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In Situ Measurement of Time-Weighted Average Concentrations of Cylindrospermopsin and Microcystin LR-YR-RR-LY in Natural Waters Using Silicone-Membrane/ Γ -Fe_2O_3-Nanoparticle-Sorbent Passive Sampling Device

Hlengilizwe Nyoni[1], Bhekie B Mamba[2] and Titus AM Msagati[2]*

[1]*Department of Applied Chemistry, Faculty of Science, University of Johannesburg, P.O. Box 17011, Doornfontein 2028, Johannesburg, Republic of South Africa*
[2]*University of South Africa, College of Science Engineering and Technology, Nanotechnology and Water Sustainability Research Unit, UNISA Science Campus, P.O. Box 392 UNISA 0003, Florida, 1709 Roodepoort, Johannesburg, South Africa*

Abstract

Preliminary use of performance reference compounds (PRC) spiked into the silicone-membrane/γ-Fe2O3 sampler for *in situ* calibration has been demonstrated to improve the quantitative nature of water concentration estimates. Hydrophobic polycyclic aromatic hydrocarbons (PAHs), though they occur at significant levels in the environment, were used as PRC because of their relatively high fugacity from the silicone membrane and evidence of their isotropic exchange kinetics. *In situ* calibrations of silicone-membrane/γ-Fe_2O_3 sampler spiked with 16 PAHs and the resulting time weighted average (TWA) concentration estimates were compared with similar values of SPE extracts from grab samples. Calibration studies were successfully done and variable environmental conditions (e.g. effects of hydrodynamics and temperature) were found to affect their elimination rates from silicone-membrane/γ-Fe_2O_3 sampler. A significant increase of elimination rates with change of hydrodynamic conditions from static to turbulent was observed for all compounds under investigation. The technique has also been successfully applied to the detection of freshwater cyanobacterial toxins such as microcystins and cylindrospermopsin.

Keywords: Performance reference compounds (PRC); Silicone-membrane/γ-Fe_2O_3 time weighted average (TWA); Microcystins; Cylindrospermopsin

Introduction

In the last two and half decades, several sampling devices have been designed and used for monitoring of various environmental contaminants. Recently, silicone-membrane/γ-Fe_2O_3-nanoparticle passive sampling device was suggested to estimate cumulative aqueous exposure to cylindrospermopsin and microcystin LR-YR-RR-LY [1]. This technique provides time-weighted average (TWA) concentrations that may be used for the application of regulatory monitoring programs to satisfy the requirements of legislative frameworks [2]. However, environmental factors such as hydrodynamics, temperature, and the build-up of a biofilm on the sampler's surface can affect the rate at which chemicals are sampled. These factors are site-specific and can greatly reduce the accuracy of the estimated water concentrations.

The most promising methods for overcoming this limitation involve addition of performance reference compound (PRC) to the samplers before deployment. By measuring the amount of PRC lost during deployment in the field, adjustments to the theoretical or experimentally derived sampling rates of targeted chemicals can be made to reflect the site-specific sampling rates [3]. Proper selection of a PRC requires knowledge of the possible occurrence of a PRC in the environment, the predicted rate of loss from the sampler, and the analytical capabilities of the laboratory. Thus, to eliminate bias of loss measurement, PRCs must not occur naturally. Ideally, deuterated or carbon-13 (^{13}C)-labelled versions of targeted chemicals are selected. In cases where labelled chemicals are not available or are cost-prohibitive, non-labelled chemicals can be used. For example, the PCB congeners 14, 29, and 50 are often used as PRCs since they do not occur in the environment. Huckins and others [4] determined that it is not necessary to have a PRC for each chemical class. Using the current models for determining PRC-derived sampling rates, a PRC can be used to calculate site specific sampling rates with increased accuracy through a range of chemical classes and log K_{OWS} [3].

This work reports the potential of using PCRs for reducing errors associated with derived water concentration estimates, of silicone-membrane/γ-Fe_2O_3-nanoparticle-sorbent passive sampler, is reported. The offload kinetics of D_{10}-phenathrene, acenaphthene, chrysene, acenaphthylene, dibenzo[ah]anthracene, anthracene, fluoranthene, benzo[a]anthracene fluorene, benzo[a]pyrene, indeno[1,2,3-cd] pyrene, benzo[b]fluoranthene, naphthalene, benzo[ghi]perylene, phenanthrene, benzo[k]fluoranthene and pyrene were performed during laboratory experiments. Afterwards, *in-situ* measurement of the time-weighted average concentrations of cylindrospermopsin and microcystin LR-YR-RR were performed and the use of PAHs as PRCs investigated.

Theory and modelling of the passive sampler

The theory of analyte uptake for the silicone-membrane/γ-Fe_2O_3-nanoparticle-sorbent passive sampling device is similar to the one

***Corresponding author:** Titus AM Msagati, University of South Africa, College of Science Engineering and Technology, Nanotechnology and Water Sustainability Research Unit, UNISA Science Campus, P.O. Box 392 UNISA 0003, Florida, 1709 Roodepoort, Johannesburg, South Africa, Tel: 27 72 311 0693; E-mail: msagatam@unisa.ac.za

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developed for the membrane assisted passive sampler [5]. It combines the coupled transport and the supported liquid membrane (SLM) uptake technique [5]. In brief, the compounds of interest dissolve into the silicone membrane from the sample and then diffuse through the membrane into the acceptor phase. Once in the acceptor phase, they adsorb onto the iron oxide nanoparticles and trapped. Lee and Walker [6] demonstrated that microcystins strongly adsorb onto iron oxide nanoparticles (γ-Fe_2O_3) thus filling silicone tubes with a suspension solution of iron oxide nanoparticles (γ-Fe_2O_3).

The mass transfer of analytes from the donor into the receiving phase of the sampler includes several diffusion and interfacial steps across all barriers. The amount of chemical accumulated with constant chemical concentration is given by the following equation [7]:

$$C_{Si/Fe}(t) = C_{Si/Fe}(0) + (C_W K_{SW} V_{Si/Fe} - C_{Si/Fe}(0))\{1-\exp(-k_{ov} A\alpha / K_{SW} V_S)t\} \quad (1)$$

where $C_{Si/Fe}$ is the concentration of analyte in the receiving phase (acceptor phase), $C_{Si/Fe}(0)$ is the amount of analyte in the sampler at the start of exposure, C_W is the water concentration of the analyte during deployment period, K_{SW} is the receiving phase-water distribution coefficient, A is the membrane surface area, α is the pore membrane area as fraction of total membrane area (membrane porosity) k_{ov} is the overall mass-transfer coefficient, $V_{Si/Fe}$ is the volume of the receiving phase (acceptor phase) and t is the exposure time. At the start of the exposure, the chemical uptake is linear and the exponential term is very small ($< < 1$) or $C_{Si/Fe}/V_{Si/Fe}C_W < < K_{SW}$. Equation 1 then reduces to [7]:

$$C_{Si/Fe}(t) = C_{Si/Fe}(0) + C_W k_{ov} A\alpha t \quad (2)$$

Equation 2 can be simplified to equation 3 which is used to measure the sampling rate or rate of accumulation, R_S in practical applications [7]:

$$C_{Si/Fe}(t) = C_{Si/Fe}(0) + C_W R_S t \quad (3)$$

where

$$R_S = k_{ov} A\alpha = K_{SW} V_S k_e \quad (4)$$

k_e is the overall exchange rate constant given by:

$$k_e = k_{ov} A\alpha / K_{SW} V_S \quad (5)$$

Mazzella et al. [8] suggested that adsorbent such as iron oxide nanoparticles may mimic first-order isotropic chemical exchange, a representative of simple kinetic derivation of the Langmuir isotherm. Hence, we can, as an approximation, apply the following two compartment model:

$$C_{Si/Fe} = C_{TWA} K_{SW}(1 - e^{-ket}) \quad (6)$$

where $C_{Si/Fe}$ is the concentration (μg g^{-1}) of the analyte in the acceptor phase, C_{TWA} is the time weighted concentration (μg L^{-1}) of the analyte in water sample, K_{SW} (L g^{-1}) is the equilibrium adsorption coefficient, which corresponds to the sample-water partition constant in partitioning media, k_e (d^{-1}) is the elimination rate constant and t is the exposure time (days).The elimination rate constant (k_e) is defined as follows [9]:

$$k_e = \frac{R_s}{K_{sw} V_{Si/Fe}} \quad (7)$$

Two different accumulation regimes, either kinetic or equilibrium, can be distinguished in the operation of the passive samplers [10]. During the kinetic regime, the elimination rate k_e is negligible compared to the uptake rate k_u (d^{-1}) and the sampler is considered as an integrative sampler (i.e. linear sorption isotherms). Equation 6 can be reduced to:

$$C_{Si/Fe} = C_{TWA} k_u t \quad (8)$$

If we introduce the volume of the acceptor phase $V_{Si/Fe}$, we can rearrange equation 8 to an equivalent relationship with the sampling rate R_S instead of the uptake rate constant k_u. In this case, the time-weighted average concentration (C_{TWA}) of an analyte can be calculated using the following equation:

$$C_{TWA} = \frac{C_{Si/Fe}}{R_s t} \quad (9)$$

The elimination rate constant k_e of a PRC (k_{ePRC}) from the passive sampler sorbent can be determined with the following first order relationship

$$C_{TWA} = \frac{C_{Si/Fe}}{R_s t} \quad (10)$$

Where $C_{PRC(t)}$ is the residual concentration (μg g^{-1}) of RCR in the receiving phase after exposure time (t) and C_{PRC0} is the concentration of PRC spiked into the receiving phase before exposure. When the elimination rate constant of a same PRC is determined under calibration ($k_{ePRCcal}$) and the field ($k_{ePRCinsitu}$) conditions, then the real value of the field sampling rate ($R_{Sinsitu}$) can be approximated with corrected value (R_{Scorr}) of the calibrated sampling rate (R_{Scal}) as follows:

$$R_{Scorr} = R_{Scal} \times \left(\frac{k_{ePRC_{insitu}}}{k_{ePRC_{cal}}} \right) \quad (11)$$

Experimental Section

Materials and methods

Chemicals and materials: CyanoBiotech GmbH, cylindrospermopsin and microcystin standards (microcystin-LR, microcystin-RR, and microcystin-YR) were purchased from Germany and supplied by Industrial Analytical (Pty) Ltd, South Africa. Certified reference standard of 16 mixed polycyclic aromatic hydrocarbons was purchased from Sigma-Aldrich South Africa. Other solvents and reagents used in this work were of high purity (Analytical grade and/or HPLC grade, > 99%) and were purchased from Sigma-Aldrich South Africa and Merck (SA). Solid-phase extraction SPE cartridges (Oasis™ HLB cartridges) were purchased from Waters Inc., USA supplied by Microsep (Pty) Ltd, SA.

Silicone membranes: The commercial silicone membranes used in this study were obtained from Technical Products Inc. (Georgia, USA) as long tubes. The identity of the commercial silicone membrane was verified by ATR-FTIR. The long chain siloxanes IR peaks and the vibration mode of the commercial silicone membrane matched the one obtained from the handbook of Infrared characteristic frequencies [11]. The strongest and broadest peaks for the membrane (Figure 1) were between 1020 and 1090 cm^{-1} which are from the stretching vibrations of Si-O-Si present in the silicone membrane backbone. The structure of the silicone membranes was analysed by SEM. The SEM images (Figure 2) showed that the silicone membrane had a smooth morphology and some scalpel creeks resulting from cutting procedure.

Microcystin mixture: With regards to relatively large amounts

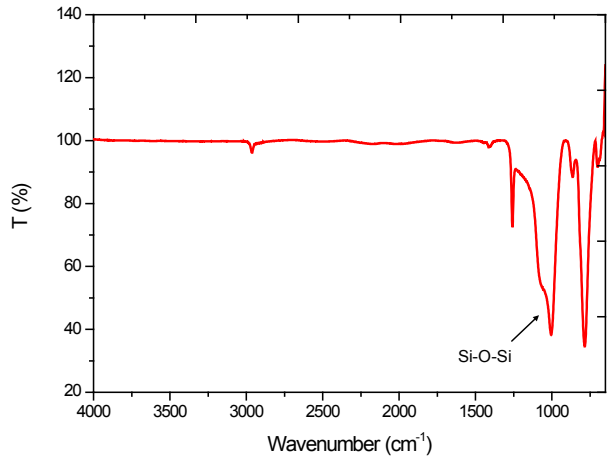

Figure 1: FTIR Spectrum of commercial silicone membrane

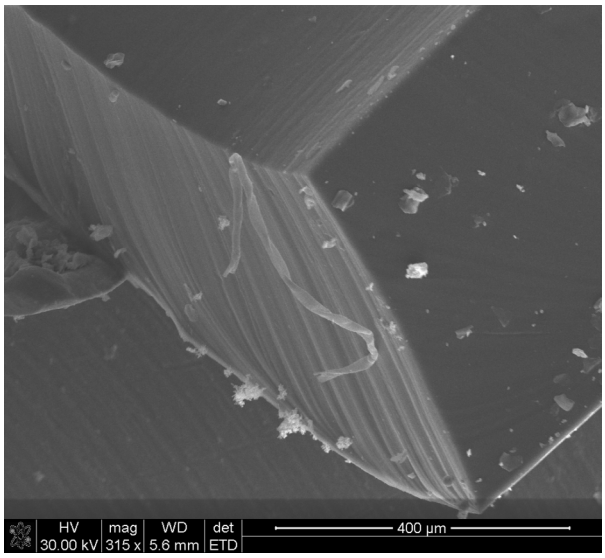

Figure 2: SEM photograph of commercial silicone membrane

of biotoxins needed for calibration experiments, and high costs of the toxin analytical standards, microcystins for the experiments were isolated from the natural cyanobacteria biomass, by repeated extraction with 10 mL of BuOH: MeOH: H_2O (1:4:15), sonicated for 3 min, then centrifuged at 7800 for 20 min at room temperature and purified with solid-phase extraction using an HLB cartridge which had been preconditioned by 100% MeOH and distilled water. The final extract (in 90% v/v methanol: water), containing cylindrospermopsin and dominant microcystin variants was aliquoted and stored at -18˚C.

Iron oxide (maghemite) nanoparticles: Synthesised iron oxide nanoparticles from our previous work [1] were used in this study without further purification. Iron oxide solution (acceptor phase) of final maghemite concentration 2.3 g/L was prepared in a pH 3.5 buffer of 0.1 M potassium hydrogen phthalate and 0.1 M hydrochloric acid and stored in the dark prior to use.

Experimental design: The exposures lasted for 14 days, during which triplicates samplers were removed after 3, 7 and 14 days and analysed. Grab samples (30 mL) of water were taken each time the samplers are removed, and the concentration of test analyte in the water determined by an Oasis HLB SPE technique as described in our previous work [1]. Figure 3 shows a depiction of the experimental set-up to measure the offload and uptake of target analytes at different combinations of exposure times, temperatures, sample matrix and hydrodynamic conditions

Fabrication of silicone-membrane/γ-Fe_2O_3-nanoparticle-sorbent passive sampler: Silicone membranes used for the optimization process were bought as long tubes and cut to appropriate lengths (48 cm × 0.1575 cm I.D × 0.2413 cm O.D giving a volume of approximately 1000 µL). Nine silicone membranes, previously soaked in deionised water, were filled with a pH 3.5 acceptor buffer of the maghemite suspension (2.3 gL^{-1}), fortified with 0.1 mL of PRCs containing 10 μgL^{-1} of each of the polycyclic aromatic hydrocarbons, using a 1000 µL micropipette. The membranes were tightened together and made in the form of a loop about 3 cm in diameter. The outside was rinsed with deionised water thoroughly to remove any buffer spills and then immersed in an appropriate sample vessel and left hanging for an appropriate time.

Response Surface Experiments

Exposure time

Silicone membranes used to assess the influence of exposure time on the uptake of the test chemicals into the sampler were cut to appropriate lengths (48 cm x 0.1575 cm I.D x 0.2413 cm O.D giving a volume of approximately 1000 µL). Twelve silicone membranes, previously soaked in deionised water, were filled with a pH 3.5 acceptor buffer of the maghemite suspension (2.3 gL^{-1}), fortified with 0.1 mL of PRCs containing 10 μgL^{-1} of each of the polycyclic aromatic hydrocarbons, using a 1000 µL micropipette. The membranes were tightened together and made in the form of a loop about 3 cm in diameter. The outside was rinsed with deionised water thoroughly to remove any buffer spills and then immersed in an appropriate sample vessel and left hanging for an appropriate time (0, 3, 7 and 14 days) at ambient temperature. A sample volume of 5 L was used and the water concentration of microcystins and cylindrospermopsin was held constant at 52.5 ± 2.5 $ngmL^{-1}$. Grab samples (30 mL) of water from the exposure tank were taken each time the samplers were removed, and the concentration of

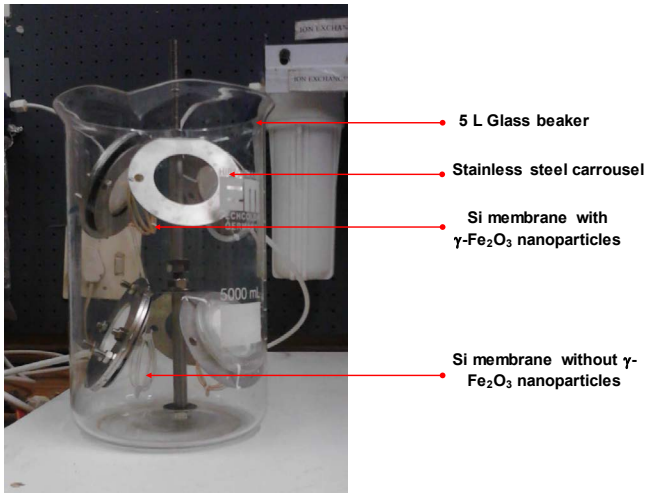

Figure 3: Experimental set-ups to measure the offload and uptake of target analytes at different combinations of exposure times, temperatures, sample matrix and hydrodynamic conditions (A photograph taken by Nyoni H in July 2014)

test analyte in the water determined by an SPE technique.

Effect of Hydrodynamics: The effect of hydrodynamics on the elimination rates of individual PAH compounds from the samplers was studied at six different stirring speeds (i.e. 0, 20, 40, 60, 80 and 100 rpm). Deionised water spiked with 50 $ngmL^{-1}$ mixtures of microcystins and cylindrospermopsin was extracted for 14 days at ambient temperature. The sample volume used was 5 L. The experiment was repeated at least three times. After exposure, the passive samplers were treated in the same way as described in the extraction procedure.

Effect of temperature: In these influence-of-temperature experiments, up to nine silicone membranes, previously soaked in deionised water, were filled with a pH 3.5 acceptor buffer of the maghemite suspension (2.3 gL^{-1}). These membranes were then fortified with 0.1 mL of PRCs containing 10 μgL^{-1} of each of the polycyclic aromatic hydrocarbons, using a 1000 µL micropipette. A set of three passive samplers were exposed in appropriate temperature-controlled systems. These systems were devised to allow calibration of the sampling devices to be compared at three different temperatures (4, 17 and 23°C). Deionized water containing 50 $ngmL^{-1}$ of a mixture of microcystins and cylindrospermopsin was used as sample solution. The stirring speed of the water sample was maintained at 60 rpm. Three sample vessels containing 5 L of spiked deionized water were placed (1) in a cooler box filled with ice maintained at 4°C, (2) in water bath held at 17°C and the other three in (3) water bath heated and maintained at 23°C. Before exposing the silicone-membrane/γ-Fe_2O_3- passive samplers, the water samples were allowed to equilibrate for at least two hours at appropriate temperature. Passive exposure period was for 14 days.

Extraction of analytes from passive samplers

After exposure, three samplers were taken out of the sample vessel, the outside flushed with deionised water and its contents transferred into a 1.5 mL vial. Prior to HPLC analysis, the extracts were sonicated in an ultrasonic bath for 5 minutes and then centrifuged for 10 min at 7500 rpm, and the supernatants were filtered through 0.45-µm polyvinylidene fluoride (PVDF) membrane syringe filters. The silicone membranes were cut to small pieces, transferred into a 15 mL centrifuge tube and extracted two times with 5 mL of aqueous methanol (90% v/v acidified with 0.1% trifluoroacetic acid) for 15 min in an ultrasonic bath. After centrifugation (10 min at 7800 rpm), supernatants were pooled, evaporated to dryness under nitrogen, and reconstituted with 500 µL of aqueous methanol (50% v/v). The extracts were either analysed immediately or stored in the refrigerator at - 18°C.

Instrument and analysis conditions

High Performance Liquid Chromatography: All extracts were analysed by the Surveyor Plus™ modular LC system and the ChromQuest™ data system, products of Thermo Fisher Scientific San Jose, on a 150 mm × 4.6 mm, 5 µm column (waters) at 30°C with isocratic elution for 5 min using acetonitrile/water (4:6) (v/v), then linear gradient elution to 100% acetonitrile over 25 min at 1.0 $mLmin^{-1}$. Chromatograms at 231nm, 238 nm 254 nm and 261 nm were recorded with the Surveyor PDA Plus Detector, and cylindrospermopsin, microcystin (Figure 4) as well as PAHs were identified by retention times and characteristic UV absorption spectra (200-300nm) according to the EPA Method 8310 [12].

GC x GC TOFMS: Methanol extracts of the silicone membranes were further analysed by gas chromatograph (Agilent Technologies, Inc., Wilmington, Delaware, USA) that was equipped with a LECO Pegasus 4D Time of Flight mass spectrometry detection and an Agilent on-column injection system. The primary oven was equipped with a Restek Rxi®-5Sil MS, 30m, 0.25mm ID, 0.25µm and the secondary oven with a Restek Rxi®-17Sil MS, 1m, 0.25mm ID, 0.25µm fused silica capillary columns. The helium carrier gas was maintained at constant flow of 1.4 mL per minute. The injection temperature was set at 300°C and the oven temperature was programmed as follows: 50°C held for 0.5 minutes; ramped from 50°C - 290°C at 25°C/minute, then 290°C - 320°C at 5°C per minute. The secondary oven and modulator temperature offset were set at 10°C and 15°C, the modulation period at 4 seconds, the hot pulse time at 0.8 seconds and the cool time at 1.2 seconds. The mass spectrometry conditions were set as follows: Transfer line temperature: 290°C; Ionization: Electron ionization at -70 eV; source temperature: 250°C; stored mass range: 50-500 um; acquisition rate: 100 spectra/second; detector voltage: -1650 V. A typical chromatogram and characteristic time of flight mass spectra of 16 PAHs are shown in Figure 5.

Quality Control

In ensuring that the concentration determined using the sampling devices reflect the true picture in the environmental media, quality control procedures to address issues such as contamination and loss of the trapped analytes, accuracy and precision of the results were conducted. Inspection for signs of puncture, discolouring or any malfunctioning upon retrieval to see any possible sources of contamination and/or loss of the trapped analytes [13,14] was performed. Procedural blanks, CRM, control samples and field blanks were used for identification of the contamination from the process [13,14].

Results and Discussion

Exposure time

During exposure the water concentration was held constant, and this was confirmed by analyses of water samples. Grab samples (100 mL) of water from the exposure tank were taken each time the samplers are removed, and the concentration of test analyte in the water

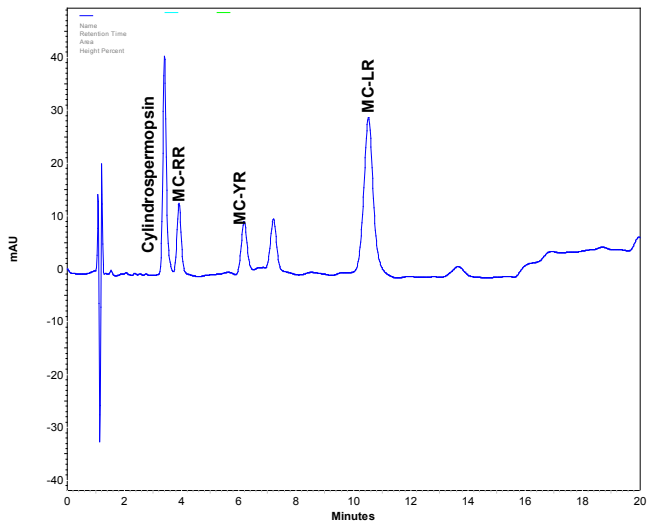

Figure 4: Typical chromatographic separation of cylindrospermopsin and microcystin on a reverse phase C18 Symmetry 300TM column (75 mm × 4.6 mm, 3.5 µm column (waters) at 30 °C) coupled with a photodiode-array detector

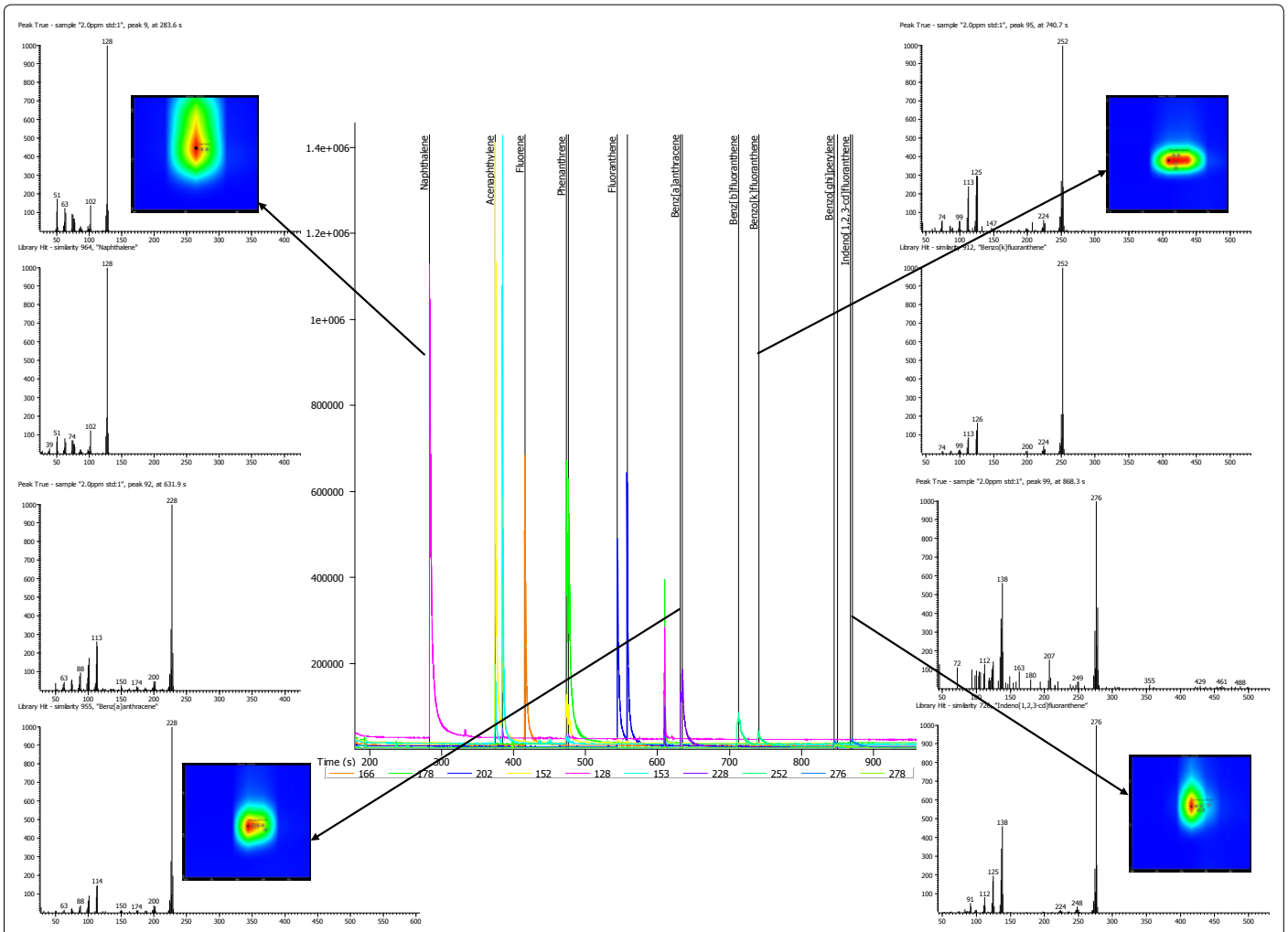

Figure 5: Typical gas chromatogram of 16 PAHs standard (2 µg mL-1) obtained using GC x GC TOFMS Pegasus 4D system

determined by an SPE technique. Characteristic analyte uptake curves for the sampler are shown in Figure 6. Satisfactory linear regression fits of the equation 3 to the uptake data of analytes from water to sampler were obtained for test compounds in all experiments. Such linear relationships have been observed in other passive samplers working in the kinetic regime, such as the POCIS [15]. The amounts quantified in the silicone membrane based passive samplers had relative standard deviations mostly between 11 and 19% (from repeat determinations), and did not exceed 24%.

Verification of isotropic exchange kinetics: Absorption versus desorption

The time courses of the amounts of individual test substances from the passive sampler are shown in Figure 7. The elimination rate constants k_{ecal} were calculated for each test PAH compound and reported in Table 1. Pseudofirst order kinetic desorption for nine PAHs of interest was observed and the determined k_{ecal} values suggested isotropic exchanges and potential application as PRCs. Generally, the silicone-membrane/γ-Fe_2O_3-nanoparticle-sorbent passive sampler exhibits isotropic exchange kinetics because both the uptake and loss of chemicals obey first-order kinetics, and the rate constants measured during uptake and loss are approximately identical (Table 1). This means that the resistance to mass transfer into and out of the sampler is the same and the loss rate constant (k_e) is proportional to the uptake rate constant (k_u).

Effect of Hydrodynamics

A significant increase of elimination rate from the passive sampler with change of hydrodynamic conditions from static to high turbulence was observed for all compounds under investigation (Figure 8). At low turbulence, the diffusion through the aqueous layer limits the mass transfer for large and more hydrophobic compounds, resulting in lower desorption rates of PAHs from the passive sampler. The extent to which the mass transfer process is influenced by turbulence is dependent on the size and polarity of the compound. For the relatively hydrophobic compound, an increase in turbulence is accompanied by an increase in the elimination rate. A similar effect of hydrodynamics has been observed and explained also for POCIS [16].

Effect of Temperature

The typical dependence of analyte elimination rate on temperature is shown in Figure 9. Because of a very low magnitude of sampling rates in stagnant water, evident temperature dependence was observed only for data obtained under conditions of turbulent water flow (40, 60, 80 and 100 rpm). In general, the magnitude of the kinetic component (k_e) increased with increasing exposure temperature. This is in agreement

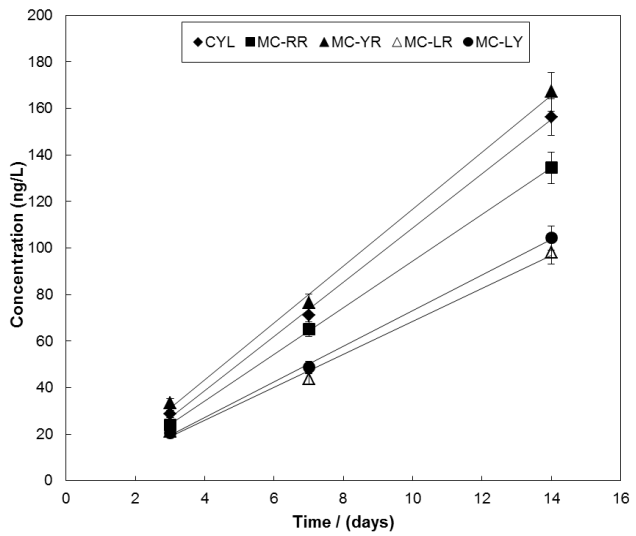

Figure 6: Typical uptake curves of the analytes in the sampler. Data are presented from the exposure conducted at 23°C and the rotation speed of 60 rpm

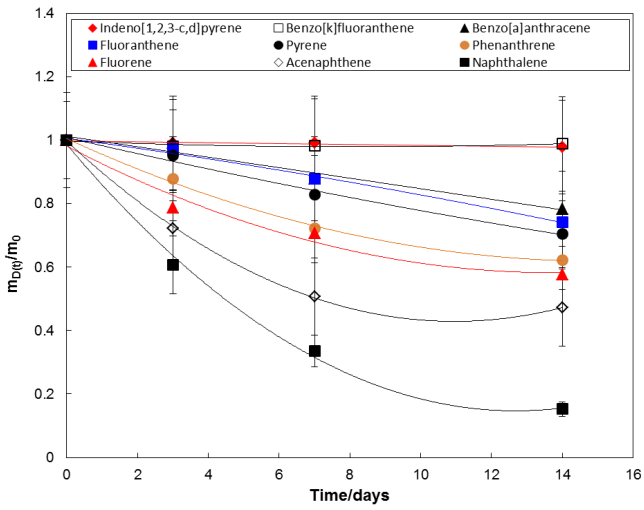

Figure 7: Desorption kinetics curves of PAHs from Silicone based passive sampler during 14 days of turbulent exposure. Data are presented from the exposure conducted at 23°C and the rotation speed of 60 rpm.

with isotropic exchange kinetics as well as with the assumptions that the increased temperature of the environmental media can enhance compounds fugacity from the silicone membrane passive sampler. The activation energies calculated using Arrhenius-type equation [7] for the uptake of microcystins and cylindrospermopsin ranged between 12 and 17 $kJmol^{-1}$ and these were in line with the average of 14 kJ mol^{-1} calculated for offload of acenaphthene, fluorene, naphthalene, pyrene and phenanthrene.

In Situ calibration of the Si/γ-Fe_2O_3 passive sampler

Replicates of silicone-membrane/γ-Fe_2O_3-nanoparticle-sorbent passive sampler were immersed in a Hartbeespoort dam, Northwest province of South Africa (Figure 10) [17] during summer (from 7th to 17th November 2014). For each compound, the concentration factor was calculated according to the ratio between the analyte amount within the sampler and the TWA concentration of the same analyte in water samples during the corresponding exposure. The *in situ* time weighted concentrations estimated with SPE, silicone-membrane/γ-Fe_2O_3 sampler with and without PRC correction are shown in (Figure 11). The corresponding $R_{Sinsitu}$ were calculated and reported in Table 2. The $R_{Sinsitu}$ are 3-4 times higher than the R_{cal}. This higher sampling rate observed in the field may be attributed to a higher flow velocity, and temperature. An average temperature of 27°C was measured during the field exposure

Conclusion

The PRC concept was validated for several PAHs in this study. The effect of temperature and water turbulence on kinetic and

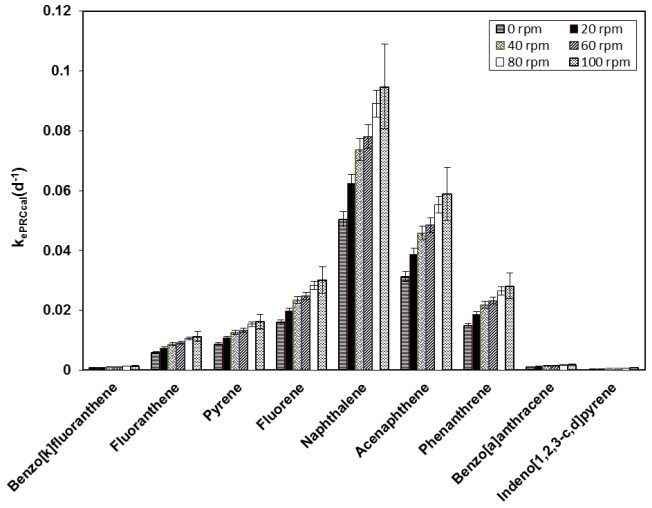

Figure 8: Effect of hydrodynamics on the PAHs elimination rate values. Data are presented from the exposure conducted at 23°C and the rotation speed of (0, 20, 40, 60, 80 and 70 rpm).

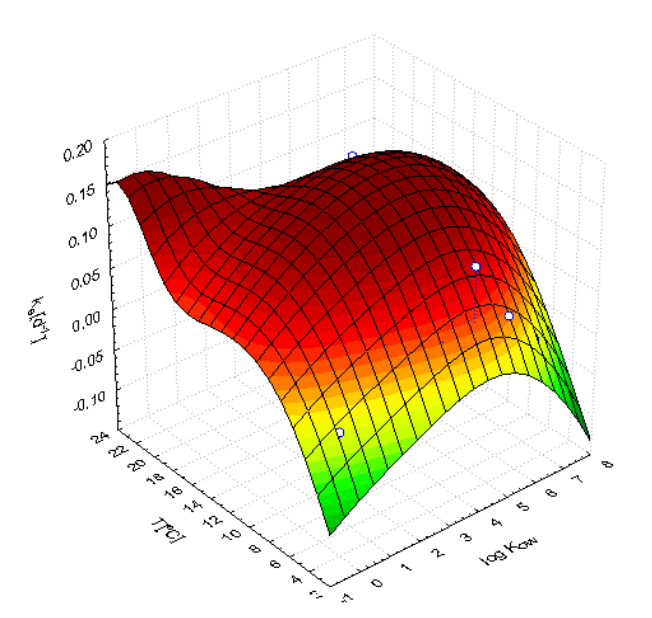

Figure 9: Effect of temperature and log KOW on analyte sampling rate values at 60 rpm rotation speed to illustrate the response surface

Figure 10: Map and GPS co-ordinates of the sampling site on the Hartbeespoort dam (A photograph taken by Nyoni H in November 2014)

thermodynamic parameters characterising the exchange of analytes between the sampler and water was studied under controlled conditions. It was found that the rate of PRC loss during 14 day exposure was used to estimate *in situ* sampling rates of the analytes (R_s) of interest. This allowed for the *in situ* calibration of the uptake of microcystins and cylindrospermopsin using offload kinetics of performance reference compounds. The sampling kinetics was dependent on temperature and for most of the tested analytes also on the flow velocity. However,

	log K_{OW}*	log K_{SW}	k_{ecal} (d^{-1})	R_{scal} /(L d^{-1})
Indeno[1,2,3-c,d]pyrene	6.58	5.6568	0.0006567 ± 0.000143	0.002938 ± 0.00013
Benzo[k]fluoranthene	6.20	5.5606	0.001192 ± 0.000314	0.006204 ± 0.00021
Benzo[a]anthracene	5.63	5.3287	0.001559 ± 0.000118	0.006995 ± 0.00009
Fluoranthene	4.90	4.8781	0.009270 ± 0.00027	0.04742 ± 0.005
Pyrene	4.88	4.8633	0.01343 ± 0.0019	0.06584 ± 0.009
Phenanthrene	4.46	4.5232	0.02322 ± 0.0010	0.09664 ± 0.009
Fluorene	4.18	4.2647	0.02482 ± 0.0024	0.09740 ± 0.008
Acenaphthene	3.98	4.0646	0.04853 ± 0.0011	0.1815 ± 0.029
Naphthalene	3.37	3.3742	0.07808 ± 0.0016	0.2423 ± 0.017
	log K_{OW}*	log K_{SW}	k_{ucal} (d^{-1})	R_{scal} /(L d^{-1})
Cylindrospermopsin	-	-	0.06739	0.1457 ± 0.027
Microcystin RR	4.40	4.47	0.05393	0.1199 ± 0.001
Microcystin YR	3.90	3.98	0.06085	0.1353 ± 0.006
Microcystin LR	4.20	4.28	0.06137	0.1364 ± 0.010
Microcystin LY	-	-	0.06543	0.1454 ± 0.016

*log K_{OW} for pH 7-8 [7,15]

Table 1: Values of log K_{SW}, log K_{OW}, $k_{ucal,}$ k_{ecal} and R_{scal} determined during *in situ* calibration of the silicone-membrane/γ-Fe_2O_3-nanoparticle-sorbent passive sampler

	$K_{ePCRcal}$ (d^{-1})	$K_{ePCRInsitu}$ (d^{-1})	$R_{S\text{-}PCRCal}$ (L d^{-1})	$R_{S\text{-}PCRInsitu}$ (L d^{-1})	$R_{S\text{-}PCRcorr}$ (L d^{-1})
Indeno[1,2,3-c,d]pyrene	0.00066	0.0315	0.002938	0.1555	0.1409
Benzo[k]fluoranthene	0.00119	0.03912	0.006204	0.1899	0.2036
Benzo[a]anthracene	0.00156	0.01257	0.006995	0.05849	0.05464
Fluoranthene	0.009270	0.01737	0.04742	0.07396	0.08885
Pyrene	0.01343	0.01767	0.06584	0.07502	0.08662
Phenanthrene	0.02322	0.06155	0.09664	0.2431	0.2561
Fluorene	0.02482	0.04942	0.09740	0.1840	0.1939
Acenaphthene	0.04853	0.08208	0.1815	0.2912	0.3069
Naphthalene	0.07808	0.1387	0.2423	0.4085	0.4303

Table 2: Values of k_{ecal}, $k_{einsitu}$, R_{scal}, $R_{sinsitu}$ and R_{scorr} determined during in situ calibration of the silicone-membrane/γ-Fe_2O_3-nanoparticle-sorbent passive sampler

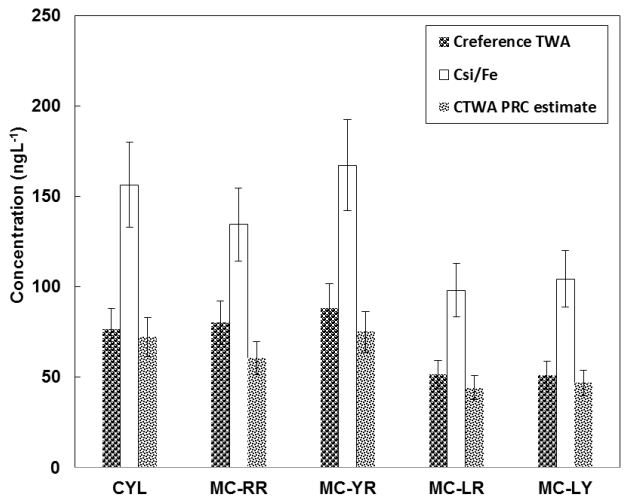

Figure 11: *In situ* 14 day time weighted average concentration estimated with SPE, silicone-membrane/γ-Fe_2O_3 sampler with and without PRC correction

careful attention must focus on the use of analytically non-interfering deuterated or ^{13}C labelled PAH compound because they do not occur at significant levels in the environment.

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