Original Article

Applicability of Passive Sampler Disks for Collection of Time-integrated River Water Samples for Toxicity Bioassay

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ABSTRACT

The applicability of Empore™ styrene-divinylbenzene reverse-phase sulfonated (SDB-RPS) passive sampler disks for integrative sampling of organic chemicals in river water was investigated to evaluate toxicity levels via bioassay using larval medaka (*Oryzias latipes*). Those disks were deployed for periods of 1, 2, 3, 7, and 10 days (PS different period), and at 2-day intervals over the 10-day sampling period (PS interval). Six 10-L grab samples were collected at the same time as PS interval sampling, and thereafter concentrated using Sep-Pak® Plus PS-2 cartridges (GS). Adsorbed chemicals were subsequently eluted from Sep-Pak cartridges and SDB-RPS disks and prepared for toxicity tests and gas chromatography/mass spectrometry analysis. Compared with all PS samples, GS samples showed strong toxicity results. None of the PS interval samples showed toxicity, even though the amount of adsorbed chemicals in the 2nd interval sample was higher than in PS 7- and 10-day samples, which showed toxicity. Furthermore, the PS 10-day sample contents were not equivalent to the accumulated amounts of adsorbed chemicals in PS interval samples. On the basis of these results, it is assumed that during long-term sampling, chemicals adsorbed on disks might be affected by desorption or decomposition, and that some might be converted to more toxic compounds.

Keywords: toxicity, bioassay, passive sampler, decomposition

INTRODUCTION

In recent years, the presence of trace chemicals, such as pesticides, pharmaceuticals, and personal care products, in the aquatic environment has emerged as one of the most urgent environmental concerns. Thus, there is a continuing need for new technologies and techniques to provide reliable data for assessing the potential threats associated with low levels of complex mixtures of environmental contaminants [1].

Since many of these contaminant compounds can pose a threat to both ecosystem and human health, it is necessary to monitor pollutants in the aquatic environment. In this regard, most water monitoring programs are based on the collection of grab, spot, or bottle samples of water at a given time. However, where pollutants are present in only trace levels,

this approach necessitates the collection of large volumes of water. Moreover, subsequent laboratory analysis of such samples provides only a snapshot of the levels of pollutants at the time of sampling. This approach accordingly has drawbacks for sampling environments where the concentration of pollutants varies over time, and thus episodic pollution events can be missed. Furthermore, spot sampling yields different apparent concentrations of pollutants depending on the pretreatment applied (e.g., filtering) and does not provide information on the actual dissolved bioavailable fraction of the contaminants to which recipients are exposed. One solution to this problem is to increase the sampling frequency or to install automatic sampling systems that can collect numerous water samples over a given time period. This, however, is costly and in many cases impractical, since a secure site and significant pretreatment of water are required. Such systems

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are therefore rarely used in widespread monitoring programs. Passive sampling can overcome these difficulties by combining sampling, analyte isolation, and preconcentration into a single step, and also enabling time-weighted average sampling of compounds during the deployment period [2].

In order to determine the concentrations of pollutants using passive samplers after field exposure, it is necessary to adopt so-called substance-specific sampling rates (i.e., a volume of water sampled per unit time), which allow users to compute time-weighted average concentrations from the compound mass in the receiving phase [3]. In this respect, toxicity is a valuable indicator of water quality, and is used to assess the effects of organic chemicals. Therefore, rather than attempting to identify the concentrations of individual contaminants, our interest in the present study was to assess the toxicity corresponding to the amounts of organic contaminants adsorbed by passive sampler disks as a simple indicator of chemical pollution. Accordingly, we did not need to identify the sampling rate for each individual organic compound.

Although the traditional approach to environmental risk assessment couples monitoring of pollutant levels with toxicity testing of individual chemicals, the application of such toxicological data to realistic environmental risk assessment is limited, as it does not address the fact that these compounds do not exist in the environment in isolation, but are instead present in complex mixtures. The difficulties associated with identifying the risks posed by mixtures of chemicals might, however, be addressed by pairing the enrichment of chemicals with the assessment of extracts via bioassays [4].

In the present study, we investigated the applicability of passive sampling (as one of the water sampling methods), using EmporeTM styrene-divinylbenzene reverse-phase sulfonated disks (hereafter SDB-RPS disks) as an alternative to grab sampling using Sep-Pak[®] Plus PS-2 cartridges, to evaluate toxicity levels via bioassays using larvae of the medaka fish (*Oryzias latipes*).

MATERIALS AND METHODS

Study area

Timor-Leste was selected as the sampling region, because it is a developing country that has inadequate pollution control facilities. Fifty-seven percent of its total population does not have access to an improved sanitation system. Moreover, there is a lack of solid waste management, and water sources are not well protected. Consequently, surface water is often polluted [5].

We conducted a preliminary survey in Dili City, the capital of Timor-Leste, and on the basis of this survey, subsequently selected Campo Alor River as our study site, as this is the city's most polluted river. Campo Alor is a freshwater stream, with a basin area of 1.6 km², width of 2 m, and water depth of 0.3–0.5 m, that runs through a residential area and is mainly exposed to the discharged wastewater from the surrounding houses. Although some streams in Dili have no flow during the dry season, Campo Alor River has a relatively high flow rate of between 0.07 and 0.13 m³/s during the dry and rainy seasons, respectively.

Sampling

For grab sampling, we used Sep-Pak[®] Plus PS-2 cartridges (Waters, Milford, USA), which contain the same sorbent material (styrene-divinylbenzene copolymer) as used in SDB-RPS passive sampler disks, to concentrate organic chemicals from river water samples. These are commonly used cartridges and we have used them in previous research [6]. For passive sampling, we selected 47-mm SDB-RPS disks (3M, Saint Paul, USA), which contain a styrene-divinylbenzene copolymer that has been modified with sulfonic acid groups to make it hydrophilic and provide selectivity for polar organic chemicals. Shaw *et al.* [4] reported that SDB-RPS disks are capable of sequestering a broad range of organic pollutants, however, the range of compounds sequestered has not been comprehensively identified.

In order to determine the necessary number of SDB-RPS disks and the length of deployment time required for sampling, preliminary tests were conducted both in the laboratory and in the field (Myojin River, Ube City, Japan). In the laboratory experiment, 5 µg/L triclosan solution was concentrated using Sep-Pak[®] Plus PS-2 cartridges, and SDB-RPS disks were deployed for 1, 2, 3, and 7 days in batches of the same solution. The results showed that the amount of triclosan adsorbed from 10 L of solution by four Sep-Pak cartridges was 31.2 µg and that adsorbed by three SDB-RPS disks that were deployed for 1, 2, 3, and 7 days was 5.14, 10.5, 29.4, and 41.9 µg, respectively. In the field experiment, three SDB-RPS disks were deployed in the river between January 8 and 11, 2016, at which time the river had an average flow velocity of 0.17 m/s, average discharge of 0.11 m³/s, average pH of 7.5, average conductivity of 0.3 ms/cm, average dissolved oxygen of 11.1 mg/L, and average water temperature of 11.6°C. During the deployment period, a 10-L grab water sample was collected each day and then concentrated using four Sep-Pak cartridges. The chemicals eluted from SDB-RPS disks and Sep-Pak cartridges showed toxicities of 0.13

Fig. 1 Sampling schedule and data logger records during the sampling period.

and 0.39 (LT_{50}^{-1} values, explained later), respectively. The amount of chemicals adsorbed by three SDB-RPS disks during 3 days was 27.4 μg , and the average amount of chemicals adsorbed by four Sep-Pak cartridges was 29.3 μg . On the basis of these results, it was concluded that in order to collect similar amounts of adsorbed chemicals and to show toxicity, it would be necessary to deploy three SDB-RPS disks in the river for at least 3 days.

Conditioned SDB-RPS disks were placed in a ChemcatcherTM passive sampler holder (3M) without a diffusion limiting membrane and this was then deployed in Campo Alor River, 0.5 km upstream from its outlet into the sea. The survey was conducted during the rainy season between March 1 and 11, 2016, at which time the river had an average flow velocity of 0.21 m/s, average discharge of 0.14 m^3/s , average pH of 7.60, average conductivity of 0.75 ms/cm , average dissolved oxygen of 4.50 mg/L , and average water temperature of 29.80°C. All sampling activities were performed between 9.00 and 11.00 AM. The sampling schedule and data logger records for water level and temperature during the sampling period are shown in **Fig. 1**. For passive sampling, SDB-RPS disks were deployed for different time periods of 1, 2, 3, 7, and 10 days (hereafter, PS different period samples) and at 2-day intervals over the 10-day sampling period (hereafter, PS interval samples), to assess how the accumulation behavior of adsorbed chemicals in the 10-day PS sample compared with those accumulated in the five 2-day interval samples. For grab sampling, six 10-L grab samples were collected—an initial sample on day 1 and then five subsequent samples

collected at the same time as the PS interval samples. These samples were concentrated using four conditioned Sep-Pak[®] Plus PS-2 cartridges (hereafter, GS samples).

Concentration and Elution of Chemical Compounds

Chemical compounds were concentrated from river water through both preconditioned Sep-Pak[®] Plus PS-2 cartridges and SDB-RPS disks. After concentration, Sep-Pak cartridges were dried by pumping air until all the water droplets inside were removed. Passive sampler SDB-RPS disks were dried in their Chemcatcher holders at room temperature (30°C), after which the holders were covered with their caps. The dried Sep-Pak cartridges and Chemcatcher samplers were wrapped in aluminum foil, refrigerated, and transferred to a cool bag until arrival in Japan. Adsorbed chemical compounds were subsequently eluted using acetone. Elution from the Sep-Pak[®] Plus PS-2 cartridges was based on the method of Ishii *et al.* [7], who reported that 9 mL of acetone could completely elute almost all organic microchemicals from each cartridge. Accordingly, 10 mL of acetone was flowed into each cartridge, and a total of 40 mL of acetone eluate was collected from the four Sep-Pak cartridges. Chemicals adsorbed onto SDB-RPS disks were eluted as recommended by the manufacturer (3M), using two 10 mL volumes of acetone for each passive sampler disk. The 60 mL of acetone eluate collected from three disks was then evaporated to a final volume of 40 mL. Acetone eluates from both SDB-RPS disks (PS samples) and Sep-Pak[®] Plus PS-2 cartridges (GS samples) were divided into two samples: 4 mL for gas

Fig. 2 Elution procedure of adsorbed chemicals, (a) from passive sampler (PS) samples, and (b) from grab samples (GS).

chromatography/mass spectrometry (GC/MS) analysis and 36 mL for the toxicity test, as shown in **Fig. 2**.

Medaka Acute Toxicity Test

In a previous study, Liu *et al.* [8] developed an efficient larval medaka assay. Organic toxicants were concentrated from 4 L of river water using disposable commercial adsorption cartridges. This concentrated solution was then diluted to prepare 10-, 20-, 50-, and 100-fold concentrated solutions and these solutions were used to examine toxicity. Toxicity was expressed as the median lethal concentration ratio (LCR_{50}). Depending on the mortality percentage of larval medaka exposed to different concentration ratios, the LCR_{50} was calculated using the TOXDAT Multi-Method Program (US EPA). The higher the LCR_{50} , the lower is the toxicity level of river water. Liu *et al.* [9] also proposed a simplified procedure for the acute toxicity test for screening purposes, in which only a 100-fold concentrated sample was used in a 48-hour test, and toxicity was expressed as the inverse of the median lethal concentration (LC_{50}^{-1}). Yamashita *et al.* [6] modified this procedure in order to evaluate toxicity as quantitatively as possible. They counted the number of dead medaka at 0.5, 1, 2, 3, 6, 12, 24, and 48 h during a test, and expressed toxicity as the inverse of the median lethal time (LT_{50}^{-1}) using Probit analysis.

Figure 3 shows the toxicity test procedure, in which 10-, 20-, 50-, and 100-fold concentrated solutions were prepared from the specified portion of acetone eluate (36 mL) for toxicity tests. Subsequently, groups of 10 individuals of 48 – 72-h post-hatch-aged larvae were exposed for 48 h to 25 mL of each test solution in a glass Petri dish of 90 mm diameter and 40 mm depth. Experimental conditions were $25 \pm 1^\circ\text{C}$ and light irradiation for 16 h per day. The control sample was 25 mL of activated carbon-treated water. No water, ventilation, or food were supplied during the test. The number of medaka deaths was recorded at 0.5, 1, 2, 3, 6, 12, 24, and 48 h.

In the present study, two toxicity indices were employed, namely, LT_{50}^{-1} and LDR_{50} (lethal dilution ratio, which is the inverse of LCR_{50}). The higher both indices are, the higher is the toxicity level of the sampled water. The reliable range of LT_{50}^{-1} is between 0.02 and 2.0, and that of LDR_{50} is between 0.01 and 0.20. Although LT_{50}^{-1} values are determined using one fourth of the test numbers, which requires conducting the toxicity test using only a 100-fold sample, LT_{50}^{-1} has a narrower range in the case of over-range toxicity samples ($LT_{50}^{-1} > 2.0$). In such cases, LDR_{50} evaluation of the toxicity test was conducted using all four folds (10-, 20-, 50-, and 100-fold samples), and then LT_{50}^{-1} values were obtained for different folds to cover the over-range toxicity samples. Le-

Fig. 3 Toxicity test procedure. (a) Preparation of different folds. (b) Test dishes with different dose levels.

thal dilution ratio (LDR_{50}) values were calculated using the same Probit analysis method as used for LT_{50}^{-1} calculation.

GC/MS Simultaneous Analysis

A gas chromatograph GC-2010 coupled with a mass spectrometer QP2010 (Shimadzu, Kyoto, Japan) was used for GC/MS analysis. The gas chromatograph was fitted with a fused silica capillary column (J&W DB-5 ms, Agilent, Santa Clara, USA; 30 mm $\times$ 0.25 mm i.d., 0.25- μ m film thickness).

The initial oven temperature was 40°C, and this was then increased to 310°C at a rate of 8°C/min. The carrier gas was helium supplied at a constant flow of 40 cm/s. Injector, interface, and ion source were maintained at 250, 300, and 200°C, respectively. The splitting ratio was 20:1. Electron impact mass spectra were obtained at 70 eV, with scans at 0.20 scans/s from 33 m/z to 600 amu. In order to identify compounds in the collected samples, a GC/MS simultaneous analysis database was used, which can identify and quantify

Table 1 Toxicity test results for passive sampler (PS) different period samples.

Deployment time	Fold (Concentration ratio)	Adsorbed amount ($\mu\text{g}/3$ disks)	(LT_{50}^{-1})*	(LDR_{50})**
1 day	100	14.2	< 0.020	< 0.010
	50		< 0.020	
	20		< 0.020	
	10		< 0.020	
2 days	100	16.7	< 0.020	< 0.010
	50		< 0.020	
	20		< 0.020	
	10		< 0.020	
3 days	100	32.5	< 0.020	< 0.010
	50		< 0.020	
	20		< 0.020	
	10		< 0.020	
7 days	100	32.2	0.20	0.014
	50		< 0.020	
	20		< 0.020	
	10		< 0.020	
10 days	100	40.8	0.26	0.020
	50		0.020	
	20		< 0.020	
	10		< 0.020	

(LT_{50}^{-1})*: inverse of median lethal time

(LDR_{50})**: lethal dilution ratio

a total of 942 chemical compounds without the need for reference standards [10].

To measure the amount of chemical adsorbed to SDB-RPS disks and Sep-Pak cartridges, the acetone eluate portion (4 mL) specified for GC/MS analysis was evaporated completely using nitrogen gas, and then 2 mL of hexane was added. Sodium sulfate was applied to remove moisture and was then removed. The hexane was subsequently evaporated to 1 mL and this volume was used for GC/MS analysis. The amounts of chemicals adsorbed to both SDB-RPS disks and Sep-Pak cartridges were calculated as the sum of the measured values of chemicals of each sample, and expressed as $\mu\text{g}/3$ disks and $\mu\text{g}/4$ Sep-Pak cartridges, respectively.

RESULTS AND DISCUSSION

Acute Toxicity Test and GC/MS Analysis Results

Tables 1, 2, and 3 show the toxicity test results for chemicals eluted from the PS different period, PS interval, and GS samples, respectively.

Table 1 shows that the chemicals eluted from the PS 10-day sample had highest toxicity at 100-fold, followed by the

7-day sample. The toxicities of PS 1-, 2-, and 3-day samples were lower than the limit of detection, even though the amount of adsorbed chemicals in the PS 3-day sample (32.5 $\mu\text{g}/3$ disks) was higher than that (32.2 $\mu\text{g}/3$ disks) in the PS 7-day sample.

Table 2 shows that no toxicity was observed in any of the PS interval samples, even though the amount of adsorbed chemicals in the PS 2nd interval sample (52.5 $\mu\text{g}/3$ disks) was higher than that in the PS 7- and 10-day samples, which both showed toxicity (**Table 1**).

The results presented in **Table 3** show that GS samples had strong toxicity at different folds, ranging from 20- to 100-fold. The LDR_{50} values were the same for the 1st and 3rd, 2nd and 4th, and 5th and 6th GS samples. However, the combination between the two indices LDR_{50} and LT_{50}^{-1} showed that the highest toxicity level was detected in the 1st grab sample, which contained the highest amount of adsorbed chemicals, whereas the 6th grab sample had the lowest toxicity level.

In spite of our pre-tests designed to determine the appropriate number of disks to use, the amounts of adsorbed chemicals in the PS 3-, 7-, and 10-day samples were lower than those in the GS samples. This might be related to the

Table 2 Toxicity test results for passive sampler (PS) interval samples.

Deployment event	Folds (Concentration ratio)	Adsorbed amount ($\mu\text{g}/3$ disks)	(LT_{50}^{-1})	(LDR_{50})
1st interval	100	19.2	< 0.020	< 0.010
	50		< 0.020	
	20		< 0.020	
	10		< 0.020	
2nd interval	100	52.5	< 0.020	< 0.010
	50		< 0.020	
	20		< 0.020	
	10		< 0.020	
3rd interval	100	26.8	< 0.020	< 0.010
	50		< 0.020	
	20		< 0.020	
	10		< 0.020	
4th interval	100	27.8	< 0.020	< 0.010
	50		< 0.020	
	20		< 0.020	
	10		< 0.020	
5th interval	100	23.2	< 0.020	< 0.010
	50		< 0.020	
	20		< 0.020	
	10		< 0.020	

Table 3 Toxicity test results for grab samples (GS).

	1st		2nd		3rd		4th		5th		6th	
Fold												
(Concentration ratio)	LT_{50}^{-1}	LDR_{50}	LT_{50}^{-1}	LDR_{50}	LT_{50}^{-1}	LDR_{50}	LT_{50}^{-1}	LDR_{50}	LT_{50}^{-1}	LDR_{50}	LT_{50}^{-1}	LDR_{50}
100	> 2.0		> 2.0		> 2.0		> 2.0		> 2.0		> 2.0	
50	> 2.0		> 2.0		> 2.0		0.91		0.71		0.42	
20	0.11	0.070	0.020	0.050	0.090	0.070	0.020	0.050	< 0.020	0.030	< 0.020	0.030
10	< 0.020		< 0.020		< 0.020		< 0.020		< 0.020		< 0.020	
Adsorbed amount ($\mu\text{g}/4$ Sep-Pak cartridges)	137		113		101		112		73.2		97.4	

difference in environmental conditions of the sampling locations, such as biofouling, flow rate, adsorbed chemicals, or high temperature. Furthermore, toxicity test results for PS 7- and 10-day samples were considerably lower than those for the GS samples. These findings are consistent with those of Tan *et al.* [11], who studied the estrogenic effect of grab samples and passive sampler extracts of different matrices of wastewater treatment plants. The authors found that the estrogenic activity obtained using passive sampler extracts

was lower than that obtained using grab samples, mainly due to biofouling.

Table 3 and **Fig. 4** show the relationship between the amounts of adsorbed chemicals and toxicity results for GS samples. The correlations between the chemical amounts and the corresponding LDR_{50} and LT_{50}^{-1} values, were not significant ($r = 0.70$, p -value = 0.12 and $r = 0.57$, p -value = 0.23, respectively).

Table 4 and **Fig. 5** show the relationship between the ad-

Fig. 4 Relationship between the adsorbed amount ($\mu\text{g}/4$ cartridges) of chemicals in grab samples (GS) and their corresponding toxicity level.

Note: Detected LT_{50}^{-1} (20 fold) values for 5th and 6th grab samples were lower than the limit (< 0.020), and therefore, we considered them to have a value of 0.010, as shown in this graph

Table 4 Adsorbed amount of chemicals in passive sampler (PS) interval and 10-day samples and average toxicity test results for grab samples (GS).

PS interval samples	1st	2nd	3rd	4th	5th	PS 10-day sample
adsorbed amount ($\mu\text{g}/3$ disks)	19.2	52.5	26.8	27.8	23.2	40.8
Average toxicity of GS samples						
	1st & 2nd	2nd & 3rd	3rd & 4th	4th & 5th	5th & 6th	1st to 6th
LT_{50}^{-1} (20 fold) *	0.065	0.050	0.050	0.020	0.010	0.040
LDR_{50}	0.060	0.060	0.060	0.040	0.030	0.050

(*) As shown in **Table 3**, LT_{50}^{-1} (100-, 50-fold) results for GS samples were mostly over the limit (> 2.0), and thus, their average values could not be calculated. Inverse of median lethal time (LT_{50}^{-1}) toxicity results at 20-fold were accordingly selected to calculate the average LT_{50}^{-1} values.

sorbed chemicals in the PS interval samples and the GS average toxicity. As shown in the sampling schedule (**Fig. 1**), GS samples were collected during the deployment time of the PS interval samples, and then the average toxicity values for GS samples were calculated to represent the toxicity conditions during the deployment times of the PS interval samples. The correlations between the chemical amounts in the PS interval

samples and the corresponding GS average toxicity (LDR_{50} and LT_{50}^{-1}) values, were not significant ($r = 0.30$, p -value = 0.55 and $r = 0.08$, p -value = 0.86, respectively).

It was noticed that the amount of adsorbed chemicals in the PS 10-day sample did not represent an accumulation of chemicals adsorbed in the individual PS interval samples. When the sum of the adsorbed amounts of each chemical

Fig. 5 Relationship between adsorbed amount ($\mu\text{g}/3$ disks) of chemicals in passive sampler (PS) interval samples and average value of toxicity results for grab samples (GS).

in PS interval samples was compared with their adsorbed amount in the PS 10-day sample for all 125 detected chemicals, a correlation between them was detected ($r = 0.91$, p -value $< 2.2 \times 10^{-16}$) (**Fig. 6**).

The above results showed that, although PS 7- and 10-day samples showed toxicity, PS samples with shorter deployment times did not show toxicity even though they contained similar or higher amounts of adsorbed chemicals. Furthermore, the amount of adsorbed chemicals in the PS 10-day sample was not equivalent to the sum of chemicals adsorbed in the individual PS interval samples. These observations suggest that longer deployment of SDB-RPS disks might be associated with desorption or decomposition of some adsorbed chemicals over the course of the deployment period, the latter of which could yield compounds of higher toxicity.

Pattern of Occurrence and Proportions of Different Chemicals

Table 5 shows the chemicals in the $\log K_{ow}$ range -0.07 to 16.5 with a maximum adsorbed amount $\geq 0.20 \mu\text{g}/3$ disks, which were detected in PS interval samples and the PS 10-day sample. The detected chemicals were categorized into five groups as shown in the table. Many compounds were absent from the PS 1st interval sample, which can be attributed to the fact that this sample was spilt during the preparation, and accordingly only 25% of the sample was

used for GC/MS analysis. Thus, it is assumed that only compounds with a high concentration were detected. **Figure 7** shows the pattern of occurrence and proportions of each chemical in the PS interval and PS 10-day samples with amounts $> 0.50 \mu\text{g}/3$ disks. The highest bars represent the highest adsorbed amount of the chemical, and the absence of a bar indicates that the chemical was not detected. There were wide variations in the occurrence and proportions of each chemical. In the PS 10-day sample, the amounts of diethyl phthalate, di-n-butyl phthalate, and nicotine represent between 60% and 140% of the accumulated amounts of these chemical in the PS interval samples. In contrast, the amounts of 2-ethyl-1-hexanol, elaidic acid methyl ester, aspirin, methyl palmitoleate, methyl palmitate, pyrethrin 2, 3-, and 4-methylphenol, and methyl myristate in the PS 10-day sample were considerably lower (or even absent) compared with the accumulated amounts of these chemicals in the PS interval samples. Pyrethrin 4 and pyrazoxyfen were only detected in the PS 10-day sample, whereas the amounts of other chemicals in the PS 10-day sample were between 10% and 50% of those accumulated in the PS interval samples. These differences in behavior do not, however, show a clear relationship with $\log K_{ow}$ values. The pattern of occurrence and proportions of different chemicals support our assumption that chemicals adsorbed onto SDB-RPS disks might undergo desorption and/or decomposition, and that some of

Fig. 6 Relationship between the amount of adsorbed chemicals in passive sampler (PS) 10-day and the sum of adsorbed amount of chemicals in passive sampler (PS) interval samples.

these could be converted to more toxic compounds.

CONCLUSION

Chemicals eluted from GS, PS different period, and PS interval samples were used in toxicity tests and subjected to GC/MS analysis, with the following results:

- Chemicals eluted from GS samples showed strong toxicity at different folds ranging from 20- to 100-fold, compared to the toxicity of those eluted from PS 7- and 10-day samples.
- Chemicals eluted from PS samples collected over a shorter period of time did not show any toxicity, especially for PS 3-day and PS 2nd interval samples even when their chemical amounts were higher than those of PS 7-day and 10-day samples, respectively.
- The amount of adsorbed chemicals in the PS 10-day sample did not represent an accumulation of the amounts of adsorbed chemicals in the PS interval samples, however, there was a correlation between the sum of adsorbed amount of each chemical in PS interval samples and their adsorbed amount in the PS 10-day sample.

- There was a wide variation in the occurrence and proportions of each chemical in the PS interval and PS 10-day samples.

On the basis of our results, it is concluded that the chemicals adsorbed onto SDB-RPS disks might be subject to desorption or decomposition during the 10-day deployment period. Accordingly, the application of SDB-RPS passive sampler disks with 10-day deployment to evaluate toxicity levels via bioassay has certain limitations and cannot be considered as a substitute for GS sampling using Sep-Pak® Plus PS-2 cartridges. In future studies, the applicability of shorter deployment periods that will not be affected by desorption and/or decomposition needs to be investigated.

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Table 5 Organic chemicals eluted from passive sampler (PS) interval and PS 10-day samples (with a maximum adsorbed amount $\geq 0.20 \mu\text{g}/3$ disks).

Name	Log K_{ow}	Category*	PS interval samples					PS 10-days	
			1st(**)	2nd	3rd	4th	5th	Sum	
Caffeine	-0.07	PPCPs	5.77	8.86	5.99	7.10	6.95	34.7	12.8
Diethyltoluamide	2.02		0.92	7.75	2.77	3.41	1.24	16.1	4.35
Aspirin	1.19		ND	ND	1.04	ND	ND	1.04	ND
L-Menthol	3.30		ND	0.06	0.07	0.87	0.04	1.04	0.12
Cholesterol	8.70	OC	3.73	14.33	4.42	4.16	6.96	33.6	5.56
Bis (2-ethylhexyl) phthalate	7.50		ND	4.37	2.20	2.47	1.82	10.9	3.92
Coprostanol	8.82		2.34	2.31	0.52	0.49	1.55	7.20	1.07
Cholestanol	8.82		ND	1.92	0.48	0.47	1.03	3.90	0.71
Di-n-butyl phthalate	4.50		0.12	0.85	0.69	0.65	0.38	2.69	1.90
beta-Sitosterol	9.65		ND	1.77	ND	ND	0.56	2.34	0.61
Elaidic acid methyl ester	7.45		1.08	1.31	0.27	0.26	ND	2.91	ND
Diethyl phthalate	2.47		0.16	0.57	0.32	0.50	0.36	1.89	1.19
Diisobutyl phthalate	4.11		0.30	0.57	0.57	0.69	0.25	2.37	1.11
Methyl palmitoleate	7.08		ND	0.96	0.16	0.17	ND	1.28	ND
Methyl palmitate	7.38		ND	0.90	0.47	0.48	ND	1.85	ND
3-&4-Methylphenol	4.74		ND	0.04	0.69	0.19	0.06	0.98	0.03
Methyl myristate	6.41		0.12	0.58	0.15	0.15	ND	0.99	ND
alpha-Terpineol	2.98		ND	0.03	0.03	0.49	0.08	0.63	0.21
3,5-Dimethylphenol	2.35		ND	0.12	0.05	0.47	0.13	0.78	0.11
Linoleic acid methyl ester	7.05		ND	0.38	0.16	0.13	ND	0.68	ND
Nonylphenol	5.76	P	ND	0.34	0.21	0.08	0.05	0.69	0.24
Stigmasterol	9.43		ND	0.34	ND	0.31	0.34	0.98	ND
Oleic acid methyl ester	7.45		0.26	0.32	0.07	0.06	ND	0.70	ND
Triclosan	4.76		ND	0.16	0.10	0.11	0.09	0.46	0.32
2-Ethyl-1-hexanol	2.73		1.60	0.14	0.10	0.20	0.06	2.09	0.10
Butyl benzyl phthalate	4.73		0.48	0.05	0.06	ND	0.01	0.60	ND
Pyrethrin 4	5.90		ND	ND	ND	ND	ND	ND	2.05
Pyrazoxyfen	5.37		ND	ND	ND	ND	ND	ND	1.20
Pyrethrin 2	4.30		ND	0.44	ND	0.74	ND	1.18	ND
Triadimenol 2	2.90		ND	ND	0.26	ND	ND	0.26	ND
Nicotine	1.17	NC	ND	0.04	ND	0.19	0.20	0.43	0.59
Acetamide, N(2-phenylethyl)-	1.19		ND	ND	0.29	ND	0.10	0.39	ND
N-Nitrosopiperidine	2.63		0.22	0.08	0.05	ND	ND	0.35	ND

Table 5 Continued

Name	Log K _{ow}	Category*	PS interval samples					PS 10-days	
			1st(**)	2nd	3rd	4th	5th	Sum	
n-C32H66	16.06		ND	0.06	0.50	0.03	ND	0.59	0.07
n-C26H54	13.11		0.06	0.03	0.39	0.11	0.02	0.60	0.15
n-C29H60	14.58		ND	0.04	0.37	0.04	ND	0.44	0.05
n-C30H62	11.94		ND	0.02	0.33	0.01	ND	0.35	0.02
n-C28H58	14.09		ND	0.03	0.33	0.04	ND	0.40	0.08
n-C27H56	13.60	HC	0.27	0.05	0.31	0.11	0.03	0.76	0.09
Squalane	14.63		ND	0.26	0.19	0.14	ND	0.59	ND
n-C24H50	12.13		0.19	0.23	0.06	0.06	0.02	0.54	0.03
2 (3H)-Benzothiazolone	2.35		ND	0.22	0.20	0.21	0.07	0.69	0.21
n-C33H68	16.50		ND	ND	0.22	ND	ND	0.22	ND

Category*: PPCPs: pharmaceutical and personal care products; OC: oxygen-containing compounds (ethers, ketones, phenols, phthalates, fatty acid ester and others); P: pesticides; NC: nitrogen-containing compounds; HC: Hydrocarbons

Log K_{ow}: Octanol-water partition coefficient

ND: Not detected

(**) 75% of the 1st passive sampler interval sample was spilt during preparation.

Compounds	Max. value of highest bar, $\mu\text{g}/3$ disks	Adsorbed chemical amounts					PS 10-day	Accumulative ratio ^(#) , %
		1 st	2 nd	3 rd	4 th	5 th		
Cholesterol	14.33							16.5
Caffeine	12.75							36.8
Diethyltoluamide	7.75							27.0
Bis(2-ethylhexyl)phthalate	4.37							36.1
Coprostanol	2.34							14.9
Pyrethrin 4	2.05							
Cholestanol	1.92							18.2
Di-n-butyl phthalate	1.90							70.6
beta-Sitosterol	1.77							26.1
2-Ethyl-1-hexanol	1.60							4.8
Elaidic acid methyl ester	1.31							0.0
Pyrazoxyfen	1.20							
Diethyl phthalate	1.19							63.0
Diisobutyl phthalate	1.11							46.8
Aspirin	1.04							0.0
Methyl palmitoleate	0.96							0.0
Methyl palmitate	0.90							0.0
L-Menthol	0.87							11.5
Pyrethrin 2	0.74							0.0
3-&4-Methylphenol	0.69							3.1
Nicotine	0.59							137.0
Methyl myristate	0.58							0.0

Fig. 7 Pattern of occurrence and proportions of each chemical in passive sampler (PS) interval and PS 10-day samples with amounts $> 0.50 \mu\text{g}/3$ disks (the highest bar represents the highest adsorbed amount; no bar indicates that compounds were not detected).

^(#)Accumulation of adsorbed chemicals in the passive sampler (PS) 10-day sample compared with the chemicals accumulated in the five 2-day PS interval samples.

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