CORRECTION OF DEPLOYMENT SPECIFIC CHEMICAL UPTAKE RATES FOR CHLORINATED PESTICIDES ACCUMULATED BY SPMD AND PDMS PASSIVE SAMPLING DEVICES USING A PASSIVE FLOW MONITOR

O'Brien D[1]*, Mueller J[2]

[1]Tropwater, James Cook University, Douglass, QLD 4810, Australia; [2] The University of Queensland, National Research Centre for Environmental Toxicology (Entox), 39 Kessels Rd, Coopers Plains, QLD 4108, Australia.

Introduction

Passive sampling devices are environmental monitoring tools developed to facilitate the assessment of chemical concentrations in environmental medium from the mass of targeted analytes sorbed within a sequestering phase (Cs) [1-4]. Advantages associated with the use of passive sampling techniques are derived from the potential to obtain a time-weighted average (TWA) measurement of a chemical concentration in the environment.

During the linear phase of chemical uptake, the calculation of a TWA pollutant concentration (Cw) in the water is given by the accumulated analyte mass in the sampler (Ms) divided by the chemical sampling rate (Rs) at deployment time (t), according to

$$C_W = \frac{M_S}{R_S t} \quad (1)$$

The accuracy of the TWA concentration obtained relies on the accurate determination of R_s for each deployment undertaken. However, R_s may be influenced by sampler configuration, the ambient temperature and the velocity of water moving across the surface of the sampling phase. As such it is necessary to have an accurate understanding of deployment conditions or to employ an *in situ* calibration method that can be used to correct R_s for the exposure conditions encountered for each deployment.

The application of performance reference compounds has been applied, with some passive sampling devices, for *in situ* correction of R_s [5, 6]. An alternative *in situ* calibration method, that employs a passive flow monitor (PFM) has been developed and is presented here.

The aim of this study was to undertake a laboratory-based calibration where the uptake of hydrophobic pesticides by the semipermeable membrane device (SPMD) and polydimethyl siloxan (PDMS) when exposed to different water velocities is correlated against co-deployed PFM devices. The herbicides and insecticides selected as part of this study are of significance for ecosystem monitoring as they are routinely applied in the agricultural industry.

Materials and methods

Sampling devices preparation:

Plaster flow monitors (PFM) are prepared from Dental Plaster (BORAL) (Fig. 1) cast into 120 mL specimen containers ([7-11]).

Semipermeable membrane device (SPMD) were prepared using lay-flat low density polyethylene tubing of approximately 60 µm thickness, 2.5 cm wide and 98 cm long. Stripes were cut and pre-extracted in redistilled hexane [12]. Each strip was injected with 1 mL of 99% pure triolein (Sigma–Aldrich T7140–50 g) that was heat seeled (surface area 460 cm^2).

Polydimethyl siloxan (PDMS) sheets of 410 µm thickness were supplied by Purple Pig Australia. PDMS were cut into strips of 92 cm long and 2.5 cm. Prior to use PDMS strips (3 pcs) were pre-extracted on a shaker in 900 mL of fresh redistilled hexane for three consecutive 24 h periods. SPMD and PDMS strips were deployed in stainless steel cages (Fig. 1).

Fig. 1. PFM devices (left) and SPMD (top) and PDMS (bottom) configuration within the deployment cages (right).

Experimental procedure:

Five experiments, each consisting of a ten day deployment, were carried out in an insulated, 1400 L stainless steel calibration tank. The sampling devices were attached to arms that extend 32 cm from the rotor of a custom built stainless steel turntable, driven by a 12 V DC motor (Hitachi, Japan). Agricultural chemicals with a wide range of log Kow (2.6–6.1) were selected for inclusion in the study. A stock of chemicals was prepared and diluted before spiking into the 1400 L chamber. The chamber was allowed to equilibriate for 24 h prior to the collection of water samples. The sampling devices were exposed to flow velocities of "0"-negligble flow, 3.4, 6.0, 16, 24 cm s^{-1}. PFMs were exposed in triplicate and the mass was recorded up to twice daily. Six SPMD and PDMS were prepared per deployment, four of which were deployed into the tank and retrieved in duplicate after 5 and 10 days of exposure. The remaining two replicates were analysed as blanks. Grab water samples (2 L unfiltered) were obtained with each sampler deployment and retrieval.

Sample extraction

SPMD: The extraction of pesticides from SPMDs was performed using an Accelerated Solvent Extractor Dionex ASE 300 (pressure: 500 psi; temperature: 40 °C, static time: 20 min; flush volume: 60%; cycles: 5) using a mixture of n-hexane Lichrosolv.[13]. **PDMS:** Prior to dialysis, the surface of each PDMS was cleaned. Each PDMS strip was extracted in 180 mL of redistilled hexane on a shaker at room temperature (21 °C) for two 24 h periods. The combined extracts from each sampler were then reduced to approximately 1 mL using rotary evaporators. Then the extract was passed through a column with 2 g of sodium sulphate to remove moisture.
Water samples: described in O'Brien et al. [11].

Analysis of extracts

The analysis of all herbicides from passive samplers and grab water samples was performed by GC–MS. Instrumental analysis was conducted by Queensland Health Scientific Services. The quantification criteria included confirmation of the retention times and selective ion monitoring of the labelled internal standards and respective analyte.

Results and discussion

Correlation of Rs with water velocity

The uptake of HCB, prothophos, chlorpyrfos, dieldrin, diazinon, metalachlor and fipronil into both the PDMS and SPMD remained linear over time when exposed to still and flowing water [r^2 ranged between 0.9 and 0.99]. The Rs for each chemical at all flow velocities investigated was calculated through the use of Eq. (1).

The uptake of all chemicals, except metalachlor and fipronil, increased with an increase in water velocity (Fig. 2). The uptake of metalachlor and fipronil by PDMS remained relatively constant for all flows of >3.5 cm s^{-1} indicating that the uptake of these chemicals is governed by the rate at which these chemicals are diffusing through the PDMS.

A one phase exponential association was used to describe the relationship between Rs and velocity, where:

$$R_s = R_{s(0\ cm\ s^{-1})} + (R_{s(max)-R_{s(0\ cm\ s^{-1})}})(1 - \exp(K_v v)) \quad (2)$$

where $R_{s(0\ cm/s)}$ is the Rs when exposed to still waters, Rs(max) is the maximum Rs for the chemical of interest, v is velocity expressed in cm s^{-1} and Kv is a rate constant expressed in reciprocal of the units of velocity.

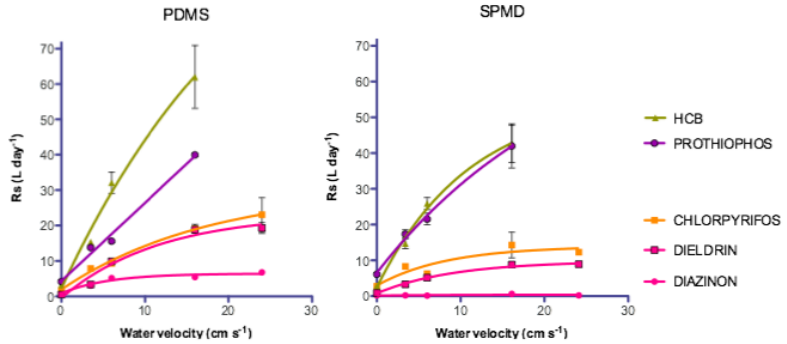

Figure 2: PDMS and SPMD sampling rates (Rs) as a function of water velocity.

The observed approach to a maximum Rs with velocity (≤ 24 cm s^{-1}) corresponds with the uptake limiting resistance shifting from the water boundary layer control to the diffusion of the analytes within the membrane of the passive samplers [14]. As the rate of diffusion across the membrane is independent from environmental conditions, the maximum Rs achievable will be equal to the constant diffusion coefficient specific to the analytes targeted and the properties and dimensions of the membrane employed.

Correlation of Rs for changes in water velocity: PFM calibration

The mass lost from the exposed PFM over each deployment period remained linear over time and ranged from 0.46 to 3.9 g day^{-1} depending on the flow rates to which the PFM were exposed. A significant linear regression produced when the daily mass lost (or rPFM) was plotted against velocity (r^2 = 0.99) allows an estimation of the water velocity where:

$$v(\text{cm s}^{-1}) = (r_{\text{PFM}} - 0.065)/0.164 \quad (3)$$

The use of the PFM is unable to distinguish between velocities of less than 3.4 cm s^{-1} (data presented elsewhere [7-11]). As such an assessment of the performance of the PFM technique for the correction of PDMS and SPMD sampling rates when exposed to a change in velocity was undertaken excluding the PFM results obtained in the absence of flow (i.e. no mechanical rotation of the table).

Fig. 3 shows a plot of PDMS and SPMD sampling rates against r_{PFM}. While the change in R_s with velocity for chloropyrifos, HCB and prothiophos appear relatively linear, a higher r^2 value is achieved for all chemicals investigated when a one phase exponential association was used to describe the relationship between R_s and velocity/r_{PFM}:

$$R_s = R_s(0 \text{ cm s}^{-1}) + (R_s(\text{max}) - R_s(0 \text{ cm s}^{-1}))(1 - \exp(K_v v))$$

Where $R_{s(0 \text{ cm s-1})}$ is the Rs when exposed to still waters, Rs(max) is the maximum Rs for the chemical of interest, v is velocity expressed in cm s^{-1} and K_v is a rate constant expressed in reciprocal of the units of velocity.

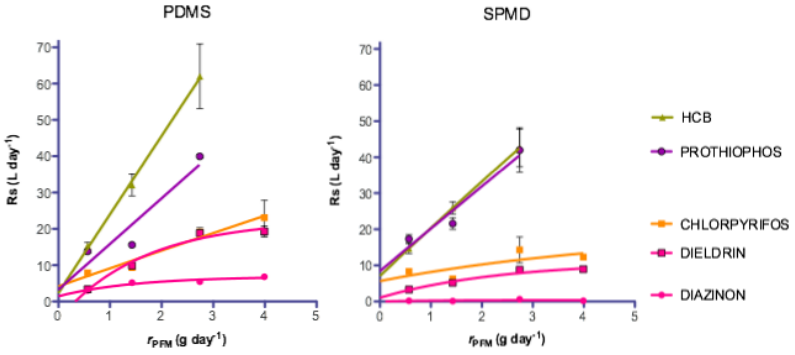

Figure 3: PDMS and SPMD sampling rates (Rs) as a function of r_{PFM}.

Discussion and conclusion

The uptake of chemicals by the PDMS and SPMD, while operating within the integrative phase of chemical uptake, was influenced by the water velocity to which the sampling devices were exposed. Few studies have investigated the change in Rs of the PDMS or SPMD when exposed to a range of flow velocities. The presented study clearly demonstrates that the application of the PFM for the measurement of water flow velocities is a cost effective, practical *in situ* calibration method that can be used to improve the accuracy of quantification achieved using SPMD and PDMS devices.

Acknowledgements

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