Validation of the Application of a Polar Organic Chemical Integrative Sampler (POCIS) in Non-steady-state Conditions in Aquatic Environments

Kazushi Noro, Yoshinori Yabuki, Arisa Banno, Yusuke Tawa, Satoshi Nakamura

Department of Environmental Research, Research Institute of Environment, Agriculture and Fisheries, Osaka Prefecture, Habikino, Japan

ABSTRACT
This study validated the chemicals monitoring ability of a polar organic chemical integrative sampler (POCIS) under non-steady-state conditions resulting from natural disasters and environmental accidents in aquatic environments via laboratory experiments. The goal of this work was to contribute toward monitoring the actual state of chemical contamination resulting from emergencies and natural disasters. A chamber replicating the chemical contamination of an aquatic environment established by a chemical exposure assessment model was set up in a clean booth. The concentrations of seven neonicotinoid pesticides were increased to a maximum of 1,000, 100, or 10 µg/L for one day and decreased by 50% per day thereafter. A POCIS was set up with polyethersulfone as the permeation membrane and a resin (Oasis hydrophilic-lipophilic balance) as the receiving phase. Calibration tests of the POCIS were also conducted. The results of this study led to the addition of six neonicotinoid pesticides to the list of POCIS-measurable targets. The results of the chamber experiments showed that a POCIS is a good tool for chemicals monitoring under non-steady-state conditions in an aquatic environment.

Keywords: polar organic chemical integrative sampler, neonicotinoid pesticides, passive sampler

INTRODUCTION

The world has faced many disasters and catastrophes. After many environmental disasters, society has realized the urgent need for countermeasures against such events. Previous studies [1] have focused on the development of resilient infrastructure to minimize the risks posed by disasters and accidents. However, Japan lacks the preparation required to tackle chemicals contamination risks resulting from disasters and accidents [2–4]. These concerns arose in Japan after the Great East Japan Earthquake, which occurred on March 11th, 2011. The aftermath of the earthquake raised various health risks resulting from fires and spills of harmful substances. Thus, studies involving observations, predictions, risk assessments, and risk management of chemical leaks resulting from natural disasters and environmental accidents are needed.

Safety engineering research aims to prevent such accidents in factories and to ensure the physicochemical safety of workers. Once chemicals are widely diffused in the environment, they pose environmental risks and must be addressed as such. However, chemical risk management research from the view point of environmental science has focused on the development of monitoring methods under steady-state environmental conditions such as those experienced in a normal environment. Continuous analyzers for each target pollutant require electricity to power the instruments, and thus, they cannot be used in emergencies. In addition, no reports exist on the validation of monitoring devices in aquatic environments under non-steady-state conditions for chemical leaks derived from large-scale accidents and natural hazards. Therefore, the development of monitoring equipment under...
non-steady-state conditions, resulting from chemical leaks due to disasters and accidents, is required. Such equipment is required for all types of environments (water, air, and soil) and targets (organics, inorganics, heavy metals, gases, and particulate matter).

This study explores monitoring of an aquatic environment via a polar organic chemical integrated sampler (POCIS), which is a passive sampler. The performance assessment of the POCIS was conducted in this study. The POCIS has a strong affinity for moderately hydrophilic organic matter (0 ≤ log \( P_{ow} \) ≤ 5) [5] such as pesticides [6–10], pharmaceuticals [11], perfluorinated compounds [12], munition [13], and drugs [14]. The POCIS can measure the time-weighted average (TWA) of chemicals in aquatic environments and thus is considered to be a useful tool during disaster-related monitoring, when frequent grab sampling is difficult. However, no previous reports exist on the performance evaluation of the POCIS under non-steady-state conditions resulting from natural disasters and environmental accidents. Therefore, our study explores whether the extreme fluctuations in concentrations typical during disasters and accidents can be captured by the POCIS.

In this study, the peak time and half-life of a leaked chemical concentrations assuming an emergency was estimated by a simulation model. Then, batch experiments were conducted to calibrate the POCIS for seven neonicotinoid pesticides. Moreover, investigations were performed to evaluate the monitoring ability of the POCIS for non-steady state conditions via laboratory chamber experiments that replicated the states of natural disasters and environmental accidents. Therefore, our study explores whether the extreme fluctuations in concentrations typical during disasters and accidents can be captured by the POCIS.

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MATERIALS AND METHODS

Estimation of chemical concentrations in an aquatic environment

The National Institute of Advanced Industrial Science and Technology’s (AIST) Standardized Hydrology-based Assessment tool for chemical Exposure Load (AIST-SHANEL) [15] was used to estimate the peak time and half-life of leaked chemical concentrations in a standard urban river affected by natural disasters and environmental accidents. Linear alkylbenzene sulfonate (LAS) was selected as the model compound, because enough scientific knowledge exists to simulate LAS concentrations resulting from chemical leaks [15]. Dissolved LAS concentrations due to an LAS leak from a hypothetical plant in a model river were simulated using AIST-SHANEL. The distance between the plant at the upper reach and the calculation point at the outlet of the river was approximately 15 km. This model provides chemical exposure concentrations in a water system using a spatial grid resolution of 1 × 1 km and a time resolution of one day by inputting easily acquired information such as Pollutant Release and Transfer Register (PRTR) release data, river basin information, and data on the basic physical properties of the chemical substance.

Chemicals

Sets of Oasis hydrophilic-lipophilic balance (HLB) sorbent and polyethersulfone (PES) microporous (0.1 μm pore size) membranes purchased from Environmental Sampling Technologies (St. Joseph, USA) were used for the study. The certified neonicotinoid standards acetamiprid, clothianidin, dinofeturan, imidacloprid, nitenpyram, thiamethoxam, and thiacloprid were purchased from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan). An acetonitrile solution containing internal standards (ISSs) of seven neonicotinoids, namely, acetamiprid-d₄, clothianidin-d₅, dinofeturan-d₅, imidacloprid-d₁₄, nitenpyram-d₅, thiamethoxam-d₃, and thiacloprid-d₄, each of 10 μg/mL concentration, were purchased from Hayashi Pure Chemical Ind., Ltd. (Osaka, Japan). Pesticide analysis grade acetone and methanol were purchased from FUJIFILM Wako Pure Chemical Corporation for the extraction and clean-up processes of the analysis.

Concentration factor and sampling rate

A sampling rate (Rₛ) should be established to estimate the aquatic environment concentrations of contaminants from the amounts collected by the POCIS. To determine \( Rₛ \), calibration experiments were conducted (see Batch sorption experiment). The POCIS consists of a receiving phase (220 mg of Oasis HLB) sandwiched by a PES membrane. In the linear phase of the POCIS uptake, the average concentration of a contaminant in water is calculated as follows:

\[ C_w = \frac{M}{R_s \times t} \]  

(1)

where

- \( C_w \): average concentration of the contaminant in the water (μg/L)
- \( M \): amount of contaminant collected by the POCIS (μg)
- \( R_s \): sampling rate (L/d)
- \( t \): sampling period (d)

Due to the membrane, only dissolved contaminants are collected by the receiving phase. Subsequently, Equation (1) is rearranged as Equation (2) to incorporate the concentration factor (CFₚ) (L).
\[ CF_i = \frac{M}{C_w} = R_i \times t \]

Thus, we can plot \( t \) versus \( \frac{M}{C_w} \) to obtain \( R_i \) within the linear phase.

**Batch sorption experiment**

To estimate the \( R_i \) of the POCIS, batch sorption experiments were conducted following the method reported by Yabuki et al. [8]. The experiments were carried out in glass beakers, each containing 1 L of the sample solution, which was stirred at 400 or 1500 rpm (HS-6DN; AS ONE Corporation, Osaka, Japan) in a constant-temperature box (MIR-554-PJ; PHC Holdings Corporation, Tokyo, Japan) at 20°C under dark conditions. The sample solution was prepared using tap water to which 200 ng/L each of the seven neonicotinoid pesticides, namely, acetamiprid, clothianidin, dinotefuran, imidacloprid, nitenpyram, thiamethoxam, and thiacloprid, were added. POCISs using HLB as the sorbent were placed in the glass beakers. The beakers were covered with aluminum foil for 1, 3, 7, 14, 21, or 28 d, and all measurements were conducted in triplicate. The sample water was replaced every day with fresh tap water to avoid the effects of pesticide self-degradation affecting the measurements.

**POCIS analysis**

The loaded POCISs from the laboratory experiments were disassembled carefully, and the membranes were detached from the disks. The receiving phase (HLB sorbent) in each POCIS was transferred into solid phase extraction tubes (6 mL) with polyethylene frits. The receiving phases in the tubes were dried with a vacuum pump to remove residual water. Then, the pesticides adsorbed on the receiving phase were eluted with 10 mL of methanol, followed by 5 mL of acetone at 1 mL/min. Subsequently, 50 µL of the IS solutions was added to these solutions. The resulting solutions were concentrated to 1 mL by blow drying with N\(_2\) gas. Then, 1.5 mL of methanol was added and the solutions were concentrated once again to 1 mL. Finally, these solutions were kept in glass vials at −20°C until liquid chromatography with mass spectrometry (LC-MS/MS) analysis.

**LC-MS/MS analysis**

LC was carried out on a Nexcera HPLC system (Shimadzu Corporation, Kyoto, Japan). Analyte separation was conducted on a Kinetex® Biphenyl column (2.6 µm, 100 × 2.1 mm\(^2\)) (Shimadzu GLC, Tokyo, Japan). Solvent A (2 mmol/L ammonium formate and 0.002% formic acid in ultrapure water) and solvent B (2 mmol/L ammonium formate and 0.002% formic acid in methanol) were used as the mobile phase. A binary gradient mode was used, with the A:B ratio varying as follows: 0 min, 97:3; 1 min, 90:10; 3 min, 45:55; 10.5, 0:100; 12 min, 0:100; 12.01 min, 97:3; 15 min, 97:3. Tandem mass spectrometry (MS/MS) was conducted on an LC-MS 8050 triple-quadrupole mass spectrometer equipped with an electrospray ionization mass spectrometer (ESI) source (Shimadzu Corporation). ESI was performed in the positive ion electrospray mode. The identification of analytes was carried out in the multiple-reaction monitoring (MRM) mode. MRM transitions of each analyte and the ISs are shown in Table 1 along with the retention time, precuror, quantitative product, and conformation product ions and their collision energies (CEs). These conditions were tuned by injecting each analyte and a mixture of the surrogate standards. Next, 2 µL aliquots of the standard solutions containing the neonicotinoid compounds at a concentration of 200 µg/mL each were injected into the MS/MS equipment. The precursor ion for each analyte was obtained by recording the mass spectra in the \( m/z \) range of 50 to 500 in the full scan mode (ESI+), and the most sensitive quantitative product and conformation product ions were procured based on each precursor ion obtained via the Q3 scan mode. The CE for each quantitative product and conformation product ions were optimized in the range of 30–60 V. To minimize potential carryover, the needle of the injector was rinsed with methanol, and subsequent rinsing was carried out after each injection with a solution of ultrapure water/formic acid/acetate (100:0.1:0.1 v/v).

**Flow velocity determination**

Flow velocity should have a significant effect for \( R_i \) of the POCIS. Because an increasing in flow will reduce the thickness of the water boundary layer, thereby reducing resistance to diffusion. Thus, measurement of the flow velocity of the batch experiment and the chamber experiment is needed to conduct these experiments with high accuracy.

According to the method reported by Booij et al. [16], flow velocities were calculated from the measured mass transfer coefficients of the water boundary layer near the surface of the POCIS devices with alabaster plates. This is because the flow velocity measured by commercial equipment or calculated by volumetric pump output does not represent the exact value of the flow velocity near the POCIS surface. The alabaster plates were fitted within a protective ring. It was clamped in a passive sampler holder. Silicone flexible spacers were put around the plate assembly to fill up empty space. The alabaster plates and the silicone flexible spacers
were purchased from Passive Sampling of Organic Compounds (Kimswerd, Netherlands). Pre-weighed alabaster plates sandwiched by stainless steel plates which is used for the POCISs were set in 1 L of tap water, which was stirred at 400 and 1500 rpm in glass beakers. Alabaster mass losses were determined after drying the plates at 60°C for 30 min, followed by cooling in ambient air. This method was applied for both the batch experiment (see Batch sorption experiment) and the chamber experiment (see Chamber experiment).

**Chamber experiment**

The LAS was selected as the model compound for the simulation (see Estimation of chemical concentrations in an aquatic environment), but it was not a suitable compound for the first step of the POCIS application validation, because the POCIS has not been developed for the LAS yet. Thus, in the chamber experiment, seven neonicotinoid pesticides (acetamiprid, clothianidin, dinotefuran, imidacloprid, nitenpyram, thiamethoxam, and thiacloprid) which is hydrophilic chemicals to be measured by the POCIS with relative ease were selected as the model chemical for the experiment in non-steady-state conditions to validate the ability of the POCIS.

Experiments were carried out in a stainless steel tank (555 × 395 × 150 mm) containing 27 L of tap water, as shown in Fig. 1 (a) and (b). A thermostat (TR-71wf; T & D Corporation; Matsumoto, Japan). A peristaltic pump (MP-3001; TOKYO RIKAKIKAI Co., Ltd., Tokyo, Japan) was used to control the chemical concentration of the solution in the tank. To ensure the existence of a peak at the end of the first day of the experiment, a solution containing seven neonicotinoid pesticides at 13.5, 1.35, or 0.135 mg/L in 2 L of tap water was injected at 1.4 mL/min on the first day. Therefore, the peak concentration should be 1,000, 100, and 10 µg/L at the end of the first day in the tank containing 27 L of tap water. Subsequently, the water was loaded in the tank by the pump at 18.8 mL/min. Concurrently, tap water was introduced by a water level controller (WLC-SA; AS ONE Corporation) to maintain a constant water volume in the tank. Thus, the concentrations of the seven neonicotinoid pesticides in the tank were decreased by 50% per day thereafter. The POCIS was placed on a stainless steel rack in the tank. The POCIS sampling periods were 0–1, 1–2, 1–3, 2–3, 3–14, and 0–14 d. The water samples were also checked several times to determine the concentrations of the seven neonicotinoid pesticides. All the equipment was set up in a clean booth (MT-01; AS ONE Corporation) to avoid contamination.

### RESULTS AND DISCUSSION

**Estimation of chemical concentrations in an aquatic environment and replication of the conditions in the chamber**

The concentration of the dissolved LAS in the aquatic

<table>
<thead>
<tr>
<th>analyte</th>
<th>retention time (min)</th>
<th>precursor ion</th>
<th>product ion 1</th>
<th>collision energy (eV)</th>
<th>product ion 2</th>
<th>collision energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetamiprid</td>
<td>4.8</td>
<td>223</td>
<td>126</td>
<td>–21</td>
<td>90</td>
<td>–35</td>
</tr>
<tr>
<td>acetamiprid-\textsuperscript{d\textsubscript{3}}</td>
<td>4.7</td>
<td>226</td>
<td>126</td>
<td>–22</td>
<td>90</td>
<td>–35</td>
</tr>
<tr>
<td>clothianidin</td>
<td>3.9</td>
<td>250</td>
<td>169</td>
<td>–13</td>
<td>132</td>
<td>–13</td>
</tr>
<tr>
<td>clothianidin-\textsuperscript{d\textsubscript{3}}</td>
<td>3.9</td>
<td>253</td>
<td>172</td>
<td>–13</td>
<td>132</td>
<td>–13</td>
</tr>
<tr>
<td>dinotefuran</td>
<td>3.2</td>
<td>203</td>
<td>113</td>
<td>–14</td>
<td>129</td>
<td>–11</td>
</tr>
<tr>
<td>dinotefuran-\textsuperscript{d\textsubscript{3}}</td>
<td>3.2</td>
<td>206</td>
<td>116</td>
<td>–14</td>
<td>132</td>
<td>–11</td>
</tr>
<tr>
<td>imidacloprid</td>
<td>4.5</td>
<td>256</td>
<td>209</td>
<td>–17</td>
<td>175</td>
<td>–21</td>
</tr>
<tr>
<td>imidacloprid-\textsuperscript{d\textsubscript{4}}</td>
<td>4.4</td>
<td>260</td>
<td>213</td>
<td>–17</td>
<td>179</td>
<td>–21</td>
</tr>
<tr>
<td>nitenpyram</td>
<td>3.8</td>
<td>271</td>
<td>189</td>
<td>–11</td>
<td>255</td>
<td>–14</td>
</tr>
<tr>
<td>nitenpyram-\textsuperscript{d\textsubscript{3}}</td>
<td>3.8</td>
<td>274</td>
<td>192</td>
<td>–11</td>
<td>258</td>
<td>–14</td>
</tr>
<tr>
<td>thiamethoxam</td>
<td>4</td>
<td>292</td>
<td>211</td>
<td>–11</td>
<td>132</td>
<td>–21</td>
</tr>
<tr>
<td>thiamethoxam-\textsuperscript{d\textsubscript{3}}</td>
<td>4</td>
<td>295</td>
<td>214</td>
<td>–11</td>
<td>132</td>
<td>–21</td>
</tr>
<tr>
<td>thiacloprid</td>
<td>5.3</td>
<td>253</td>
<td>126</td>
<td>–21</td>
<td>90</td>
<td>–41</td>
</tr>
<tr>
<td>thiacloprid-\textsuperscript{d\textsubscript{4}}</td>
<td>5.3</td>
<td>257</td>
<td>126</td>
<td>–21</td>
<td>90</td>
<td>–41</td>
</tr>
</tbody>
</table>
environment was found to be at its maximum on the first day of the accident. Moreover, the reduction rate of the LAS was approximately 50% per day, in other words, the half-life of the dissolved LAS was approximately one day. As expected, chemicals with high water solubility are more prevalent in an aquatic environment compared to hydrophobic chemicals.

In this study, seven neonicotinoid pesticides (acetamiprid, clothianidin, dinotefuran, imidacloprid, nitenpyram, thiamethoxam, and thiacloprid) were chosen as model chemicals to replicate LAS. Typically, when a large volume of a chemical is leaked in a river as a result of a natural disaster or accidents, its concentration reduces naturally as a result

Fig. 1 (a) Schematic experimental setup used for the reproducing non-steady-state conditions. (b) Figure of the experimental setup used in this study.
of the dilution effect of the water body. Thus, the result derived from AIST-SHANEL for LAS can be applied for other chemicals. Based on this result, we considered that the half-life of the chemicals is one day for the chamber experiment conditions. We considered the peak concentration following to a previous report [17]. In this report, triple-digit concentration as the peak concentration was shown with a condition which assuming a chemical leak accident from a chemical solution tank in a hypothetical plant. In this condition, it was assumed that 34.4 m$^3$ of chemical solution was leaked from the tank and pipe in one day. Another condition in the report, the maximum concentration was double-digit decreasing compared to the first condition. In the second condition, 0.05 m$^3$ of the chemical solution was leaked from the tank with emergency shut-off valve. Thus, we adopted 1,000, 100, or 10 µg/L as the maximum concentrations to evaluate the performance of the POCIS under a wide concentration range assuming several condition.

**Batch sorption experiment and calculation of $R_s$**

The results of the batch sorption experiment are shown in Fig. 2 (a–d) and Table 2. Fig. 2 (a) and (c) show the amounts of seven neonicotinoid pesticides collected by the POCIS for 1 to 28 d under 400 and 1500 rpm, respectively.
Nitenpyram was not captured by the POCIS in both cases. Moreover, the collected amounts of dinotefuran were relatively lower than those of the others pesticides (except nitenpyram). This difference in the collected amounts can be attributed to log $P_{ow}$, which is a reference index of hydrophobic/hydrophilic character. Among the seven neonicotinoid pesticides, dinotefuran and nitenpyram are relatively hydrophilic, implying that the POCIS may be unable to collect hydrophilic chemicals ($log P_{ow} < 0$) when using HLB sorbent as the receiving phase. Clothianidin, which is also characterized as a hydrophilic chemical ($log P_{ow} = -0.55$) was, however, collected by the POCIS. The same was true of thiamethoxam, imidacloprid, acetamiprid, and thiacloprid, which are relatively hydrophobic chemicals. Furthermore, it has been demonstrated that no or a poor relationship exists between log $P_{ow}$ and $R_s$ for pesticides and selected endocrine disruptors when using Chemcatcher and POCIS, respectively [8,18–20].

$CF_t$ was calculated to estimate $R_s$ for each neonicotinoid pesticide, as shown in Fig. 2 (b) and (d), and Table 2. $CF_t$ was calculated only in the linear range to evaluate the POCIS in the kinetic phase, that is, until the half saturation of the POCIS [21]. The values of $R_s$ at 1500 rpm were higher than those at 400 rpm. This tendency is consistent with the findings of several previous studies [5,11,12,22–26]. In general, the mass transfer of chemicals from water to sorbent under low flow conditions is governed by the water boundary layer. Conversely, the water turbulence prevalent under high flow conditions decreases the thickness of the water boundary layer. However, at some point, which is reported to be approximately 6 cm/s [25], an increase in turbulence no longer affects the sampling rate [23]. The flow velocities in the 1 L glass beaker under 400 rpm and 1500 rpm were calculated to be 1.0 cm/s and 18 cm/s, respectively (Table 2). These values correspond to those in previous reports [25]. The value of 1.0 cm/s at 400 rpm is said to denote a calm state. Thus, the ranges of $R_s$ shown in Table 2 refer to the maximum and minimum values of the six collected neonicotinoid pesticides for an aquatic environment under any flow velocity condition. The $R_s$ values of the six neonicotinoid pesticides are consistent with those of other pesticides when using HLB sorbent as the receiving phase [8]. Thus, these values are considered to be reasonable and appropriate for this study. As a consequence, the TWA of the neonicotinoid pesticides can be monitored by the POCIS in an aquatic environment. In addition, the linear range under 1500 rpm is typically shorter than the corresponding value under 400 rpm. This phenomenon is also attributed to the difference in the water boundary layer thickness. A thick water boundary layer plays the role of a filter. Thus, the chemical diffusion from the solution to the sorbent is repressed by the presence of a thick water boundary layer.

### Table 2 Log $P_{ow}$ of neonicotinoid pesticides, rotation speed, linear range of $CF_t$, $R_s$, and flow velocity under the triplicate batch experiments.

<table>
<thead>
<tr>
<th></th>
<th>Dinotefuran</th>
<th>Clothianidin</th>
<th>Nitenpyram</th>
<th>Thiamethoxam</th>
<th>Imidacloprid</th>
<th>Acetamiprid</th>
<th>Thiacloprid</th>
</tr>
</thead>
<tbody>
<tr>
<td>$log P_{ow}$</td>
<td>−0.66</td>
<td>−0.55</td>
<td>−0.13</td>
<td>0.57</td>
<td>0.70</td>
<td>0.80</td>
<td>1.26</td>
</tr>
<tr>
<td>Rotation speed (rpm)</td>
<td>400</td>
<td>400</td>
<td>400</td>
<td>400</td>
<td>400</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>Linear range (d)</td>
<td>3</td>
<td>7</td>
<td>n.d.</td>
<td>7</td>
<td>28</td>
<td>28</td>
<td>28</td>
</tr>
<tr>
<td>$R_s$ (L/d)</td>
<td>0.105</td>
<td>0.115</td>
<td>n.d.</td>
<td>0.124</td>
<td>0.089</td>
<td>0.078</td>
<td>0.077</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.040</td>
<td>0.028</td>
<td>n.d.</td>
<td>0.019</td>
<td>0.004</td>
<td>0.003</td>
<td>0.005</td>
</tr>
<tr>
<td>Confidence limit*</td>
<td>0.127</td>
<td>0.078</td>
<td>n.d.</td>
<td>0.048</td>
<td>0.009</td>
<td>0.008</td>
<td>0.013</td>
</tr>
<tr>
<td>Flow velocity (cm/s)</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Rotation speed (rpm)</td>
<td>1500</td>
<td>1500</td>
<td>1500</td>
<td>1500</td>
<td>1500</td>
<td>1500</td>
<td>1500</td>
</tr>
<tr>
<td>Linear range (d)</td>
<td>3</td>
<td>14</td>
<td>n.d.</td>
<td>14</td>
<td>14</td>
<td>14</td>
<td>14</td>
</tr>
<tr>
<td>$R_s$ (L/d)</td>
<td>0.106</td>
<td>0.242</td>
<td>n.d.</td>
<td>0.202</td>
<td>0.257</td>
<td>0.239</td>
<td>0.214</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.051</td>
<td>0.044</td>
<td>n.d.</td>
<td>0.007</td>
<td>0.041</td>
<td>0.039</td>
<td>0.024</td>
</tr>
<tr>
<td>Confidence limit*</td>
<td>0.094</td>
<td>0.050</td>
<td>n.d.</td>
<td>0.008</td>
<td>0.047</td>
<td>0.045</td>
<td>0.029</td>
</tr>
<tr>
<td>Flow velocity (cm/s)</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
</tr>
</tbody>
</table>

n.d.: not determined, *P = 0.05.
Incidentally, due to the short linear range of dinotefuran, the 95% confidence limit for this chemical is relatively greater than the corresponding values of the other chemicals. The data required to calculate $R$ and its error for dinotefuran comprise only three points: 0, 1, and 3 d.

To summarize the results, the values of $R$, with the confidence limits of the POCIS for dinotefuran, clothianidin, thiamethoxam, imidacloprid, acetamiprid, and thiacloprid were obtained from the batch test. It is clear that the POCIS would be an appropriate device for sampling such chemicals under steady-state conditions. Additionally, the measurement periods for these pesticides using the POCIS were also obtained.

**Evaluation of the POCIS in non-steady-state conditions**

The evaluation results of the POCIS in the chamber reproducing non-steady-state conditions at the maximum values for 1,000, 100, and 10 µg/L are shown in Figs. 3, 4, and 5, respectively. The values are also shown in Tables S1–6.
The periods of the TWA values of the aqueous solution are obverse for the sampling period of the POCIS. Thus, the TWA values are ideal values, which can be compared to the POCIS values in the same sampling period. The $R_s$ estimated by batch experiments at 1500 rpm was used to calculate the POCIS value for the chamber experiment, because the flow velocity conditions of the chamber experiment were close to those of the batch experiment at 1500 rpm. As the linear range of $R_s$ for dinotefuran was less than 7 d, the POCIS values of dinotefuran for the sampling periods of 3–14 and 0–14 d are advisory. Thus, these values should be used with caution.

At the maximum value of 1,000 µg/L (Fig. 3), the POCIS captured all the changes in the neonicotinoid pesticide concentrations. However, all the average concentrations determined by the POCIS were lower than the TWA values at 1500 rpm. As the linear range of $R_s$ for dinotefuran was less than 7 d, the POCIS values of dinotefuran for the sampling periods of 3–14 and 0–14 d are advisory. Thus, these values should be used with caution.

Fig. 4 Comparison of POCIS-measured values to TWAs from aqueous solution concentrations under the 100 µg/L maximum concentration condition for (a) dinotefuran, (b) clothianidin, (c) thiamethoxam, (d) imidacloprid, (e) acetamiprid, and (f) thiacloprid (all measurements in triplicate). Horizontal error bars for the red squares, and vertical error bars for the red squares represent periods for the TWAs, sampling periods of the POCIS, and plus and minus one standard deviations, respectively.
the maximum value of 1,000 µg/L. It appears that saturation of the HLB sorbent (the receiving phase) caused the underestimation. To summarize, the upper limit of the POCIS for the six neonicotinoid pesticides is less than 1,000 µg/L. To utilize the POCIS in non-steady-state conditions in the aftermath of disasters and accidents, some measures must be taken to avoid the saturation of the HLB sorbent.

When the maximum values were 100 and 10 µg/L (Figs. 4 and 5), the POCIS captured the concentration changes of the neonicotinoid pesticides more clearly than under the maximum value of 1,000 µg/L. Therefore, the POCIS is a suitable tool for capturing concentration spikes when the

Fig. 5 Comparison of POCIS-measured values to TWA values from aqueous solution concentrations under the 10 µg/L maximum concentration condition for (a) dinotefuran, (b) clothianidin, (c) thiamethoxam, (d) imidacloprid, (e) acetamiprid, and (f) thiacloprid (all measurements in triplicate). Horizontal error bars for the red squares, and vertical error bars for the red squares represent periods for the TWAs, sampling periods of the POCIS, and plus and minus one standard deviations, respectively.
maximum concentrations are less than 100 µg/L. Almost all the POCIS-measured values of the 95% confidence interval for 0–1 and 1–2 d included the TWA value as the ideal POCIS value. These encouraging results showed that under non-steady-state conditions, the POCIS can be used for collecting samples for concentrations lower than 100 µg/L for as less as one day. On the other hand, the POCIS values for longer sampling periods, such as 3–14 and 0–14 d, were relatively lower than the TWA value. Moreover, the results for dinotefuran indicated significant error resulting from the statistical confidence limit established as a result of the batch experiment (Table 2) rather than experimental error. As only three available values (for days 0, 1, and 3) were used for the calculation of $R_s$ for dinotefuran, its confidence limit is relatively high. Thus, the average value of dinotefuran is close to the TWA value as well as the other values.

To discuss the accuracy of the POCIS, POCIS/TWA values of the aqueous solution for seven neonicotinoid pesticides (Table 2) were calculated (Fig. 6). As referred to above, the POCIS values of dinotefuran for the sampling periods of 3–14 and 0–14 d are advisory. Firstly, the POCIS/TWA values under the maximum concentration condition of 1,000 µg/L, especially for 0–1 and 1–2 d which are in peak time, were obviously lower than the other two low concentration condition values. This is because of the saturation of HLB, as mentioned above. Secondly, the POCIS/TWA value under the maximum concentration conditions of 100 and 10 µg/L, for long sampling periods of 3–14 and 0–14 d, were relatively lower than those for short sampling periods of 0–1, 1–2, 2–3, and 1–3 d. In addition, the POCIS/TWA values in concentration decreasing period from the first day to the end of the chamber experiments (Figs. 3–5) are relatively lower than those in concentration increasing period from the start to the end of the first day of the experiments.

Presumably, the tendency stated above which is: lower POCIS/TWA value for higher concentration conditions and longer sampling periods imply that the apparent uptake rate decreases because the diffusive path length from the surface of the filter increases and the concentration gradient becomes gentler in the curve phase. These aspects were apparent from the results of the batch experiment from the 14th day to the 28th day (Fig. 2) [27]. The curve phase was observed in the linear range due to the difference in the concentrations between the batch and chamber experiments. Put simply, the higher concentrations of the seven neonicotinoid pesticides in the chamber experiments would fill up absorbed site on the HLB sorbent more quickly compared to the batch experiments. Additionally, if the response of the POCIS value was slow, a lag time required to establish steady state condition across water boundary layer, PES filter, and HLB could be reasons for the lower POCIS/TWA value [28]. However, the lag time and slow response was not observed in the batch (Fig. 2) and chamber experiments (Figs. 3–6). Thus, the effect of the lag time is negligible.

The underestimation for concentration decreasing periods compared to concentration increasing periods could be explained by a mechanistic model described by Endo et al. [27]. According to the model, the direction of chemical diffusion in the concentration increasing period is constant from the aquatic boundary layer to HLB via PES. Conversely, the direction of chemical diffusion in the concentration decreasing period is not constant, because the highest concentration point is in the filter or in the water boundary layer when the concentration is decreasing. In short, chemicals can move to both, the HLB and aqueous solution, from the filter or from the water boundary layer by diffusion. Therefore, this reverse transfer could be a reason for underestimating the concentration decreasing periods.

If the batch experiments were conducted over a wider concentration range, the underestimation of the POCIS measurements for long sampling periods would not be observed. This solution, however, is not realistic, because the experiments would be too costly to implement. Thus, we should explore possibility of underestimation when we conduct POCIS measurements for long sampling periods. In other words, POCIS measurements for long sampling periods can possibly miss a concentration spike. Therefore, further studies are required to solve the issue of underestimation, albeit at low cost. There are two ways to solve this problem. First, the estimation of $R_s$ should become possible at a low cost, and second, a new adsorbent with a longer linear range should be identified.

Indeed, the apparent uptake rate is a result of the absorption and desorption rates. Previous studies using a Catcher or diffusive gradient in thin film (DGT) focused on the absorption-desorption kinetics [28–30]. For comparison, a collected amount of the POCIS sample to the sum of collected amounts of the POCIS samples (e.g., compared the collected amount of POCIS sample for 1–3 d to sum of it for 1–2 d and 2–3 d) to discuss the effect of desorption; the comparison results are shown (Figs. 7, S7–9). The sum of the collected amount of the POCIS samples for 0–1, 1–2, 2–3, and 3–14 d should be equal to that for 0–14 d in linear phase. Likewise, the sum of the collected amount of the POCIS samples for 1–2 and 2–3 d also should be equal to that for 1–3 d. The decrease in the collected amount for long sampling
periods because of the desorption from the POCIS was apparent for the result of dinotefuran for 0–14 d, which is out of the linear range (Table 2). The weak decreasing trend of the collected amount for long sampling periods was apparent for the results of clothianidin, thiamethoxam, imidacloprid, and acetamiprid for 0–14 d compared to the sum of the collected amounts for 0–1, 1–2, 2–3, and 3–14 d. The trend was independent of the concentration range. Therefore, the sampling phase for the long sampling period would not be in linear phase but in curve phase and equilibrium phase (e.g., 14–28 d of the batch experiment for clothianidin), which was described in a previous study [27]. This explains why the POCIS/TWA value for the longer sampling periods was lower than for shorter periods as shown in Fig. 6. Additionally, the reason for the lower POCIS/TWA values was not only the curve phase sampling period, but also desorption of chemicals. Because the collected amount of the POCIS sample for 0–14 d was lower than its sum for 0–1, 1–2, 2–3,
and 3–14 d for clothianidin, thiamethoxam, imidacloprid, and acetamiprid (Fig. 7). However, the collected amount for 0–14 d of thiacloprid, whose Log $P_{ow}$ is the highest among the seven neonicotinoid pesticides, was not lower than the sample sum for 0–1, 1–2, 2–3, and 3–14 d. In short, the desorption effect for long sampling periods was not observed for thiacloprid.

In contrast, a significant decreasing trend for the collected amount for the short sampling period, comparing the sum of the collected amount 1–2 and 2–3 d to that of 1–3 d, was not observed for all neonicotinoid pesticides except dinofuran whose linear phase was only for three days. Thus, the

Fig. 7 Amounts collected by the POCIS in the chamber experiments under the 1,000, 100, and 10 µg/L maximum concentration conditions for (a) dinofuran, (b) clothianidin, (c) thiamethoxam, (d) imidacloprid, (e) acetamiprid, and (f) thiacloprid.
sampling for short period should be in linear phase with high accuracy.

Overall, the POCIS is a good tool for monitoring aquatic environments in non-steady-state conditions with limitations. The upper limit of the POCIS with high accuracy measurements is between 100 and 1,000 µg/L. Though the POCIS has limitations, it can measure the concentration spike in a qualitative manner in non-steady-state conditions at maximum values for 1,000 µg/L, which is the worst case in the Osaka prefectural report [17]. Therefore, we concluded that the POCIS is useful for aquatic monitoring in emergency situations. In addition, the POCIS can measure concentration fluctuations with high accuracy for the smaller accident in the report [17]. Moreover, underestimations were observed for long sampling periods, which was attributed to the decrement in the adsorption rate due to the gentle concentration gradient from the surface of the filter to the HLB and the desorption. Our results and discussion thus explain the mechanism of the error in the POCIS-measured values compared to the grab sampling values reported in previous studies [31–33], and show consistency with previous validations for fluctuating water concentrations [28,30].

CONCLUSIONS

We investigated the calculation of \( R_s \) values of POCIS measurements for seven neonicotinoid pesticides and evaluated the performance of the device in non-steady-state conditions in an aquatic environment. This study makes several contributions to the existing literature. First, we added six neonicotinoid pesticides to the list of chemicals that can be measured using POCIS. Second, we investigated the mechanism of underestimation for the POCIS for long sampling periods. Overall, we revealed the ability of the POCIS to monitor neonicotinoid pesticides, thus shedding new light on the accuracy of the POCIS in non-steady-state conditions. In real situations, many types of chemicals can be leaked into aquatic environments due to disasters and accidents. Therefore, further studies are needed to expand the types of chemical contaminants that can be measured by the POCIS under non-steady-state conditions in aquatic environments.

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SUPPLEMENTARY MATERIALS

Supplementary Materials for this article can be accessed at the journal website as a separate file.


REFERENCES


