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Development of a new time-integrative sampler using *in situ* solvent extraction

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ABSTRACT

Despite the great success of time-weighted average passive sampling of hydrophobic contaminants, such as PCBs and PAHs, the sampling of polar organic compounds still presents a challenge because the equilibrium between water and most sampling phases is attained in a relatively short time. In this study, we proposed a new time-integrative sampler using *in situ* solvent extraction (TISIS) for polar organic chemicals. The sampler was composed of a 15 cm poly(dimethylsiloxane) (PDMS) tubing, with an internal diameter of 0.5 mm and wall thickness of 0.5 mm, through which an extraction solvent (acetonitrile) was passed. Four polar organic contaminants, caffeine, atrazine, diuron and 17α-ethynylestradiol, were chosen for the evaluation of the performance of the sampler. Without the use of *in situ* solvent extraction, the PDMS tubing when exposed to a constant aqueous concentration of the four model compounds was able to linearly accumulate those compounds for less than 12 h and equilibrium between the PDMS tubing and water was attained in 2 d under our laboratory conditions. However, TISIS when exposed to a constant aqueous concentration was able to linearly accumulate all the model compounds without any exposure time limitation. The measured sampling rates at three different extraction flow rates (0.2, 0.5, 1.5 mL min^{-1}) were similar, regardless of the chemicals, indicating that the overall mass transfer from aqueous solution to the extraction solvent was most likely dominated by partitioning to the PDMS tubing and the internal diffusion within PDMS. In addition, a pulsed exposure experiment confirmed that TISIS operated in a time-integrative mode when the environmental concentration was highly fluctuated.

1. Introduction

Time-integrative sampling provides a very useful tool for measuring the time-weighted average concentrations of environmental contaminants when the level of chemical contaminants has significant temporal variations (Vrana et al., 2005; Söderström et al., 2009). Although sampling kinetics depends on the physicochemical properties of chemical contaminants as well as those of the sampling phases, a two-phase model is often used for simplicity to explain the accumulation kinetics of chemicals within the sampling material (Huckins et al., 1999; Vrana et al., 2005; Mazzella et al., 2007; ter Laak et al., 2008; Bayen et al., 2009; Söderström et al., 2009; Shaw and Mueller, 2009; Hawker, 2010). Many factors can affect sampling kinetics, such as the sampler geometry, hydrodynamic conditions around the sampler, temperature and fouling on the surfaces, as well as the distribution coefficient between the sampler and water (K_{SW}). Of these, K_{SW} is considered one of the most important parameters in determining whether a sampler is suitable for evaluating the time-weighted average concentration, as the time required to attain equilibrium between the sampler and water increases with increasing K_{SW} (Huckins et al., 1999; Stuer-Lauridsen, 2005; Mazzella et al., 2007; Bayen et al., 2009; Llorca et al., 2009). Most passive samplers can run in a time-integrative mode, without much modification, for compounds with a high K_{SW}. For example, passive samplers, such as semi-permeable membrane devices (SPMDs) and other partitioning-based samplers consisted of hydrophobic sorbing phases, have been used to determine the time-weighted average concentration of hydrophobic contaminants, including polycyclic aromatic hydrocarbons, polychlorinated biphenyls and polychlorinated biphenyl ethers (Huckins et al., 1999; Adams et al., 2007; Ouyang et al., 2007; Anderson et al., 2008; ter Laak et al., 2008).

However, the equilibration time will be much shorter for less hydrophobic chemicals, with a low 1-octanol–water partition coefficient (K_{OW}) because the $\log K_{SW}$ values for most passive sampling materials are linearly related with $\log K_{OW}$ (Huckins et al., 1999; ter Laak et al., 2008). As more and more attention has been paid to polar organic chemicals (POCs) (Mills et al., 2007; Söderström et al., 2009), many passive samplers accumulating POCs in a time-integrative mode have been developed (Kingston et al., 2000; Alvarez et al., 2004; Hyne and Anistrope, 2008). Polymeric phases having higher sorption capacities for POCs have been employed (Kingston et al., 2000; Alvarez et al., 2004; Mazzella et al., 2007; Shaw et al., 2009) or diffuse mem-

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branes making mass transport slower in the aqueous boundary layer have been used (Ouyang et al., 2007; Vermeirssen et al., 2009). However, K_{SW} values vary significantly between various POCs, making sampling times that guarantee time-integrative uptake highly dependent on the target analytes. Because environmental sampling is usually aimed at monitoring many compounds of interests simultaneously (Kolpin et al., 2002; Loos et al., 2010), it is difficult to apply passive sampling techniques for this purpose.

Thus, we proposed a new type of time-integrative sampler using *in situ* solvent extraction (TISIS) by the flow of an organic solvent through the polymer tubing lumen. The chemical concentration in the sampling phase in contact with the extraction solvent could be reduced much lower than the equilibrium concentration. Therefore, sampling could be constantly conducted within a linear uptake regime. Poly(dimethylsiloxane) (PDMS) tubing and acetonitrile were chosen for the model polymer support and extraction solvent, respectively. Partition coefficients between PDMS and water (K_{PDMSw}) and sampling rates (R_S) were measured without using the extraction solvent to obtain sampling parameters. The performance of TISIS was evaluated using four model polar organic chemicals, caffeine, atrazine, diuron and 17α-ethynylestradiol. The sampling rates were determined in a constant aqueous exposure concentration. The amounts sampled under a pulsed exposure condition were also experimentally measured and compared with those calculated from the sampling rates obtained under the constant exposure study.

2. Theory

For a sampler consisted of a single phase or that can be assumed as a single phase, the accumulation of chemicals from water to the sampler can be described by a simple differential equation:

$$\frac{dC_S}{dt} = k_u C_w - k_e C_S \tag{1}$$

where C_S and C_w are the concentrations of a chemical in the sampler and water (mg L^{-1}), respectively, and k_u and k_e are the uptake and elimination rate constants (d^{-1}). The ratio of k_u to k_e equals to the equilibrium partition coefficient between the sampler and water (K_{SW}). If C_w is considered to be a constant, the concentration of a chemical accumulated in the sampler (C_S) is given by:

$$C_S = \frac{k_u}{k_e} C_w (1 - e^{-k_e t}) = K_{SW} C_w (1 - e^{-k_e t}) \tag{2}$$

Thus, C_S increases linearly with C_w when $k_e t$ is sufficiently small. When this condition is met, the sampling rate (R_S, L d^{-1}) is defined as:

$$R_S = k_u V_S = K_{SW} k_e V_S \tag{3}$$

where V_S is the volume of the sampler (L). The uptake and elimination rate constants (k_u and k_e) can be approximated using a film-diffusion model composed of two thin films of water and the sampler.

$$k_u = \frac{1}{\frac{\delta_w}{D_w}\frac{r}{\delta_w + r} + \frac{\delta_S}{D_S K_{SW}}} \frac{A_S}{V_S} \tag{4}$$

$$k_e = \frac{1}{\frac{\delta_w}{D_w}\frac{r}{\delta_w + r} K_{SW} + \frac{\delta_S}{D_S}} \frac{A_S}{V_S} \tag{5}$$

where δ represents the thickness of boundary layer (m), D is the diffusion coefficient (m^2 d^{-1}), the subscripts S and w represent the sampler and water, r is the radius of curvature of the sampler surface and A_S is the surface area of the sampler (m^2). Thus, R_S can be written as:

$$R_S = \frac{A_S}{\frac{\delta_w}{D_w}\frac{r}{\delta_w + r} + \frac{\delta_S}{D_S K_{SW}}} \tag{6}$$

The exponential term in Eq. (2) should be sufficiently small to allow time-integrative sampling. Thus, the elimination rate constant, k_e, needs to be minimized. Because a small A_S/V_S or large δ_S (i.e., thick passive sampler) is undesirable for handling, investigations have attempted to increase K_{SW} by modifying the sorbing phase for POCs (Kingston et al., 2000; Alvarez et al., 2004) or to increase δ_w by installing a diffuse membrane (Ouyang et al., 2007; Vermeirssen et al., 2009).

3. Materials and methods

3.1. Materials

Four model chemicals were chosen for the development of a new time-integrative sampler for polar organic chemicals. Caffeine, two herbicides, atrazine and diuron, and a synthetic estrogen, 17α-ethynylestradiol (EE2), were chosen for the evaluation of the sampler as these were very frequently detected in wastewaters and river waters worldwide (Kingston et al., 2000; Alvarez et al., 2004; Tran et al., 2007; Focazio et al., 2008; Hyne and Anistrope, 2008; Loos et al., 2010; Yoon et al., 2010). They are also electronically neutral under environmentally relevant conditions and polar, due to their logK_{ow} values, which range between 0.07 (caffeine) and 3.67 (EE2) (Table 1). All four chemicals were of high purity (>98%) and purchased from Sigma–Aldrich (St. Louis, MO). Poly(dimethylsiloxane) (PDMS) tubing, with an external diameter of 1.5 mm and internal diameter of 0.5 mm, was purchased from a local manufacturer (Dong-Bang Silicone Inc., Gimpo, Republic of Korea). PDMS, frequently used as a sampling material (Ouyang et al., 2007; Kwon and Escher, 2008; ter Laak et al., 2008; Llorca et al., 2009), was chosen because it is highly permeable to organic chemicals (Rusina et al., 2007) and possesses high stability in water and many organic solvents.

3.2. Design of the sampler

A schematic diagram of the sampler is shown in Fig. 1. The extraction solvent was passed through the PDMS tubing (i.d. = 0.5 mm) at the desired flow rate controlled by a syringe pump (KDS 100, KD Scientific Inc., Holliston, MA). An aqueous solution containing the chemical species was allowed to flow through a three-necked glass round flask. The hydraulic retention time in the flask was measured as 7.08 h, satisfying that the aqueous concentration of the selected chemical species remained constant during the constant exposure experiment. The solution was gently agitated by stirring at 120 rpm, using a Teflon coated magnetic stirring bar (51 mm × 8 mm diameter), to mimic turbulent sampling conditions and to increase the sampling rates by decreasing the thickness of the aqueous boundary layer (Kwon et al., 2006a). All sampling experiments were conducted at 25 ± 2 °C.

3.3. Chemical analyses

All the experiments were conducted in a mixture of two chemicals. Mixture 1 was composed of caffeine and atrazine and mixture 2 of diuron and EE2. An HPLC system, equipped with a Waters quaternary gradient pump (Waters 600E, Milford, MA, USA), an autosampler (Waters 717+) and a photodiode array detector (Waters 2996), was used for the quantification of the compounds. Deionized water and acetonitrile were used as the eluent solvents, in a gradient mode, at a flow rate of 1 mL min^{-1}: 40% acetonitrile (3 min), ramp to 60% acetonitrile in 6 min, hold for 2 min. The chemical mixture was separated on a reverse-phase C18 col-

Table 1
Physico-chemical properties, PDMS–water partition coefficients and sampling rates of the three selected model compounds.

Compound	CAS Reg. No.	MW (g mol^{-1})	LogK_{ow}[a]	pK_a	LogK_{PDMSw}[b]		Sampling rate, R_S (L d^{-1})			
					Batch	Kinetic	PDMS only	TISIS		
								0.2 mL h^{-1}	0.5 mL h^{-1}	1.5 mL h^{-1}
Caffeine	58–08-2	194.19	0.07	−0.13∼1.22[c]	0.26 ± 0.01	0.31 ± 0.02	0.000578	0.000530	0.000502	0.000372
Atrazine	1912–24-9	215.68	2.61	–	2.17 ± 0.02	2.15 ± 0.02	0.0410	0.0134	0.0107	0.00950
Diuron	330–54-1	233.10	2.78	–	1.65 ± 0.01	1.78 ± 0.01	0.0220	0.00890	0.00797	0.00742
EE2	57–63-6	296.41	3.67	10.04[d]	1.40 ± 0.02	1.53 ± 0.01	0.0221	0.00571	0.00761	0.00751

[a] Suggested values by Sangster Research Laboratory, 2011.
[b] Mean ± standard error.
[c] From Brittain and Pronkerd, 2007.
[d] From Kwon et al., 2006b.

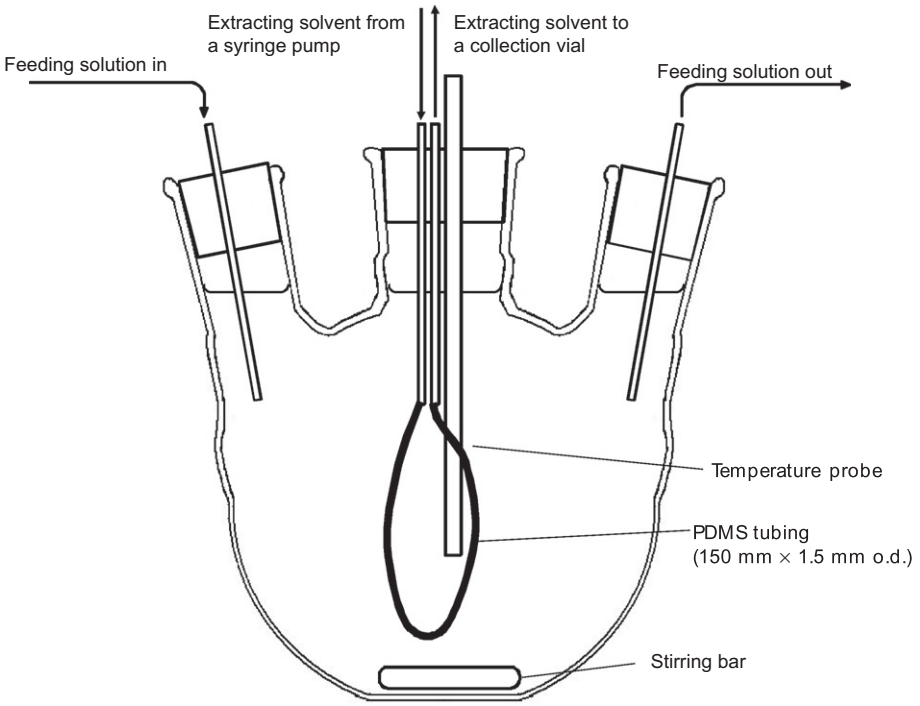

Fig. 1. Experimental design of the time-integrative sampler.

umn (Thermo ODS Hypersil 150 mm × 4.6 mm, 5 μm particle size, 120 Å pore size, end-capped; Thermo Fischer Scientific, Waltham, MA, USA) at room temperature. The detection wavelengths and retention times of caffeine, atrazine, diuron and EE2 were 272, 220, 248 and 227 nm and 3.1, 6.9, 7.5 and 9.3 min, respectively.

3.4. Determination of distribution coefficients between PDMS tubing and water (K_{PDMSw}) and sampling rates

The K_{PDMSw} values of the four selected chemicals were determined using a batch equilibrium partitioning test and a kinetic uptake method. In the batch experiment, one piece of cleaned 15 cm PDMS tubing was placed in a 4 mL glass vial containing an aqueous solution of the chemicals. The ranges of the initial aqueous concentrations spiked into the solution were 5–100, 0.2–4, 0.05–5 and 0.5–5 mg L^{-1} for caffeine, atrazine, diuron and EE2, respectively. Although phase equilibrium was obtained less than 24 h by shaking the vials in an orbital shaker at 150 rpm and 25 °C (see Fig. S1, Supplementary Material), equilibrium partition coefficients were measured after 72 h. The PDMS tubing was taken and extracted using 2 mL of acetonitrile. A preliminary experiment showed that over 98% of the extractable chemicals were extracted in the first extraction. Both aqueous samples and acetonitrile extracts were subjected to HPLC analysis for the determination of C_w and C_{PDMS}. The K_{PDMSw} values were obtained from the slope of a plot of C_{PDMS} versus C_w.

Kinetic K_{PDMSw} and the kinetic rate constant (k_e) were determined using PDMS tubings as passive samplers in a flow-through condition. Less than 10 pieces of custom-cut PDMS tubing (15 cm) were submerged in the aqueous solution, in which constant concentrations of the chemicals were maintained by flowing the feed water containing a constant chemical concentration. The total volume of PDMS tubings in the vessel was sufficiently small so that the partitioning of chemicals from the aqueous solution did not noticeably decrease the aqueous concentration. Routine measurements of the aqueous concentrations showed that the aqueous concentrations remained unchanged during the kinetic experiment. Amount of chemicals accumulated in PDMS was determined using the same extraction and HPLC quantification procedure described above. Obtained values of C_{PDMS} were plotted with respect to the exposure time and the uptake rate constant (k_u) and K_{PDMSw} were determined by a non-linear regression using Eq.

(2) using OriginPro ver. 8.0 (OriginLab Co., Northampton, MA). The sampling rates were then calculated using the volume of PDMS (Eq. (3)).

3.5. Time-integrative sampling in a constant aqueous concentration

A sampler, described in Fig. 1, was used for time-integrative sampling using *in situ* solvent extraction. Acetonitrile was chosen as the extraction solvent as it dissolves all four chemicals well, with minimal swelling of the PDMS. The swelling ratio of PDMS in acetonitrile was 1.01, smaller than those in other alternative organic solvents, such as methanol (1.02), ethanol (1.06) and acetone (1.06) (Lee et al., 2003). The sampling rates of the four selected chemicals were evaluated at three different extraction flow rates (0.2, 0.5 and 1.5 mL h^{-1}). The amounts of acetonitrile recovered in collection vials were 66%, 82% and 89% at 0.2, 0.5 and 1.5 mL h^{-1}, respectively. The sampled acetonitrile was then evaporated under a gentle nitrogen stream, with the final volume adjusted to 0.1 mL h^{-1} for the HPLC analysis. Potential loss of chemicals due to the evaporation and re-dissolution steps was neglected because all chemicals have low vapor pressure and their recoveries in this step were close to 100%. The total mass of chemicals sampled was then calculated from the concentration measured by HPLC and the collection recovery of acetonitrile. The aqueous exposure concentrations were approximately 10, 0.4, 0.5, and 0.7 mg L^{-1} for caffeine, atrazine, diuron and EE2, respectively. The sampling rates (in L h^{-1}) were determined by plotting the amount recovered by the sampler (in mg) divided by the aqueous concentration (mg L^{-1}) versus time (in h).

3.6. Flow-through experiment with a pulse exposure

In order to further evaluate the performance of the sampler, it was exposed to the aqueous solution, which received pulses of chemicals to simulate the variable concentration. To generate a pulsed exposure in the reaction vessel, the two different feed solutions were alternated. The solution containing the chemical mixture was allowed to flow into the vessel for 24 h and de-ionized water flowed for the next 48 h. This cycle of a pulse was repeated three times, with the experiment conducted for 9 d. The aqueous concentrations were approximately 9, 0.3, 1.0 and 1.2 mg L^{-1} for caffeine, atrazine, diuron and EE2, respectively. The aqueous concentration of the model chemicals in the feed tank was continuously monitored.

To predict the chemical concentration in the vessel and the total amount of chemical extracted, it was assumed that: (1) the solution in the vessel was well-mixed, (2) the decrease in the concentration in the vessel due to the extraction by the polymeric phase and acetonitrile was negligibly small, and (3) the sampling rate was independent of the aqueous concentration. Based on these three assumptions, the aqueous concentration ($C(t)$) and the sampled amount ($M(t)$) were theoretically derived, as follows (see Supplementary Material A for further details):

Constant input concentration (C_{in}):

$$C(t) = C_{in} - (C_{in} - C_0)\exp\left(-\frac{t}{\tau}\right) \quad (7)$$

$$M(t) = M_0 + R_S(C_{in}t + \tau(C_{in} - C_0)\exp\left(-\frac{t}{\tau}\right) - \tau(C_{in} - C_0)) \quad (8)$$

No chemical input:

$$C(t) = C_0\exp\left(-\frac{t}{\tau}\right) \quad (9)$$

$$M(t) = M_0 + R_S C_0\tau\left(1 - \exp\left(-\frac{t}{\tau}\right)\right) \quad (10)$$

where C_0 and M_0 are the initial aqueous concentration (mg L^{-1}) and the initial amount of a chemical sampled (mg), respectively, and τ is the hydraulic retention time (h).

4. Results and discussion

4.1. Determination of sampler–water partition coefficients

Fig. 2 shows the changes in C_{PDMS} with exposure time when PDMS tubing was exposed to a constant aqueous concentration of the four chemicals. The broken lines represent the best-fit curves of the theoretical model (Eq. (2)). The K_{PDMSw} values obtained by a batch shaking method are also presented in Table 1 (see also Fig. S2, Supplementary Material). The values from the batch test were close to those kinetically determined. As shown in Fig. 2, equilibrium between PDMS and water was attained within 3 d for all compounds. The time domain for determining the time-weighted average concentration is often assumed that the sampler accumulates chemicals linearly until C_{PDMS} reaches the half equilibrium concentration (Huckins et al., 1999; Stephens et al., 2005). According to this assumption, the time domain for integrative sampling was shorter than 20 h under our experimental condition. However, the time-integrative sampling regime can be extended by lowering the surface area to volume ratio (Bayen et al., 2009) or increasing the thickness of the diffusion boundary layer (Ouyang et al., 2007; Vermeirssen et al., 2009), although decreased mass transport may cause analytical difficulties due to limited mass accumulated.

The sampling rates (R_S) were also determined using Eq. (3) (Table 1), with the highest rate found for atrazine, followed by EE2, diuron and caffeine, which coincided with the decreasing values of K_{SW}. Because the thickness of the diffusion boundary layer (δ_w) does not depend on the chemical properties (Levich, 1962) and the diffusion coefficients in water and PDMS are unlikely to differ by orders of magnitude, the differences in the sampling rates were most likely due to the different K_{SW}, with measured difference in R_S well-explained by the K_{SW} values.

The sampling rates in this study (Table 1) were generally lower than those reported in the literature. The reported sampling rates of atrazine and diuron ranged between 0.0077 and 1.8 L d^{-1} using POCIS (Alvarez et al., 2004; Mazzella et al., 2007), various configurations of SDB-RPS (Shaw et al., 2009; Shaw and Mueller, 2009) and SDB-XC (Hyne and Anistrope, 2008) Empore disks and cellulose sampling device (Tran et al., 2007). Although many other factors affect the sampling rate, the smaller surface area of the PDMS tubing and lower sorbing capacity of PDMS compared with other sampling phases seem to be the main causes of the lower sampling rates. The surface area of TISIS using 15 cm PDMS tubing is 7.1 cm^2 smaller than other passive samplers tested (18–60 cm^2)

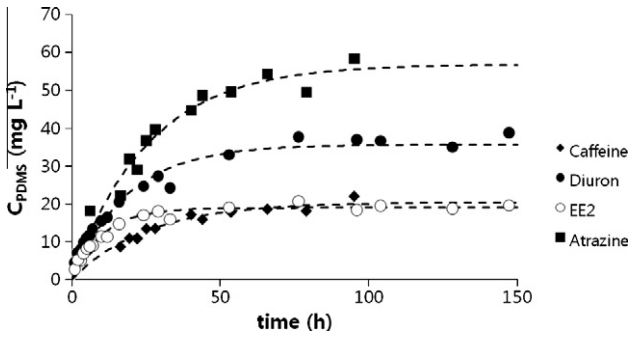

Fig. 2. Chemical concentrations in the PDMS tubing exposed to constant chemical concentrations. Broken lines represent the model-fit using Eq. (2).

(Alvarez et al., 2004; Mazzella et al., 2007; Shaw and Mueller, 2009). Although PDMS, a non-polar polymer, was used as the polymeric support in this study, it would increase the sampling rate of polar organic chemicals by using an alternative support material with higher sorption capacity for them.

4.2. Effects of the extraction flow rate

Because an ideal time-integrative sampler should be far from phase equilibrium with ambient water, a reasonably short residence time of the extraction solvent (acetonitrile) is required. However, minimizing the amount of solvent is also advantageous due to the ease of handling and potential experimental losses associated with concentrating the solvent in a laboratory. Therefore, the performance of TISIS at three different extraction flow rates was evaluated (Fig. 3). As indicated above, the loss of the extraction solvent increased with decreasing flow rate because the solvent caused slight swelling of the PDMS (Lee et al., 2003) and may diffuse out. However, the sampling rate obtained at three flow rates did not differ much for all the tested chemicals (Fig. 3 and Table 1), indicating that the concentration (or chemical potential) in the extraction solvent was much lower than that in the aqueous solution regardless of the changes in the flow rates tested. The concentration gradient or the change in chemical potential, the main driving force of mass transport from the aqueous solution to extraction solvent, was thought to be remained unchanged within the range of the flow rates of acetonitrile. Fig. 4 schematically describes the driving force of the mass transport from the ambient water to the extraction solvent.

The sampling rates obtained using TISIS were lower than the initial sampling rate obtained in the experiment with PDMS tubing only, whereas the difference was small for caffeine, with R_S values for atrazine, diuron, and EE2 using TISIS lower by factors between 2.5 and 4.3. The effective thickness of the PDMS tubing passive sampler should be thinner than that of TISIS. The diffusion film thickness of a polymeric phase can be approximated as half of its physical thickness for a flat surface (Salaün and Buffle, 2004). With the agitation of aqueous phase and relatively lower K_{PDMSw} values of the test chemicals, it is likely that the mass transport resistance in the PDMS tubing would be rate-limiting. Although additional acetonitrile phase may also contribute the overall mass transfer resistance by adding a third term in the denominator in Eq. (6), the effects would be negligible because all the test compounds dissolve much better in acetonitrile than in PDMS. Thus, the decreased sampling rates for the model compounds were likely to be caused by the increased thickness of the PDMS film and experimental results fell within the reasonable range expected. Another factor that might lowered the sampling rate of TISIS compared to PDMS was the axial change in the concentration gradient. However, this was unlikely to decrease the sampling rate because

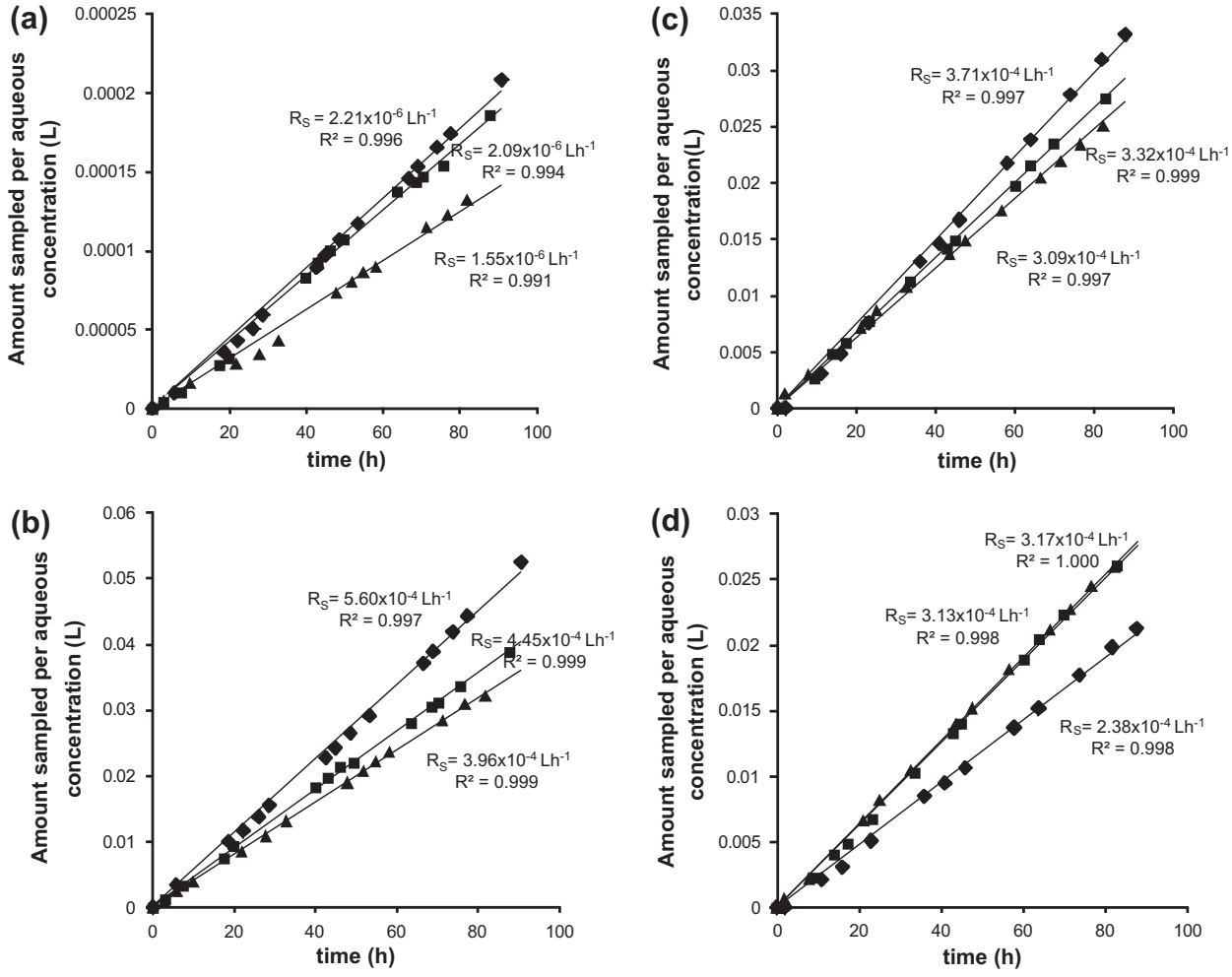

Fig. 3. Cumulative amount sampled using TISIS divided by the aqueous exposure concentration (L) with respect to exposure time for: (a) caffeine, (b) atrazine, (c) diuron, and (d) 17α-ethynylestradiol at three different extraction flow rates, 0.2 (diamonds), 0.5 (squares) and 1.5 mL h^{-1} (triangles). The dashed lines represent the linear best-fit lines. The sampling rate (R_S; L h^{-1}) was determined from the slope of the regression line.

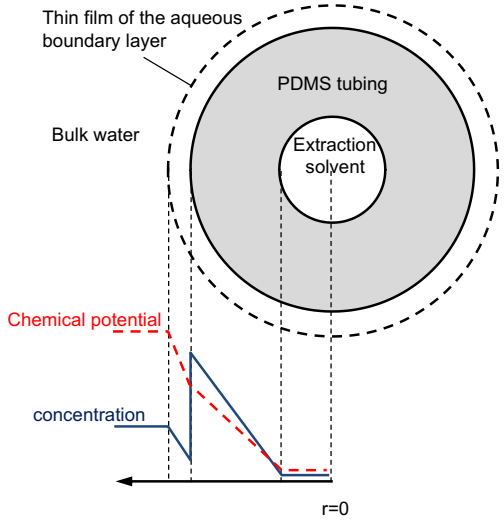

Fig. 4. Schematic diagram of the cross section of TISIS. The solid and dashed lines represent the concentration gradient and change in the chemical potential in the *r*-coordinate, respectively.

the sampling rate was not increased by increasing the flow rate of acetonitrile (Table 1 and Fig. 3). This suggests that the lowest flow rate of the extraction solvent was sufficient to extract the test chemicals, without disturbing the concentration gradient, as shown in Fig. 4.

It should be also noted that the sampling rate of TISIS may be too low for many polar organic chemicals with low sampler-water partition coefficient such as caffeine in this study. Although sampling rate may be increased by increasing surface area, it would be desirable for using alternative polymeric phase with higher sorption capacity for such chemicals.

4.3. Pulsed exposure

Fig. 5 shows the results from the time-integrative sampling using TISIS when the aqueous concentration changed over time. The open diamonds represent the measured aqueous concentrations and dashed lines indicate the theoretical curves using Eqs. (7) and (9). For all the test chemicals, the measured aqueous concentrations coincided very well with the predicted curves, confirming that the aqueous concentration was modeled by assuming a complete continuously-stirred tank reactor. The filled squares represent the cumulative amount of chemicals sampled using TISIS and the solid curves the model results using Eqs. (8) and (10). For the derivation of the theoretical curve, pre-determined kinetic distribution coefficients (K_{PDMSw}) and sampling rates (R_S), at the extraction flow rate of 0.5 mL h^{-1} (Table 1), were used. Although the experimental data were slightly lower than the theoretical model prediction except for caffeine, the overall deviations were less than 10% for all the test chemicals. Thus, it was confirmed that

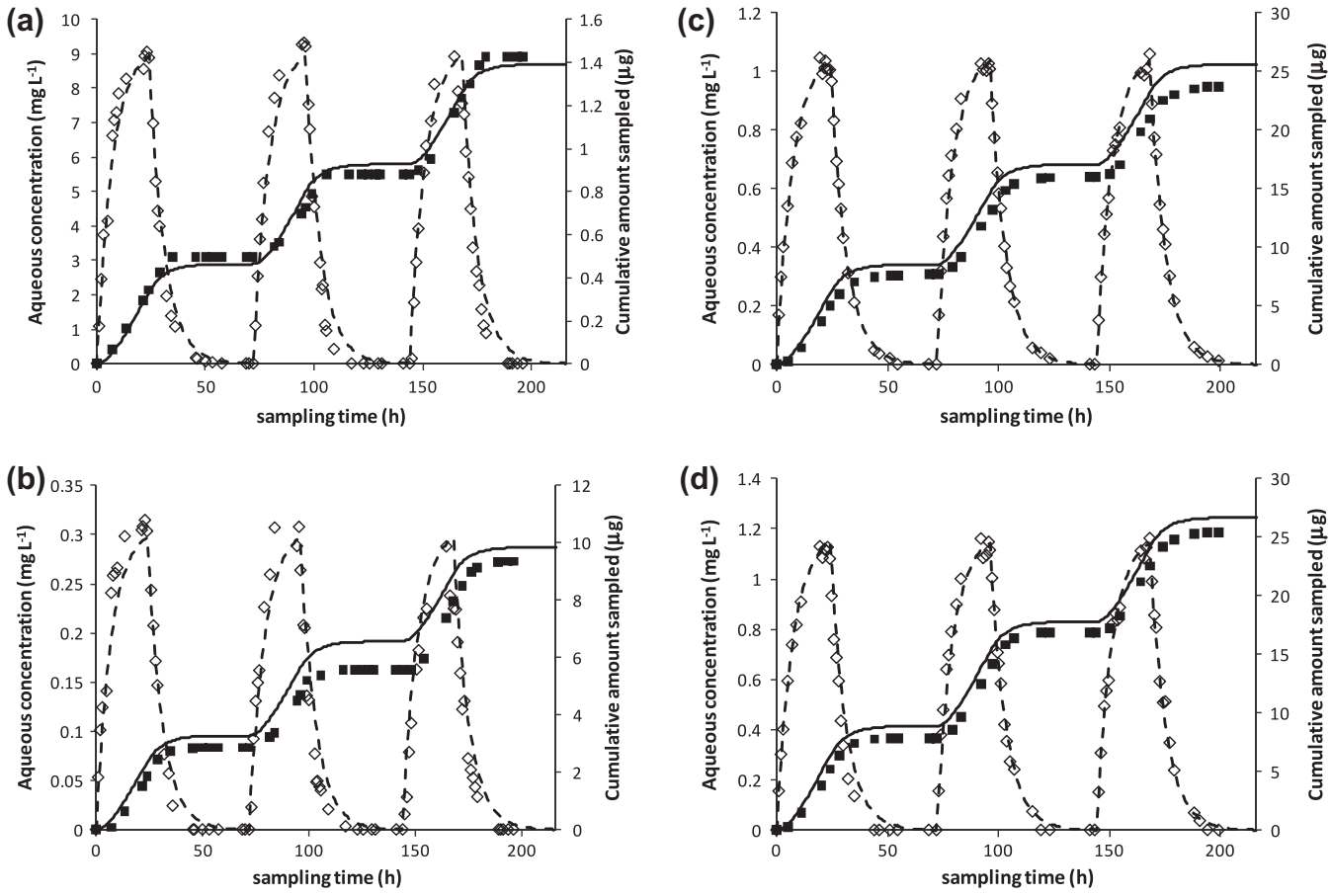

Fig. 5. Evaluation of the performance of TISIS under pulsed exposure conditions during 200 h for: (a) caffeine, (b) atrazine, (c) diuron, and (d) 17α-ethynylestradiol. The open diamonds represent the measured aqueous concentration and the filled squares the cumulative amount of the chemical sampled using TISIS. The dashed and plain lines are predicted aqueous concentrations using Eqs. (7) (constant input condition) and (9) (zero input condition) and the predicted sampled amount using Eq. (8) (constant input condition) and Eq. (10) (zero input condition).

TISIS can accumulate polar organic chemicals in a time-integrative regime, regardless of the distribution coefficient between the polymeric passive sampling phase and water (K_{SW}).

4.4. Implication of the study to environmental monitoring of polar organic chemicals

As shown in this work, TISIS was able to linearly accumulate all of the model compounds, regardless of the K_{SW} values and varying aqueous concentrations under laboratory conditions. Although the device is not ready for the field deployment as its current form, this study has provided some important insights into the determination of time-weighted average concentrations of POCs. A sampler may be designed so that the overall mass transport of chemicals from water is limited by diffusion in the polymeric support so that the overall sampling rate would be nearly constant for a given compound with variable turbulent conditions in the field. Therefore, a simple laboratory calibration may replace the use of performance reference compounds. Another advantage of TISIS would be the selective preconcentration of analytes because large molecules in the sample matrix do not pass through the PDMS tubing.

5. Conclusions

A new time-integrative sampler using *in situ* solvent extraction (TISIS) was found to be able to determine time-weighted average concentration of polar organic compounds in water. Time-domain for integrative sampling was not limited by the partition coefficient of a compound by extracting the chemicals sorbed in the polymer tubing using an organic solvent. The major advantages of the sampler were: (1) the invariance of the sampling rate with changing environmental conditions and (2) the separation of analytes from sampling matrix. Although the sampling rates of POCs were low using non-polar PDMS as a polymeric support, this study provide new insights on the determination of time-weighted average concentration using *in situ* solvent extraction.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2011.10.011.

References

Adams, R.G., Lohmann, R., Fernandez, L.A., Macfarlane, J.K., Gschwend, P.M., 2007. Polyethylene devices: passive samplers for measuring dissolved hydrophobic organic compounds in aquatic environments. Environ. Sci. Technol. 41, 1317–1323.

Alvarez, D.A., Petty, J.D., Huckins, J.N., Jones-Lepp, T.L., Getting, D.T., Goddard, J.P., Manahan, S.E., 2004. Development of a passive, in situ, integrative sampler for hydrophilic organic contaminants in aquatic environments. Environ. Toxicol. Chem. 23, 1640–1648.

Anderson, K.A., Sethajintanin, D., Sower, G., Quarles, L., 2008. Field trial and modeling of uptake rates of in situ lipid-free polyethylene membrane passive sampler. Environ. Sci. Technol. 42, 4486–4493.

Bayen, S., Ter Laak, T.L., Buffle, J., Hermens, J.L.M., 2009. Dynamic exposure of organisms and passive samplers to hydrophobic chemicals. Environ. Sci. Technol. 43, 2206–2215.

Brittain, H.G., Pronkerd, R.J., 2007. Profiles of drug substances, excipients and related methodology. Critical Compilation of pKa Values for Pharmaceutical Substances, vol. 33. Burlington, MA, USA.

Focazio, M.J., Kolpin, D.W., Barnes, K.K., Furlong, E.T., Meyer, M.T., Zaugg, S.D., Barber, L.B., Thurman, M.E., 2008. A national reconnaissance for pharmaceuticals and other organic wastewater contaminants in the United States – II. Untreated drinking water sources. Sci. Total Environ. 402, 201–216.

Hawker, D.W., 2010. Modeling the response of passive samplers to varying ambient fluid concentrations of organic contaminants. Environ. Toxicol. Chem. 29, 591–596.

Huckins, J.N., Petty, J.D., Orazio, C.E., Lebo, J.A., Clark, R.C., Gibson, V.L., Gala, W.R., Echols, K.R., 1999. Determination of uptake kinetics (sampling rates) by lipid-containing semipermeable membrane devices (SPMDs) for polycyclic aromatic hydrocarbons (PAHs) in water. Environ. Sci. Technol. 33, 3918–3923.

Hyne, R.V., Anistrope, M., 2008. Calibration and field application of a solvent-based cellulose membrane passive sampling device for the monitoring of polar herbicides. Chemosphere 71, 611–620.

Kingston, J.K., Greenwood, R., Mills, G.A., Morrison, G.M., Persson, L.B., 2000. Development of a novel passive sampling system for the time-averaged measurement of a range of organic pollutants in aquatic environments. J. Environ. Monit. 2, 487–495.

Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B., Buxton, H.T., 2002. Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999–2000: a national reconnaissance. Environ. Sci. Technol. 36, 1202–1211.

Kwon, J.-H., Escher, B.I., 2008. A modified parallel artificial membrane permeability assay for evaluating the bioconcentration of highly hydrophobic chemicals in fish. Environ. Sci. Technol. 42, 1787–1793.

Kwon, J.-H., Katz, L.E., Liljestrand, H.M., 2006a. Use of a parallel artificial membrane system to evaluate passive absorption and elimination in small fish. Environ. Toxicol. Chem. 25, 3083–3092.

Kwon, J.-H., Liljestrand, H.M., Katz, L.E., 2006b. Partitioning of moderately hydrophobic endocrine disruptors between water and synthetic membrane vesicles. Environ. Toxicol. Chem. 25, 1984–1992.

Lee, J.N., Park, C., Whitesides, G.M., 2003. Solvent compatibility of poly(dimethylsiloxane)-based microfluidic devices. Anal. Chem. 75, 6544–6554.

Levich, V.G., 1962. Physicochemical Hydrodynamics. Prentice-Hall, Englewood Cliffs, NJ, USA.

Llorca, J., Gutiérrez, C., Capilla, E., Tortajada, R., Sanjuán, L., Fuentes, A., Valor, I., 2009. Constantly stirred sorbent and continuous flow integrative sampler: new integrative samplers for the time weighted average water monitoring. J. Chromatogr. A 1216, 5783–5792.

Loos, R., Locoro, G., Comero, S., Contini, S., Schwesig, D., Werres, F., Balsaa, P., Gans, O., Weiss, S., Blaha, L., Bolchi, M., Gawlik, B.M., 2010. Pan-European survey on the occurrence of selected polar organic persistent pollutants in ground water. Water Res. 44, 4115–4126.

Mazzella, N., Dubernet, J.-F., Delmas, F., 2007. Determination of kinetic and equilibrium regimes in the operation of polar organic chemical integrative samplers: application to the passive sampling of the polar herbicides in aquatic environments. J. Chromatogr. A 1154, 42–51.

Mills, G.A., Vrana, B., Allan, I., Alvarez, D.A., Huckins, J.N., Greenwood, R., 2007. Trends in monitoring pharmaceuticals and personal-care products in the aquatic environment by use of passive sampling devices. Anal. Bioanal. Chem. 387, 1153–1157.

Ouyang, G.F., Zhao, W.N., Bragg, L., Qin, Z.P., Alaee, M., Pawliszyn, J., 2007. Time-weighted average water sampling in Lake Ontario with solid-phase microextraction passive samplers. Environ. Sci. Technol. 41, 4026–4031.

Rusina, T.P., Smedes, F., Klanova, J., Booij, K., Holoubek, I., 2007. Polymer selection for passive sampling: a comparison of critical properties. Chemosphere 68, 1344–1351.

Söderström, H., Lindberg, R.H., Fick, J., 2009. Strategies for monitoring the emerging polar organic contaminants in water with emphasis on integrative passive sampling. J. Chromatogr. A 1216, 623–630.

Salaün, P., Buffle, J., 2004. Integrated microanalytical system coupling permeation liquid membrane and voltammetry for trace metal speciation. Theory and applications. Anal. Chem. 76, 31–39.

Sangster Research Laboratory. LOGKOW – A databank of evaluated octanol–water partition coefficient (logP). <http://logkow.cisti.nrc.ca/logkow/index.jsp> (accessed 1.05.11).

Shaw, M., Eaglesham, G., Mueller, J., 2009. Uptake and release of polar compounds in SDB-RPS Empore™ disks; implications for their use as passive samplers. Chemosphere 75, 1–7.

Shaw, M., Mueller, J., 2009. Time integrative passive sampling: how well do chemcatchers integrate fluctuating pollutant concentrations? Environ. Sci. Technol. 43, 1443–1448.

Stephens, B.S., Kapernick, A., Eaglesham, G., Mueller, J., 2005. Aquatic passive sampling of herbicides on naked particle loaded membranes: accelerated measurement and empirical estimation of kinetic parameters. Environ. Sci. Technol. 39, 8891–8897.

Stuer-Lauridsen, F., 2005. Review of passive accumulation devices for monitoring organic micropollutants in the aquatic environment. Environ. Pollut. 136, 503–524.

ter Laak, T.L., Busser, F.J.M., Hermens, J.L.M., 2008. Poly(dimethylsiloxane) as passive sampler material for hydrophobic chemicals: effect of chemical properties and sampler characteristics on partitioning and equilibration times. Anal. Chem. 80, 3859–3866.

Tran, A.T.K., Hyne, R.V., Doble, P., 2007. Calibration of a passive sampling device for time-integrated sampling of hydrophilic herbicides in aquatic environments. Environ. Toxicol. Chem. 26, 435–443.

Vermeirssen, E.L.M., Bramaz, N., Hollender, J., Singer, H., Escher, B.I., 2009. Passive sampling combined with ecotoxicological and chemical analysis of pharmaceuticals and biocides – evaluation of three chemcatcher™ configurations. Water Res. 43, 903–914.

Vrana, B., Mills, G.A., Allan, I.J., Dominiak, E., Svensson, K., Knutsson, J., Morrison, G., Greenwood, R., 2005. Passive sampling techniques for monitoring pollutants in water. Trends Anal. Chem. 24, 845–868.

Yoon, Y., Ryu, J., Oh, J., Choi, B.-G., Snyder, S.A., 2010. Occurrence of endocrine disrupting compounds, pharmaceuticals, and personal care products in the Han River (Seoul, South Korea). Sci. Total Environ. 408, 636–643.