Determining the suitability of a polar organic chemical integrated sampler (POCIS) for the detection of pesticide residue in the Ishikawa River and its tributary in Osaka, Japan

Yoshinori YABUKI,1,3,* Junko ONO,1 Takashi NAGAI,2 Keiya INAO2 and Shinji TANIMORI3

1 Research Institute of Environment, Agriculture and Fisheries, Osaka Prefecture, 442 Shakudo, Habikino, Osaka 583–0862, Japan
2 Institute of Agro-Environmental Sciences, NARO, 3–1–3 Kannondai, Tsukuba, Ibaragi 305–8604, Japan
3 Osaka Prefecture University, 1–1 Gakuen-cho, Naka-ku, Sakai, Osaka 599–8531, Japan

(Received September 20, 2017; Accepted November 1, 2017)

The monitoring of pesticide concentrations in Japanese rivers was conducted via a grab sampling method and a passive sampling method using the polar organic chemical integrated sampler (POCIS). The results showed that cumulative detections were 84 with grab sampling and 98 with the POCIS. All of the pesticides detected by grab sampling could be quantified with a POCIS except for one (although its traces were detected). In addition, 15 detections quantified by POCIS were undetected by grab sampling. The average concentrations of pesticides detected by both the POCIS and grab sampling during the investigation period were compared. A good correlation was observed between the two methods with a slope of 1.00 and a coefficient of correlation (r) of 0.897 (n=79). Although high temporal variability was observed in the pesticide concentrations by grab sampling, the average pesticide concentrations obtained by the two methods showed similar values during the investigation period. © Pesticide Science Society of Japan

Keywords: pesticides monitoring, passive sampling, comparison with grab sampling, POCIS, river water.

Electronic supplementary material: The online version of this article contains supplementary material (Supplemental Tables S1–S7), which is available at http://www.jstage.jst.go.jp/browse/jpestics/

Introduction

In order to increase food production, pesticides are indispensable. On the other hand, pesticides discharged from agricultural fields have been detected in the aquatic environment. In particular, herbicides used in paddy fields flow out from the fields directly into rivers through drainage channels. Under a worst-case scenario, more than 50% of applied pesticides can run off from paddy fields into open aquatic systems. In order to assess the environmental risks due to the presence of pesticides in aquatic systems and to implement measures necessary to reduce them, it is necessary to monitor the pesticides in aquatic environments. The conventional sampling method for aquatic pesticides has been grab sampling. Grab sampling is a method in which a single sample is collected at a particular time. These spot samplings provide only a snapshot of the pesticide residue in the water at the time of sampling, and they often are insufficient for detecting and quantifying trace levels of aquatic pesticides. In addition, pesticide discharge is temporal, depending on the actual pesticide use and other factors, such as precipitation. Therefore, frequent sampling is required to evaluate aquatic pesticide levels and their effect on aquatic organisms. However, increasing the sampling frequency is time consuming, laborious, and expensive.

Passive sampling methods have been developed to monitor environmental contaminants such as heavy metals, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons in aquatic environments. Various types of samplers with different characteristics, such as polar organic chemical integrative samplers (POCISs), semipermeable membrane devices (SPMDs), and Chemcatcher, have been developed for the sampling of aquatic pesticides. Due to its ability to detect polar organic compounds, the POCIS has been considered an appropriate sampler for monitoring aquatic pesticides. Passive sampling methods could be used to determine the time-weighted average (TWA) concentrations of environmental contaminants with a wide range of octanol–water partition coefficients (log Pow) between 0 and 3 over long periods, as well as to obtain trace contaminant concentrations at detectable levels. In order to estimate the concentration of contaminants in the river from the amount accumulated in the POCIS, a sampling rate (Rs) of each chemical is required. The Rs values of 48 pesticides and the temperature dependency were obtained in our previous
Materials and Methods

1. The sampler

A pharmaceutical POCIS obtained from Environmental Sampling Technologies (USA) was used for this study. The POCIS consisted of a solid sequestration phase (220 mg of Oasis hydrophilic–lipophilic balance [HLB] resin) enclosed between two hydrophilic microporous polyethersulfone (PES) membranes (porosity 0.1 µm). In the linear region of the POCIS uptake, the average concentration of pesticides in water (C_w; µg/L) can be described by the following equation:

$$C_w = \frac{M}{R_s \cdot t}$$

where $R_s$ is the sampling rate (L/day), $M$ (µg) is the amount of pesticides accumulated by the sampler, and $t$ is the exposure time (d). The $R_s$ values of pesticides obtained in the previous study were used in this study. We had previously performed the calibration experiment to obtain sampling rates at 18, 24, and 30°C. In this study, the $R_s$ values at 24°C were used because of their similarity to the water temperatures of the two rivers used for sampling (see Results and Discussion).

2. Field research

The Ishikawa River and its tributary, the Sabigawa River in southeastern Osaka, Japan, were selected for this study (Fig. 1). Their watershed is predominantly agricultural near the headwaters, becoming heavily urbanized in the lower reaches. The river basin area and the agricultural area of the Ishikawa River were approximately 222 km² and 10 km², respectively, while those of the Sabigawa River were approximately 17 km² and 2.2 km², respectively. The agricultural areas were mainly used as paddy fields. Sites 1 and 2 were in the Ishikawa River, while sites 3 and 4 were in the Sabigawa River. Site 1 was approximately 9 km downstream from the confluence of the Ishikawa and Sabigawa rivers; site 2 was approximately 11 km upstream from site 1; site 3 was approximately 0.3 km upstream from the confluence; and site 4 was near the riverhead.

The investigation was carried out in June 2012 and August 2012 at site 3 and in June 2013 at sites 1, 2, 3, and 4. At each site, a protective canister containing two POCIS devices was deployed for 14 days. Seven to eight water samples were collected by grab sampling at about 1- to 3-day intervals throughout the POCIS deployment period. In order to determine the fluctuations of pesticides, it would be desirable to collect samples every day or to perform continuous sampling using an automatic water sampler. In this study, even though grab sampling was performed at the sites as much as possible, it is possible that this method could not fully catch the pesticide peaks. At each site, 1 L of water samples was collected in pre-cleaned amber glass
bottles. Water temperature, pH, and flow velocity were measured directly in the rivers. The DOC concentration was determined using a TOC analyzer (TOC-L, Shimadzu, Japan) after filtration using 0.7 µm glass fiber filters (GF/F, Whatman, UK).

3. Analytical procedure for obtaining pesticides from a POCIS and water samples

The analytical procedure to obtain pesticide samples from a POCIS and the water samples from grab sampling was the same as in the previous study. Water samples for grab sampling were filtered through 0.7 µm glass fiber filters (GF/F, Whatman, UK). Four hundred milliliters of the filtrate was passed through an Oasis HLB Plus cartridge (225 mg/cartridge, Waters, USA) at a flow rate of 10 mL/min after the cartridge had been conditioned with 10 mL of methanol and 20 mL of pure water in succession. The cartridge was rinsed with 20 mL of pure water and then dried using nitrogen with a vacuum pump for 30 min to remove water from the cartridge. The components retained in the cartridge was performed using the Oasis HLB Plus cartridge (225 mg/cartridge, Waters, USA) at a flow rate of 10 mL/min after the cartridge had been conditioned with 10 mL of methanol and 20 mL of pure water in succession. The cartridge was rinsed with 20 mL of pure water and then dried using nitrogen with a vacuum pump for 30 min to remove water from the cartridge. The components retained in the cartridge were eluted with 15 mL of methanol at a flow rate of 1 mL/min. The eluted components were then evaporated to approximately 0.5 mL with a rotary evaporator (Buchi, Switzerland) and dried under a nitrogen stream. The residue was then dissolved in 2 mL of acetone for gas chromatography with tandem mass spectrometric detection (GC-MS/MS) analysis.

The exposed POCISs from the field were disassembled carefully and the membranes detached from the disk. The resin (Oasis HLB) in each POCIS was carefully transferred into an empty, solid-phase-extraction glass tube (6 mL) with polyethylene (PE) frits. Then the cartridge was dried using nitrogen and a vacuum pump to remove water from the resin. The elution of components retained in the cartridge was performed using the same method as for the water sample, after which the residue was dissolved in 2 mL of acetone for GC-MS/MS analysis. All of the samples were analyzed using a GC-MS/MS system (7890 and 7000, Agilent Technologies, USA) operated in multiple reaction monitoring (MRM) mode under the analytical conditions.

The pesticide mixture standard solution WQ-1, which includes 68 pesticides and analytical standards (purity >98%) of oxaziclomefone, pyriminobac-methyl (E), pyriminobac-methyl (Z) and butachlor, which are commonly found in rivers in Japan, was obtained from Wako Pure Chemical Industries (Japan). Fifty-seven pesticides that reached appropriate recovery (70 to 100%) and coefficients of variation (within 10%) by the above method were selected for monitoring in this study (Table S-1). The limit of quantification (LOQ) of pesticides in the water sample was 0.0025 to 0.05 µg/L (Table S-1). The LOQs of the POCIS were calculated using the following equation:

\[ \text{LOQ} = \text{IQL} \cdot V_r / V_f \]  

where IQL is the instrument quantification limit (µg/L), \( V_r \) is final volume of acetone (mL) and \( V_f \) is the volume of the water sample (mL). The LOQs of the POCIS were obtained from the product IQL and \( V_f \). The recoveries of pesticides were obtained by a recovery test of the analyzed pesticides, which was conducted with triplicate extractions from filtered, uncontaminated river water, which spiked at 0.5 µg/L.

Time series of pesticide concentrations detected via grab sampling were used to calculate TWA concentrations. TWA concentrations were calculated using the following equation:

\[ \text{TWA} = \sum_{i=1}^{n} (C_i \cdot T_i) / T \]  

where \( C_i \) is the average of concentrations (µg/L) during period \( i \), \( T_i \) is the day during period \( i \) and \( T \) is the day of the total investigation period of grab sampling. If the concentration of pesticides was below the LOQ, the values used were evaluated as zero µg/L. The TWA concentrations of the POCIS were calculated using Eq. (1).

Results and Discussion

1. Water quality of the Ishikawa and Sabigawa rivers

The averages of water temperature, pH, and dissolved organic carbon (DOC) at each site are shown in Table 1. Li et al. reported that the \( R_s \) values significantly increased with the flow velocity,22–24) one report suggested that there was less than a twofold increase in accumulated amounts between 0.026 and 0.37 m/s.25) Harman et al.26) concluded that flow correction might not be necessary in some studies where water flow rates varied over the range studied; therefore, we did not adjust the \( R_s \) values.

The average flow velocities at sites 1, 2, 3, and 4 were around 0.3, 0.5, 0.1, and 0.2 m/s, respectively. Although some reports suggested that the \( R_s \) values significantly increased with the flow velocity,22–24) one report suggested that there was less than a twofold increase in accumulated amounts between 0.026 and 0.37 m/s.25) Harman et al.26) concluded that flow correction might not be necessary in some studies where water flow rates varied over the range studied; therefore, we did not adjust the \( R_s \) values.

2. Detection of aquatic pesticides via POCIS and grab sampling methods

No pesticides were detected from the blank POCIS that was not deployed in the river. Table S-2 to S-7 show the detailed characteristics of pesticides detected by the POCIS and grab sampling methods.

Eighteen pesticides were detected by grab sampling, while

| Table 1. Averages of water temperature, pH, and DOC at each site |
|-----------------|-------------|-------------|-------------|-------------|-------------|
|                 | June 2012   | Aug. 2012   | June 2013   |
| Water Temp. (°C) | 23          | 27          | 25          | 24          | 25          | 17          |
| pH              | 8.2         | 8.1         | 8.1         | 8.2         | 8.1         | 8.1         |
| DOC (mg/L)      | 3.1         | 3.4         | 2.0         | 1.9         | 3.1         | 1.5         |
21 pesticides were detected by the POCIS at site 3 in June 2012 (Table 2 and S-2). All of the pesticides detected by grab sampling were also detected by the POCIS, which detected three additional pesticides (metalaxyl, iprodione, and methidathion) undetected by grab sampling. The TWA concentrations obtained by grab sampling were a maximum of 0.00084 \(\mu g/L\) for procymidine. At site 3 (Tables 2 and S-6), 19 and 21 pesticides were detected by grab sampling and the POCIS, respectively. All the pesticides detected by grab sampling were also detected by POCIS, which detected two additional pesticides (malathion and cafenstrole) undetected by grab sampling. The TWA concentrations obtained by grab sampling were a maximum of 3.3 \(\mu g/L\) for bromobutide and a minimum of 0.0012 \(\mu g/L\) for fenobucarb. The POCIS concentrations obtained by the POCIS were a maximum of 3.5 \(\mu g/L\) for bromobutide and a minimum of 0.0029 \(\mu g/L\) for cafenstrole. At site 4 in June 2013 (Tables 2 and S-7), two and four pesticides were detected. All of the pesticides detected by grab sampling were also detected by the POCIS except for methidathion (although its traces were detected); the POCIS also detected three pesticides (fenobucarb, bromobutide, and pyriminobac-methyl) that were undetected by grab sampling. The TWA concentrations obtained by grab sampling were a maximum of 0.047 \(\mu g/L\) for mefenacet and a minimum of 0.0013 \(\mu g/L\) for methidathion. The TWA concentrations obtained by the POCIS were a maximum of 0.013 \(\mu g/L\) for mefenacet and minimum of 0.00035 \(\mu g/L\) for fenobucarb. The better detectability of pesticides by the POCIS might be explained by the lower LOQs (Tables 2 and S-1). Furthermore, there might have been a pulsed discharge of the pesticides during the grab sampling period.

3. Comparison of the TWA concentrations of pesticides by POCIS and grab sampling methods

The relationship between the TWA concentrations of pesticides obtained by the POCIS and by grab sampling is shown in Fig. 2 for all of the sites in June and August 2012 and 2013. When the TWA concentrations obtained by grab sampling were greater than or equal to 0.01 \(\mu g/L\), a good correlation was observed between the two methods with a slope of 1.00 and a coefficient of correlation \((r)\) of 0.938 \((n=32)\), showing there was not much difference between the values in the two methods of detecting pesticides at this concentration range. On the other hand, when the TWA concentrations obtained by grab sampling were less than 0.01 \(\mu g/L\) (near the LOQ), the correlation was weak between the methods, with a slope of 2.28 and \(r\) of 0.369 \((n=47)\), as the TWA concentrations obtained by the POCIS were slightly higher than those obtained by grab sampling. The difference in the TWA concentrations between grab sampling and the POCIS in the low concentration range was likely due to the low reliability of grab sampling at that range, since it is not fully functional in capturing samples at the LOQ levels and responds poorly to extremely short spike peaks. The results indicated that the POCIS could calculate TWA concentrations of the pesticides at 0.01 \(\mu g/L\) or larger as accurately as grab sampling. The results also suggested that the POCIS could detect pesticides at concentrations below 0.01 \(\mu g/L\) more sensitively than grab sampling.

### Table 2. Number of pesticides detected by POCIS and grab sampling at each investigation

<table>
<thead>
<tr>
<th></th>
<th>June 2012</th>
<th>Aug. 2012</th>
<th>June 2013</th>
<th>Site 3</th>
<th>Site 3</th>
<th>Site 1</th>
<th>Site 2</th>
<th>Site 3</th>
<th>Site 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>POCIS</td>
<td>21</td>
<td>16</td>
<td>19</td>
<td>17</td>
<td>21</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grab</td>
<td>18</td>
<td>14</td>
<td>17</td>
<td>14</td>
<td>19</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Vol. 43, No. 1, 18–23 (2018) Determining the suitability of a POCIS for the detection of pesticide

21 pesticides were detected by the POCIS at site 3 in June 2012 (Table 2 and S-2). All of the pesticides detected by grab sampling were also detected by the POCIS, which detected three additional pesticides (metalaxyl, iprodione, and methidathion) undetected by grab sampling. The TWA concentrations obtained by grab sampling were a maximum of 0.00084 \(\mu g/L\) for procymidine. At site 3 (Tables 2 and S-6), 19 and 21 pesticides were detected by grab sampling and the POCIS, respectively. All the pesticides detected by grab sampling were also detected by POCIS, which detected two additional pesticides (malathion and cafenstrole) undetected by grab sampling. The TWA concentrations obtained by grab sampling were a maximum of 3.3 \(\mu g/L\) for bromobutide and a minimum of 0.0012 \(\mu g/L\) for fenobucarb. The POCIS concentrations obtained by the POCIS were a maximum of 3.5 \(\mu g/L\) for bromobutide and a minimum of 0.0029 \(\mu g/L\) for cafenstrole. At site 4 in June 2013 (Tables 2 and S-7), two and four pesticides were detected. All of the pesticides detected by grab sampling were also detected by the POCIS except for methidathion (although its traces were detected); the POCIS also detected three pesticides (fenobucarb, bromobutide, and pyriminobac-methyl) that were undetected by grab sampling. The TWA concentrations obtained by grab sampling were a maximum of 0.047 \(\mu g/L\) for mefenacet and a minimum of 0.0013 \(\mu g/L\) for methidathion. The TWA concentrations obtained by the POCIS were a maximum of 0.013 \(\mu g/L\) for mefenacet and minimum of 0.00035 \(\mu g/L\) for fenobucarb. The better detectability of pesticides by the POCIS might be explained by the lower LOQs (Tables 2 and S-1). Furthermore, there might have been a pulsed discharge of the pesticides during the grab sampling period.

3. Comparison of the TWA concentrations of pesticides by POCIS and grab sampling methods

The relationship between the TWA concentrations of pesticides obtained by the POCIS and by grab sampling is shown in Fig. 2 for all of the sites in June and August 2012 and 2013. When the TWA concentrations obtained by grab sampling were greater than or equal to 0.01 \(\mu g/L\), a good correlation was observed between the two methods with a slope of 1.00 and a coefficient of correlation \((r)\) of 0.938 \((n=32)\), showing there was not much difference between the values in the two methods of detecting pesticides at this concentration range. On the other hand, when the TWA concentrations obtained by grab sampling were less than 0.01 \(\mu g/L\) (near the LOQ), the correlation was weak between the methods, with a slope of 2.28 and \(r\) of 0.369 \((n=47)\), as the TWA concentrations obtained by the POCIS were slightly higher than those obtained by grab sampling. The difference in the TWA concentrations between grab sampling and the POCIS in the low concentration range was likely due to the low reliability of grab sampling at that range, since it is not fully functional in capturing samples at the LOQ levels and responds poorly to extremely short spike peaks. The results indicated that the POCIS could calculate TWA concentrations of the pesticides at 0.01 \(\mu g/L\) or larger as accurately as grab sampling. The results also suggested that the POCIS could detect pesticides at concentrations below 0.01 \(\mu g/L\) more sensitively than grab sampling.
4. Variation of TWA concentrations of the POCIS

The effect of the pattern of temporal fluctuation of the pesticide concentration obtained by grab sampling on the consistency of TWA concentrations between grab sampling and the POCIS was examined. Bromobutide, which increased in concentration in a consistent manner during the investigation period, was detected from site 3 in June 2012 (Fig. 3). The average concentrations of bromobutide obtained by the POCIS and grab sampling were similar, at 4.9 µg/L and 4.4 µg/L, respectively. Pretilachlor, which decreased in concentration, was detected from site 3 in June 2012 (Fig. 4). The average concentrations of pretilachlor obtained by POCIS and grab sampling were similar, at 0.11 µg/L and 0.10 µg/L, respectively. Fenobucarb was detected only once by grab sampling from site 3 in June 2013 (Fig. 5). The average concentrations of fenobucarb obtained by the POCIS and grab sampling were 0.001 µg/L and 0.006 µg/L, respectively, with the concentration obtained by the POCIS being six times higher than that obtained by grab sampling. The insecticide fenobucarb is used for vegetables and rice. In this region, fenobucarb is normally used on a random day throughout the cultivation period, while herbicides (for example, bromobutide and pretilachlor) are used during a limited period from May to June. Therefore, the concentration of fenobucarb in river water is likely to be found in pulses. For this reason, the temporal variability in the concentration of fenobucarb may not be appropriately determined by grab sampling. This could explain the higher TWA concentration of fenobucarb obtained by the POCIS.

These results suggest that a POCIS could be useful for the detection of pesticides in situations such as temporary runoff or the presence of trace-level concentrations during sampling. Moreover, pesticides detected by the POCIS in this study had a wide range of octanol-water partition coefficients (log $P_{ow}$) between 1.6 and 4.8. Therefore, it appears that a POCIS could be applicable for a wide range of pesticides. On the other hand,
a recent study\textsuperscript{27, 28} reported that the sampling rates of some of neonicotinoid insecticides (log $P_{ow}$ of $-0.66$ to $1.26$) could not be obtained due to the saturation of adsorption. Thus, the applicability of a POCIS to more highly soluble pesticides should be a subject for further study, such as inserting a different type of sorbent inserted into the POCIS.

Conclusions

The POCIS was able to measure all of the pesticide concentrations detected by grab sampling except for one (although its traces were detected). In addition, the POCIS detected a total of 15 pesticides undetected by grab sampling. A comparison of the average concentrations of pesticides detected by both the POCIS and grab sampling during the investigation period showed that there was approximately a 1:1 relationship between the two methods. These pesticides exhibited a pattern of wide fluctuations, such as the tendency to increase and decrease. Therefore, the POCIS was highly effective as a method to calculate on-site TW A concentrations, regardless of the fluctuation in pesticide concentrations expected in the environment.

Acknowledgements

This work was supported in part by JSPS KAKENHI Grant Number 26740015.

The authors are grateful to Mr. Satoshi Nakamura, Mr. Mitsuhashi Tamazawa, Dr. Nobuyuki Aiiko, Dr. Motonori Okumura and Ms. Arisa Banno of the Research Institute of Environment, Agriculture and Fisheries, Osaka Prefecture, for providing valuable advice concerning this study. The authors would also like to thank Ms. K. Goto, Mr. M. Obata and Mr. H. Nakanishi of the Research Institute of Environment, Agriculture and Fisheries, Osaka Prefecture, for help with sample collection and technical assistance.

References