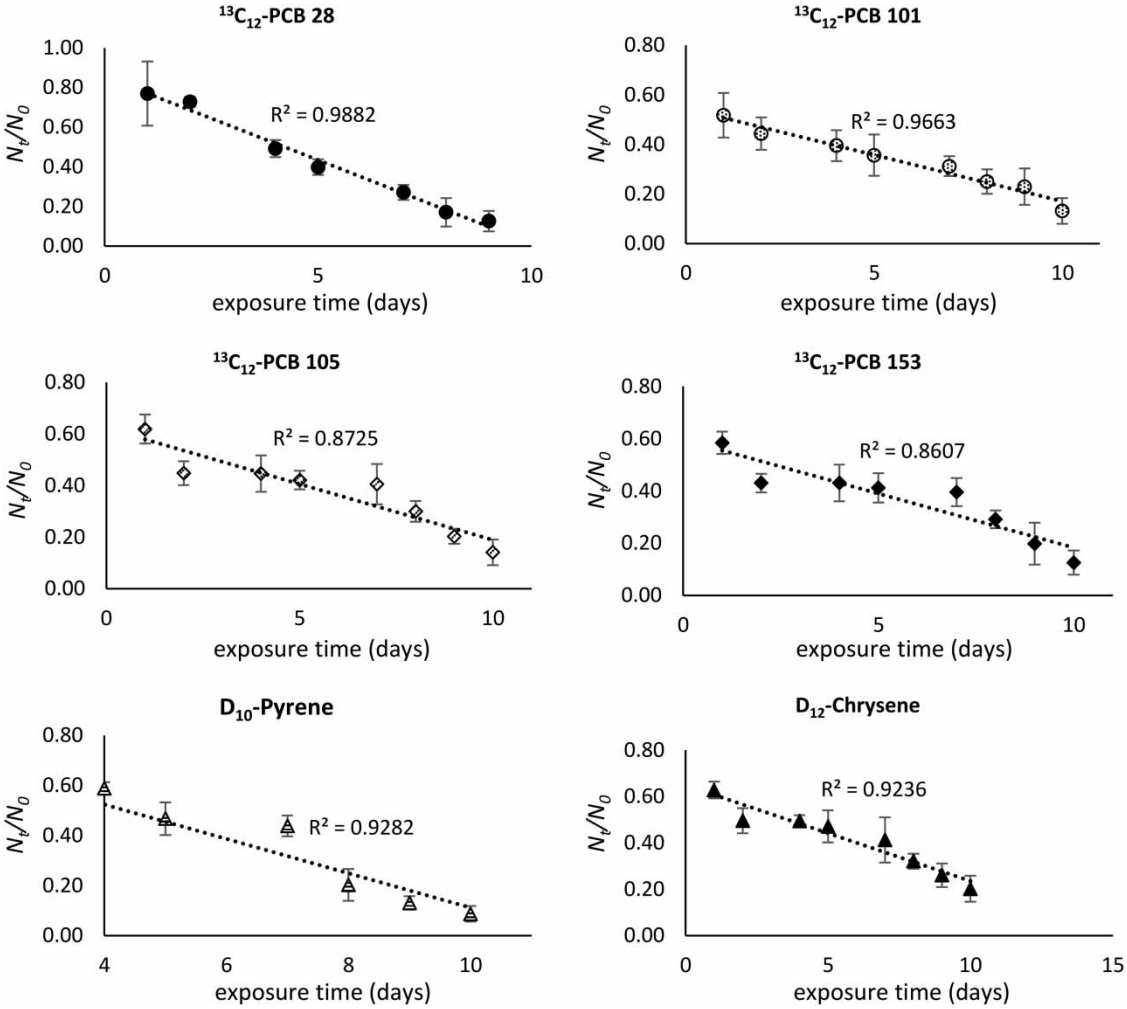


**Figure 2** | PRC offload curves from the MIM-based sampler over a ten-day exposure period (18 °C, 40 cycles/min). The results show an average over three separate measurements.

PRC (Alvarez 2010). PCB sampling rates for the different congeners ranged between 20.7 and 71.3 L/d over the three different temperatures investigated. Whilst those obtained under different hydrodynamic conditions ranged between 15.3 and 95.6 L/d for the different congeners. Sampling rates are largely affected by the physicochemical properties of analytes under investigation. The less chlorinated and moderately hydrophobic PCBs had higher sampling, whilst the more chlorinated congeners had the lowest sampling rates. This is consistent with observations from Estoppey *et al.* (2014) in which silicone rubber passive samplers were used for PCB uptake from water. The highest sampling rates were recorded for PCB 28, followed by PCBs 52, 101, 118, 138, 153 and 180. The decrease in sampling rates with higher log $K_{ow}$ values is believed to be due to a decrease in diffusion coefficients and mass transfer kinetics resulting from an increased molecular size (Huckins *et al.* 2002).

## Verification of isotropic exchange kinetics

Isotropic exchange kinetics apply when target analytes diffuse from the bulk solution and into the sampler receiving phase, followed by subsequent dissipation of its PRC or labelled analogue from the receiving phase (Huckins *et al.* 2002). Since analyte diffusion and PRC dissipation are governed by the same mass transfer kinetics when measured under the same conditions, PRCs can be used to correct for the effects of environmental conditions during sampling (Vrana *et al.* 2006a, 2006b). When dissipation ($k_e$) and accumulation rates ($R_s$) are measured under the same conditions, it is assumed that isotropic exchange kinetics apply, and the PRCs can be used to correct for the effects of environmental conditions during sampling.

Application of the MIM-based sampler under different conditions of water velocities and temperature using seven

different PRCs showed sufficient correlation between PCB sampling and PRC dissipation rates (Figure 3). This also demonstrated that PCB uptake and PRC dissipation remained in the linear phase under the different sampler calibration conditions investigated.

This data set represents the sampling and dissipation rates associated with each of the five experiments conducted. The results show the average over three separate measurements. In fact, a correlation was observed for a wider scope of PCB and PRC analogue combinations. This was crucial as it allows for the estimation of sampling rates for PCBs without the use of their carbon-13 labelled PRC analogues. The estimation of sampling rates for PCBs 52, 118, 138 and 180 was determined without the use of their carbon-13 labelled analogues as PRCs. The four $^{13}C_{12}$-labelled PCBs ($^{13}C_{12}$-PCBs 28, 101, 105 and 153) used as PRCs in this study, had sufficient correlation with PCBs 52, 118, 138 and 180 (0.947, 0.987, 0.997 and 0.850) to be used as PRCs.

## Effects of temperature and hydrodynamic conditions on sampling rates

The effects of temperature and hydrodynamic conditions on sampling rates were investigated as highlighted in Table 1, and the effects are illustrated in Figure 4. Experiments performed at 18 °C resulted in the lowest sampling rates for all PCBs investigated. Increasing the temperature from 18 to 21 °C resulted in an increase in sampling rates by a factor 1.37. A further increase from 21 to 26 °C had a less notable effect, as the sampling rates only increased by a factor of 1.16 for the different PCBs investigated. Furthermore, increasing the temperature from 16 to 26 °C led to an increase in PCB sampling rates by a factor of 1.60, which was more notable. Increasing temperature results in increased mass transfer kinetics of PCBs towards the sampler receiving phase, thus increasing sampling rates. Increasing temperature also resulted in increased dissipation rate constants ($k_e$) of PRCs, which further demonstrates the existence of isotropic exchange kinetics between PCBs and PRCs.

Increasing stirring speeds from 0 to 40 cycles/min and 40 to 70 cycles/min increased the sampling rates by a factor of 1.86 and 1.56, respectively. The lowest sampling rates were obtained under static conditions (Figure 4). Increasing stirring speeds from 40 to 70 cycles/min had a less notable effect compared to increasing from 0 to 40 cycles/min. It is likely that the sampler approaches equilibrium with increasing stirring speeds, which could have led to minimal effects on the sampling rates of PCBs. In general, increasing stirring speeds increases mass transfer kinetics, favouring the diffusion of PCBs from the bulk

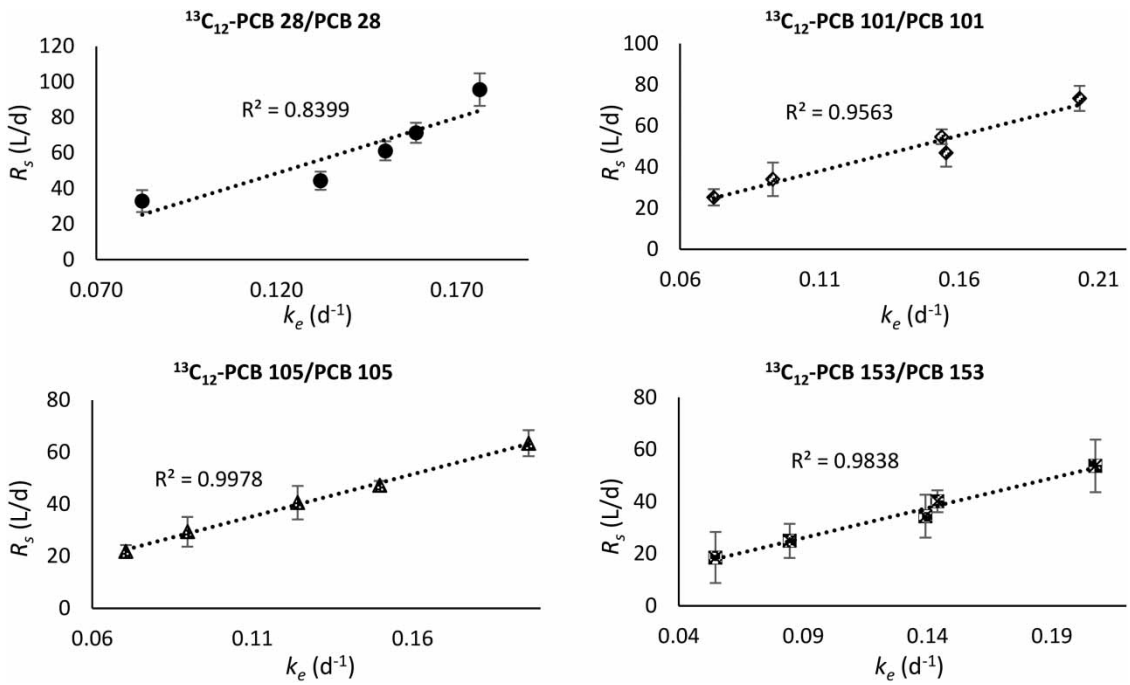


**Figure 3** | The verification of isotropic exchange kinetics through correlation between sampling rates ($R_s$) of PCBs and the dissipation rate constants ($k_e$), their PRC analogues.

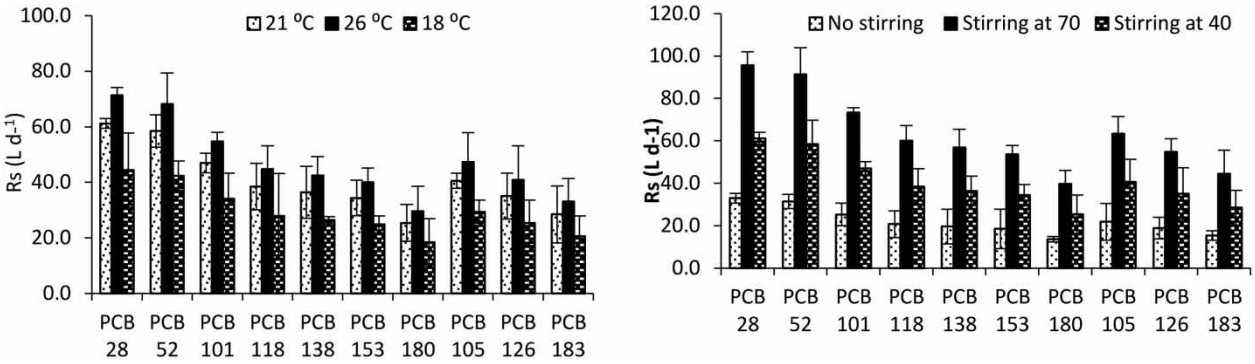


**Figure 4** | The effect of temperature (at 40 cycles/min) and hydrodynamic conditions (at 18 °C) on PCB sampling rates. An average of three measurements for each experiment were recorded.

aqueous solution and into the receiving phase of the sampler, thus increasing sampling rates at higher stirring speeds. The high sampling rates suggest suitability of the sampler for PCB sampling. High sampling rates are crucial for PCB sampling, due to their ultra-trace levels in water (Vrana *et al*. 2006a, 2006b).

## Deployment of the passive samplers

The newly-developed sampler was deployed at the Hartbeespoort and Roodeplaat Dams to evaluate performance and to determine TWA concentrations of the seven indicator PCBs. Prior to deployment, the samplers were spiked with six PRCs at known concentrations, covering a log $K_{ow}$ range of 4.46 to 6.92. PCBs and PRCs in deployed samplers and water samples collected were quantified through isotope dilution. Concentrations were adjusted according to the PCB recoveries obtained. The absolute recoveries, limit of detection (LOD), limit of quantification (LOQ), TWA concentrations and %RSD of the samples analysed are summarised in Table 2.

### Roodeplaat Dam

Over the ten-day sampling period, the samplers had sequestered PCBs 28, 52, 101, 138 and 180 in varying concentrations at the different sampling points. Quantifiable concentrations of PCBs 28, 101 and 138 were found in the water samples, with PCB 28 having the highest freely dissolved concentration. PCB 28 is characterised by a lower log $K_{ow}$ (5.67) (Mackay *et al.* 1992a, 1992b). Therefore, its freely dissolved concentration in water tends to be higher than its more chlorinated counterparts. There was no detectable amount of PCB 52, 118, 153 and 180 in the water samples. These more chlorinated congeners tend to occur in soils and sediments, as opposed to occurring in their freely dissolved form (Agency for Toxic Substances and Disease Registry 2000), thus accounting for their lower detectability in water samples. Using laboratory-derived sampling rates, TWA concentrations were determined from the amounts of PCBs accumulated by the samplers during deployment. Field blanks taken to the Roodeplaat Dam during deployment and retrieval of the samplers had ultra-trace levels of PCB 52 and 101, whilst PCBs 28, 118, 138, 153 and 180 were not detected. Concentrations accumulated in the field blanks were subtracted from amounts in the deployed samplers, which gives more accurate TWA concentrations in the dam.

A comparison of PRC amounts in the samplers before ($N_0$) and after deployment ($N_t$) was used to determine dissipation rate constants ($k_e$), as demonstrated by Equation (2). PRC dissipation rates are sampling-site dependent, due to an intrinsic variation of conditions between aquatic environments. These variations are accounted for by comparing site-specific dissipation rate constants to those obtained under controlled laboratory conditions, as demonstrated by Equation (8). This correction factor gives a more accurate calculation of TWA concentrations. PCB 28 had the highest TWA concentrations (Table 2) across the different samplers in both harbour points. This was followed by PCBs 180, 101, 138 and 52, whilst PCBs 118 and 153 were not detected. The higher concentration of PCB 28 in the samplers could be attributed to a greater abundance in water or a higher sampling rate associated with this congener, or a combination of both factors.

It was interesting to note a presence of PCB 52 and PCB180 in the samplers, which was not detected in the water samples. The lower detectability of PCB 180 in water samples could be attributed to higher log $K_{ow}$ values (Mackay *et al.* 1992a). It has been well established that

**Table 2** | Summary of results obtained from MIM-based samplers deployed at the Roodeplaat and Hartbeespoort Dams

| PCBs | LODs (ng/mL) | LOQs (ng/mL) | $R^2$ | Mean recoveries | (%RSD) | Roodeplaat TWA concentration | | | | Roodeplaat water sample concentration | | | | Hartbeespoort TWA concentration | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Harbour 1 (ng mL $d^{-1}$) | Harbour 1 (%RSD) | Harbour 2 (ng mL $d^{-1}$) | Harbour 2 (%RSD) | Harbour 1 (ng $mL^{-1}$) | Harbour 1 (%RSD) | Harbour 2 (ng $mL^{-1}$) | Harbour 2 (%RSD) | Harbour 1 (ng mL $d^{-1}$) | Harbour 1 (%RSD) | Harbour 2 (ng mL $d^{-1}$) | Harbour 2 (%RSD) |
| 28 | 0.353 | 1.18 | 0.966 | 81.3 | 2.70 | 0.828 | 112 | 1.52 | 36.0 | 4.51 | 173 | 0.0051 | 170 | 0.754 | 18.2 | 0.336 | 29.8 |
| 52 | 0.307 | 1.02 | 0.979 | 75.5 | 20.9 | 0.047 | 79.1 | 0.0569 | 37.7 | ND | ND | ND | ND | ND | ND | ND | ND |
| 101 | 0.306 | 1.02 | 0.979 | 103 | 20.4 | 0.310 | 47.7 | 0.347 | 33.9 | 4.42 | 173 | 4.75 | 4.51 | ND | ND | 0.0599 | 70.5 |
| 118 | 0.182 | 0.606 | 0.990 | 110 | 3.84 | ND | ND | N.D. | N.D. | ND | ND | ND | ND | ND | ND | ND | ND |
| 138 | 0.150 | 0.500 | 0.994 | 121 | 35.4 | 0.291 | 62.6 | 0.578 | 13.9 | 2.83 | 173 | ND | ND | 0.0530 | 56.6 | 0.0157 | 70.5 |
| 153 | 0.0984 | 0.328 | 0.998 | 84.1 | 35.9 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| 180 | 0.111 | 0.369 | 0.997 | 95.9 | 16.0 | 0.436 | 53.5 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |

ND = not detected.

highly chlorinated PCBs tend to occur in higher concentrations in soils and sediments, as opposed to water, due to their higher log $K_{ow}$ values (Faroon *et al.* 2003). The detection of PCB 52 and PCB 180 in the samplers highlights their presence in water. However, they were not present in concentrations that are easily detectable through spot-and-grab sampling. This demonstrates the enrichment capability of the MIM-based sampler, and its ability to enhance the detection limits of PCBs that would normally occur at ultra-trace levels in aquatic environments. The individual PCBs detected were combined to obtain a sum of the concentrations in the harbour points (1.9124–2.5021 ng $mL^{-1}$ $d^{-1}$). It is evident that the newly-developed MIM-based sampler enhances the detectability of PCBs occurring in low concentrations in water, in considerably shorter deployment times.

The concentrations detected through spot sampling appear to be highly variable (Table 2), and this could be due to the hydrodynamic properties of the dam. Furthermore, an unrealistically large number of water samples would have to be collected and analysed to get TWA concentrations from spot sampling. Therefore, concentrations obtained from the collected water samples can only be used as an indicator for the presence of PCBs in aquatic systems. The PCB concentrations detected through the MIM-based samplers also showed a great degree of variation, with %RSD ranging between 13.9 and 112.3% (Table 2). This could be attributed to a lack of uniformity across the different membranes in the samplers during MIM fabrication. However, the newly-developed sampler gives a good indication of the presence of PCBs in aquatic environments, and this is achieved through minimal sample preparation, as opposed to spot sampling.

## Hartbeespoort Dam

The amount of PRCs before and after deployment were compared and used to correct for sampling-site specific conditions using Equations (2) and (8). Field blanks taken to the deployment site during deployment and retrieval of the samplers showed no quantifiable amounts of any of the seven indicator PCBs. The samplers sequestered PCBs 28, 101 and 138 in varying concentrations over the deployment period, and from these accumulated amounts, TWA concentrations were determined. PCB 28 showed the highest TWA concentration (Table 2), followed by PCBs 101 and 138. There were no quantifiable amounts of PCBs 52, 118, 153 and 180 in the samplers after deployment. PCB 28 appears to have the greatest detectability, which could

be attributed to higher sampling rates and a higher freely dissolved concentration in water, or a combination of both factors. Since PCBs 101 and 138 have much higher log $K_{ow}$ values, they tend to partition away from the water and into soils and sediments (Faroon *et al.* 2003). In addition to lower concentrations in water, they have lower sampling rates, which could account for the lower concentrations detected.

The TWA concentrations determined are slightly higher than those obtained by Amdany and co-workers using SPMDs over a 14 day deployment period (Amdany *et al.* 2014). For a more direct comparison, TWA concentrations were compared to those by Amdany and co-workers over the winter period, since the MIM-based sampler were also deployed in winter. They found PCB 28 (0.019 ng/mL) in the highest concentration, followed by PCBs 52 (0.006 ng/mL), 138 (0.003 ng/mL) and 101 (0.003 ng/mL), which is consistent with the findings using the newly-developed MIM sampler. However, they also found PCBs 153, 118 and 180 in varying concentrations, which were not detected using the MIM-based sampler. The variation in concentrations between the MIM-based sampler and those determined by Amdany and co-workers could be due to numerous factors. TWA concentrations could vary from time to time due to hydrodynamic conditions and weather patterns. The samplers were deployed over different times, which could account for the slight variation in concentrations.

## CONCLUSION

The study provided the development and evaluation of a new MIM-based passive sampler for sampling PCBs, based on the concept of molecular imprinting. The study also provided calibration data for the newly-developed sampler towards different environmental conditions using PRCs. PCBs were sampled at considerably high sampling rates, which was necessary due to their occurrence at ultra-trace levels in aquatic environments. The sampler was deployed at two dams, the Roodeplaat and Hartbeespoort Dams, to evaluate PCB sampling performance. PRC dissipation rates of the deployed samplers were compared to those obtained under controlled laboratory conditions in order to correct for sampling-site specific variables, and to allow for more accurate estimations of TWA concentrations of PCBs. The newly-developed sampler enhanced the detectability of certain PCB congeners present at ultra-trace levels in aquatic environments, which ultimately minimised the sample preparation required to detect such levels. Furthermore, the sampler provided simplified extraction of sequestered PCBs, with minimal solvents required. The shorter deployment times (10 days) associated with the sampler also eliminates the need for collecting large volumes of water samples frequently. This could minimise costs and the turnaround time for analysis. The MIM-based sampler demonstrated the existence of isotropic exchange between PCBs with different PRC analogues. However, more efforts are still required in the sampler fabrication to achieve less variation in the concentrations obtained.

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