Original Article

Development and Evaluation of the Performance of the Polar Organic Chemical Integrative Sampler for Linear Alkylbenzene Sulfonate

Kazushi Noro, Yoshinori Yabuki, Junko Ono, Satoshi Nakamura

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

ABSTRACT

A polar organic chemical integrative sampler (POCIS) was developed for the detection of linear alkylbenzene sulfonates (LASs), which are one of the most widely used chemicals globally and represent a type of surfactant agent. In the present study, the LASs were significantly sorbed onto the polyethersulfonate (PES) membrane, suggesting that the less sorptive polytetrafluoroethylene (PTFE) membrane is suitable for application in the POCIS device. Calibration experiments showed that the POCIS device with Oasis WAX as the sorbent and PTFE as the membrane filter had linear ranges > 28 d and sampling rates ranging from 0.035 ± 0.007 (tetradecylbenzenesulfonate) to 0.139 ± 0.024 (dodecylbenzenesulfonate) L d^{-1} . Furthermore, this POCIS device was validated under non-steady-state conditions via both field and chamber tests. The time-weighted average concentrations of dodecylbenzenesulfonate measured using the POCIS agreed well with those obtained via grab sampling within 21% over the sampling period of 14 d in both the field and chamber tests. Therefore, the POCIS can be successfully applied in the detection of LASs in LAS-contaminated aquatic environments.

Keywords: passive sampling, surfactants, monitoring

INTRODUCTION

Linear alkylbenzene sulfonates (LASs) are one of the most widely used chemicals globally and represent a type of surfactant agent [1]. They are produced and imported into Japan in enormous quantities; hence, there is concern that they might leak into natural environments in the event of disasters and accidents. In 2005, Japan produced and imported 62,088 and 5,472 t of LASs, respectively [2]. Therefore, leaked LASs can be hazardous to some aquatic organisms. Indeed, recent study demonstrated that chemical leak accidents may induce high LASs concentrations ($< 10 \text{ mg L}^{-1}$) in rivers, which may be above the lowest values of reliable acute LC50/EC50/ErC50 values [3]. A review of the aquatic toxicity data on commercially representative LASs revealed that the lowest values of reliable acute LC50/EC50/ErC50 for fish, *Daphnia magna*, and algae are 1.67, 1.62, and 29.0 mg L^{-1} , respectively [4]. In addition, the sodium dodecylbenzenesulfonate

(C₁₂-LAS) was the most common LAS. The abundance ratio of the C₁₂-LAS was 20–50% among LASs [4].

In recent years, polar organic chemical integrative samplers (POCIS), which is a type of passive sampler, have been devised for monitoring aquatic contaminants such as pesticides, pharmaceuticals, and munitions [3,5–12]. In the POCIS sampling, POCIS are deployed in the aquatic environment for a certain period, then the target compounds adsorbed on the sorbent are analyzed in the laboratory. The POCIS sampling is a simple and low cost method and gives time-weighted average (TWA) concentrations of the target compounds, which are advantages for the aquatic monitoring. The POCIS can be customized as selecting the sorbents and membrane filters for the target chemicals.

The application of POCIS for LASs can be challenging, even though the log octanol-water partition coefficients (log K_{ow}) values of LAS (0.45 to 3.32) are within the range of log K_{ow} for the POCIS sampling (0 to 5) [5,13–15]. This is

Corresponding author: Kazushi Noro, E-mail: NoroK@mbox.kannousuiken-osaka.or.jp

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because the LAS concentration in rivers may change four digits ($1 \mu\text{g L}^{-1}$ to 10 mg L^{-1}), when LAS leaked accidentally into rivers [3]. Conventional methods for detecting LASs include the methylene blue active substances method, high-performance liquid chromatography and mass spectrometry (LC-MS), and the use of biosensors [1,16,17]. However, passive sampling methods have not yet been applied in the detection of LASs.

In this study, we selected two sorbents and two membrane filters to develop POCIS devices for LAS detection in accordance with the optimization method reported by Noro *et al.* (2020) [8]. Thereafter, the performance of the POCIS devices were investigated in a field test and a chamber test. The most suitable sorbent for LAS detection was selected from the two sorbent candidates based on sorption and recovery experiments. Further, the permeation properties of the LASs with respect to the two membranes types were evaluated to identify the most suitable membrane filter. The POCIS device was then calibrated by performing static renewal experiments. Furthermore, a field test was conducted using the POCIS device to evaluate its performance under real conditions. Finally, a chamber test was conducted to validate the performance of the POCIS devices with respect to the detection of LASs under non-steady-state conditions.

MATERIALS AND METHODS

Materials

To develop the POCIS device for LAS detection, two candidate sorbents were considered initially, including Oasis WAX (Waters Corp., Milford, USA), which is an ion-exchange polymer-type sorbents, and Oasis HLB (Waters Corp.), which is a polymer-type sorbent. The WAX sorbent has been used for solid-phase extraction for LASs in biological samples (National Institute for Environmental Studies, 2017) and the HLB sorbent is the most widely used sorbent for POCIS. To pre-clean all the sorbents, acetone and methanol (10 mL each) was used, after which the cleaned sorbents were dried using a stream of nitrogen.

Microporous polyethersulfone (PES) membranes (pore size, $0.1 \mu\text{m}$; thickness, $102\text{--}158 \mu\text{m}$) and hydrophilic polytetrafluoroethylene (PTFE)-type membrane filters (pore size, $0.1 \mu\text{m}$; thickness, $35 \mu\text{m}$) were obtained from Nihon Pall Ltd. (Tokyo, Japan) and Toyo Roshi Kaisha, Ltd. (Tokyo, Japan), respectively.

An anionic surfactant mixture methanolic standard solution containing sodium decylbenzenesulfonate (C_{10} -LAS), sodium undecylbenzenesulfonate (C_{11} -LAS), sodium

dodecylbenzenesulfonate (C_{12} -LAS), sodium tridecylbenzenesulfonate (C_{13} -LAS), and sodium tetradecylbenzenesulfonate (C_{14} -LAS), each with a concentration of 1 g L^{-1} , was purchased from Fujifilm Wako Pure Chemical Corp. (Osaka, Japan). The sodium 4-dodecylbenzenesulfonate (RING- $^{13}\text{C}_6$) methanolic solution (10 mg L^{-1}), which was used as an internal standard, was purchased from Cambridge Isotope Laboratories, Inc. (Tewksbury, USA). Sodium dodecylbenzenesulfonate (C_{12} -LAS) of extra pure grade was purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Further, LC/MS-grade ultrapure water and ammonium formate solution (1 mol L^{-1}) as well as pesticide-analysis-grade acetone, methanol, hexane, and toluene (Fujifilm Wako Pure Chemical Corp.) were used for extraction and clean-up during the analysis. Ammonia solution, sodium chloride, and formic acid of guaranteed reagent grade were also purchased from Fujifilm Wako Pure Chemical Corp.

Sorption experiments

To estimate the sorption ability of the sorbent candidates for C_{10} -LAS, C_{11} -LAS, C_{12} -LAS, C_{13} -LAS, and C_{14} -LAS ($\text{C}_{10\text{--}14}$ -LAS), batch experiments were performed followed by the execution of an optimization method for the development of POCIS devices [8]. To conduct the batch experiment, the anionic surfactant mixture solution containing $\text{C}_{10\text{--}14}$ -LAS at a concentration of $1,000 \mu\text{g L}^{-1}$ was prepared using the methanolic standard solution (1 g L^{-1}) and ultrapure water. Thereafter, 10 mL of the mixture solution and 10 mg of the sorbent were loaded into a 10-mL glass centrifugation tube in triplicates. A horizontal shaking apparatus was allowed to shake the glass tube containing the solution and sorbent at 150 rpm for 48 h. The supernatant (1 mL) was then transferred into a vial with the internal standard (IS) solution ($100 \mu\text{g L}^{-1}$, $25 \mu\text{L}$) after 10 min of the centrifugation process. $\text{C}_{10\text{--}14}$ -LAS concentrations in the supernatant were analyzed using LC-MS/MS. A control experiment was also conducted concurrently.

Recovery experiments

The efficiency of $\text{C}_{10\text{--}14}$ -LAS recovery from the sorbents was estimated via extraction using a mixture of acetone:hexane:toluene (30:65:5 in volume ratio) containing 0.3% ammonium proposed as an optimized solvent for LASs extraction [18]. The sorbent loaded with $\text{C}_{10\text{--}14}$ -LAS was prepared in a similar manner as the case with the sorption experiments. Specifically, the loaded sorbent was placed in an empty solid-phase extraction (SPE) reservoir containing a polypropylene frit. The residual water in the

collected sorbent was then removed using an SPE vacuum manifold. The C_{10-14} -LAS were then eluted using 40 mL of the acetone:hexane:toluene mixture containing 0.3% ammonium. This was followed by the addition of 25 μL of the IS solution ($100 \mu\text{g L}^{-1}$) to the solutions. A stream of N_2 was allowed to evaporate the solution to 0.5 mL. Thereafter, the solution was diluted to 10 mL by adding methanol and evaporated again to 1 mL. The resulting solution was then stored in a glass vial at -20°C .

Permeation experiments

The permeation properties of the two membrane types used in this study (PES and PTFE) were evaluated as previously described [18]. The device used for the permeation experiments is shown in **Fig. S1**. The membranes were used to separate two solutions in glass cells. A mixed C_{10-14} -LAS solution (32 mL, $100 \mu\text{g L}^{-1}$ each) and a NaCl solution (32 mL, $84 \mu\text{g L}^{-1}$) were added to the donor and acceptor cells, respectively. Thereafter, the solution in the cells was agitated for 48 h at room temperature and 200 μL of the sample solution was collected at specific intervals to determine C_{10-14} -LAS concentrations. The obtained solution was then diluted five times using methanol containing the IS solution (25 μL). The obtained data was fitted to the first-order model (Equation 5 in Endo and Matuura, 2018) [19]. The equations are as follows.

$$C_{\text{don}} = \frac{C_{\text{don},0}}{2} \left(1 + e^{-\frac{2k}{V}t} \right) \quad (1)$$

$$C_{\text{acc}} = \frac{C_{\text{don},0}}{2} \left(1 - e^{-\frac{2k}{V}t} \right) \quad (2)$$

where V (m^3) is the volume of the solution, C_{don} and C_{acc} ($\mu\text{g L}^{-1}$) are the concentration of the LAS in the donor cell and the acceptor cell, respectively, t (h) is the time, and k ($\text{m}^3 \text{h}^{-1}$) is the mass transfer coefficients.

Analytical conditions

The LC-20 system (Shimadzu Corporation, Kyoto, Japan) was used to perform the LC-MS/MS analysis. An InertSustain C18 column (5 μm , $150 \text{ mm} \times 2.1 \text{ mm}$) (GL Sciences Inc., Tokyo, Japan) was used to separate the C_{10-14} -LAS at 40°C . Solvents, A (5 mmol L^{-1} ammonium acetate in 0.1% formic acid solution) and B (acetonitrile), were used as the mobile phase. The ratio of A to B ratio was 65:35 (isocratic) and the total flow rate was 0.2 mL min^{-1} . A Triple-QuadTM 4500

system, which is a tandem mass spectrometer, equipped with an electrospray ionization mass spectrometer source (AB Sciex LLC., Framingham, USA) in the negative ion electrospray mode was used. The mass spectrometric conditions are shown in **Table S1** along with the retention time, precursor ion, quantitative ion, collision energies, and detection limits.

Static renewal experiments

Static renewal experiments were conducted to determine the sampling rate (R_s) as well as the linear ranges of the POCIS device as previously described [3,8]. The POCIS device (outer diameter, 102 mm; inner diameter, 54 mm) contained dried Oasis WAX (220 mg) with PTFE membrane filters and PES membrane filters.

The sample solution (1 L) containing 200 ng L^{-1} each of the C_{10-14} -LAS mix solution was added into glass beakers in which the POCIS device was installed. The solution was agitated at 18.0 cm s^{-1} , which was determined using an alabaster mass transfer sensor at 20°C under dark conditions [3]. R_s was estimated under 1500 rpm (18 cm s^{-1}), which was the same stirring condition that was employed in previous studies [3,8]. The experiment was conducted at 1, 3, 7, 14, 21, and 28 d in triplicate. Changes in the concentrations of C_{10-14} -LAS were avoided by replacing the solutions daily.

The membrane containing the sorbent in the POCIS devices were carefully ejected from the metal rings after the experiments. The sorbent was obtained and eluted in a same manner as the recovery experiments (see Recovery experiments).

The amount of contaminant that accumulated in the sorbent could be described based on the following first-order kinetics model.

$$M = mK_d C_w (1 - e^{-\frac{R_s t}{mK_d}}) \quad (3)$$

where M (ng) represents the amount of the contaminants that collected in the sorbent, m (kg) represents the sorbent mass, K_d (L kg^{-1}) represents the sorbent-water sorption coefficient, C_w (ng L^{-1}) represents the concentration of the contaminants in solution, R_s (L d^{-1}) represents the sampling rate, and t (d) represents the sampling period.

The duration of the kinetic sampling stage, which represents the period during which the model can be approximated as a linear formula is called the “linear range” (d) ($t_{1/2}$), calculated as

$$t_{1/2} = \frac{\ln 2 \times mK_d}{R_s} \quad (4)$$

Field test

A field test was conducted at the Ishikawa River in southern Osaka, Japan. The basin area (222 km²) and agricultural area (10 km²) of the river were reported in a previous study [10]. To perform the field test, a downstream point of this river was selected as the sampling spot.

To carry out the sampling at the Ishikawa River, which was conducted in June 2020, a protective canister containing three POCIS devices was deployed for 14 days (June 3–17, 2020). Grab samples were also collected seven times at intervals of 2–3 d within the 14 days of the POCIS deployment. The grab samples (750 mL) were collected in cleaned glass bottles. The flow rate at the sampling spot was measured four times, and were determined to be 29, 24, 40, and 29 cm s⁻¹ on June 3, 8, 10, and 15, 2020, respectively. Additionally, the water temperature was ranged from 24.2 to 28.7°C.

Reportedly, R_s is basically constant, above the flow rate at 6 cm s⁻¹ [20]. The flow velocity in the static renewal experiments (18 cm s⁻¹) and the field tests (24–40 cm s⁻¹) were above 6 cm s⁻¹. In addition, the temperature in the field test (24.2 to 28.7°C) was similar to those in the static renewal experiments (20°C). Therefore, in this study, it was reasonable to apply this determined R_s based on a static renewal experiment in the field test.

Chamber tests

Chamber tests were conducted as previously described [3]. Specifically, the peak concentration and half-life of the LASs in an LAS-contaminated river owing to a chemical leak were estimated as 10 mg L⁻¹ and 1 d, respectively, using a previously reported simulation model [3,21].

A stainless-steel tank containing tap water (volume, 27 L; flow rate, 9 cm s⁻¹) was used as the test chamber. The POCIS devices were installed on a metal rack in the chamber for 0–1, 1–3, 3–14, and 0–14 d. Using a pump (MP-3001; Tokyo Rikakikai Co., Ltd., Tokyo, Japan), 2 L of the C₁₂-LAS solution (13.5 mg L⁻¹) was introduced into the chamber at a flow rate of 1.4 mL min⁻¹. By the end of the first day, it is expected that the concentration of the C₁₂-LAS in the chamber should be at 1 mg L⁻¹, which is below the critical micellar concentration of 1.1 mg L⁻¹ [22]. Subsequently, the solution in the chamber was removed at 18.8 mL min⁻¹ using the same pump, and concurrently, the water volume was kept constant using a water level controller (WLC-SA; AS ONE Corporation, Osaka, Japan). Therefore, the concentration of C₁₂-LAS in the chamber decreased by half every day from the start of the second day. In short, the half-life period of the C₁₂-LAS concentration was 1 d. The water samples (1 mL) that were

collected twelve times to check the C₁₂-LAS concentration in the tank were transferred into LC vials spiked with the IS solution (25 µL). These vials were kept at 4°C until LC-MS/MS analysis.

RESULTS AND DISCUSSION

Sorption and recovery experiments

The log of the apparent sorption coefficient (K_d ; L kg⁻¹) values calculated based on the results of the sorption experiment. The C_{10–14}-LAS was sorbed effectively onto Oasis WAX, while Oasis HLB showed a weaker sorption performance (Table S2). The log K_d values of the sorbents were determined as 6.0 (C₁₂-LAS) to 6.9 (C₁₀-LAS) for Oasis WAX and 4.3 (C₁₀-LAS) to 6.1 (C₁₄-LAS) for Oasis HLB (Table S3). Thus, these Oasis WAX was selected as candidate sorbents for the recovery experiment. The results of the recovery experiments showed that a C_{10–14}-LAS recovery rate of 78–104% (Table S4). Therefore, in this study, Oasis WAX, which showed strong sorption and high recovery efficiency, was selected as the sorbent for the POCIS device.

Permeation experiments

With the PTFE membrane, the concentrations of C₁₀-LAS, C₁₁-LAS, and C₁₂-LAS reached equilibria rapidly (Fig. 1, Table S5). Further, the results corresponding to C₁₃-LAS and C₁₄-LAS showed that the PTFE filter absorbed longer-chain LAS only slightly (Fig. 1). The results corresponding to C₁₀-LAS and C₁₁-LAS in relation to the PES membrane were similar to those obtained using the PTFE membrane. Additionally, the equilibrium concentrations of C₁₂-LAS, C₁₃-LAS, and C₁₄-LAS in the acceptor cell with the PES membranes installed were 50% (C₁₂-LAS) to 88% (C₁₄-LAS) lower than those in the cell with the PTFE membranes installed. These observations indicate that these longer-chain LASs were strongly absorbed onto the PES membrane. Therefore, the PES membrane may not be suitable as a filter in POCIS devices meant for the detection of LASs in aquatic environments.

All the LAS types in the acceptor cell showed a short lag time (ca. 1 h) with both the PTFE and PES membranes. The model described in a previous study was fitted to the results (Eq. 1 and 2) [19], and it was observed that the fitted first-order rate constants of C₁₁-LAS were 86% higher for PTFE than for PES, and this could be attributed to the greater thickness of the PES membrane (100–150 µm) compared with the PTFE membrane (35 µm); these results agree with those reported in previous studies [8,19]. In summary, the

Fig. 1 Permeation experiments with polytetrafluoroethylene (PTFE) and polyethersulfone (PES) membrane filters. The target chemicals were sodium decylbenzenesulfonate (C_{10}), sodium undecylbenzenesulfonate (C_{11}), sodium dodecylbenzenesulfonate (C_{12}), sodium tridecylbenzenesulfonate (C_{13}), and sodium tetradecylbenzenesulfonate (C_{14}). The lines indicate the first-order model fit (Eq. 1 and 2). The dashed lines and solid lines indicate the results of the donor cell and the acceptor cell, respectively.

inert and thin PTFE filter was found to be most suitable as a membrane filter given that it is associated with a lower risk of the adsorption of LASs onto the membranes.

Sampling rates and linear ranges

The static renewal experiment was conducted using the POCIS with Oasis WAX as the sorbent and with either PES or PTFE as the membrane filter. The results corresponding to the POCIS device with the PTFE membrane (PTFE POCIS) are presented in **Fig. 2** and **Tables 1, S6**.

The R_s values and linear ranges of the LASs corresponding to the PTFE POCIS device were estimated using the model shown in Eq. 3 based on the K_d values obtained following the sorption experiment (**Table S4**). The obtained R_s values of the LASs ranged from 0.035 ± 0.007 (C_{14} -LAS) to 0.139 ± 0.024 (C_{11} -LAS) ($L d^{-1}$), and their linear ranges were determined to be > 28 d.

The amounts of C_{10} -LAS, C_{11} -LAS, and C_{12} -LAS that

accumulated in the PTFE POCIS device rapidly increased within the first seven days, after which the uptake rates decreased gradually. Therefore, it is possible that the PTFE POCIS would overestimate the concentrations of C_{10} -LAS, C_{11} -LAS, and C_{12} -LAS within the first seven days. This uptake shape would appear to be due to sorbent saturation. However, the linear range of the PTFE POCIS device for LAS detection was evidently above 28 d, as mentioned above, implying the adsorption did not reach the saturation.

Uncertainties of the collected amount estimation compared to the measured values on 7 d were calculated as;

$$U = \frac{|M_{7d} - t_u C_c R_s|}{t_u C_c R_s} \times 100 \quad (5)$$

where U (%) is the uncertainty (%), t_u (d) is the time for the U estimation, C_c ($ng L^{-1}$) is the concentration for the calibration tests, M_{7d} (ng) is the collected amount on the time of t_u for the calibration tests (**Table S6**). The t_u and C_c values were 7 (d) and 200 ($ng L^{-1}$), respectively. The U values ranged from 5.4 (C_{13} -LAS) to 93 (C_{11} -LAS)%. The U values were higher than the relative standard deviations of the R_s values (**Table 1**). Therefore, applying R_s values to estimate the LASs concentrations may induce a larger error than those expected from the standard deviations of R_s values in short deployment periods (< 7 d).

When the dry POCIS devices were deployed in the solution, the water penetrated into the POCIS device which enhanced the permeation of the LASs [23]. The effect was found in the previous study using the POCIS devices with glass bars to estimate the permeation rate [23]. The effect has not been considered, because the lag-time may counteract. When the sorption of the chemicals onto the membranes are weak, the effect should become marked.

The static renewal experiment for C_{14} -LAS seemed to show a time lag (**Fig. 2**), possibly due to the sorption of C_{14} -LAS on the PTFE filter, as mentioned in the permeation experiment (**Fig. 1**). Therefore, such a time lag should be considered when the PTFE POCIS is used in monitoring C_{14} -LAS for a short time period (< 3 d).

Besides, the POCIS device with the PES membrane (PES POCIS) accumulated 0.4 (C_{14} -LAS) to 54.1 (C_{11} -LAS) ng of LAS for a period of over three days. This is ca. 80% less than the accumulated LAS associated with the PTFE POCIS device. This is because the strong sorption of the LAS on the PES is a limiting factor in LAS uptake by the PES POCIS device. Thus, Oasis WAX and the PTFE membrane were identified as the most promising combination for LAS

Fig. 2 Amounts of linear alkylbenzene sulfonates accumulated in the polar organic chemical integrative sampler. The target chemicals were sodium decylbenzenesulfonate (C_{10}), sodium undecylbenzenesulfonate (C_{11}), sodium dodecylbenzenesulfonate (C_{12}), sodium tridecylbenzenesulfonate (C_{13}), and sodium tetradecylbenzenesulfonate (C_{14}). In all cases, the temperature was maintained at 20°C and the experiments were conducted under dark conditions. The concentration of each analyte in the solution was 200 ng L⁻¹. The error bars show 1 σ ($n = 3$), and the dotted line indicates model fitting (Eq. 3) with the K_d values based on the sorption experiments. R^2 values are the coefficients of determination.

Table 1 Linear ranges and sampling rates (R_s) of linear alkylbenzene sulfonates at 20°C and 1500 rpm. The concentration of each analyte in the solution was 200 ng L⁻¹.

	C_{10} -LAS ^a	C_{11} -LAS ^b	C_{12} -LAS ^c	C_{13} -LAS ^d	C_{14} -LAS ^e
Linear range (d)	> 28	> 28	> 28	> 28	> 28
R_s (L d ⁻¹)	0.101 ± 0.007	0.139 ± 0.024	0.110 ± 0.007	0.071 ± 0.010	0.035 ± 0.007

$n = 3$, error = 1 σ

^asodium decylbenzenesulfonate

^bsodium undecylbenzenesulfonate

^csodium dodecylbenzenesulfonate

^dsodium tridecylbenzenesulfonate

^esodium tetradecylbenzenesulfonate

Table 2 Results of the field test.

	^a C ₁₀ -LAS	^b C ₁₁ -LAS	^c C ₁₂ -LAS	^d C ₁₃ -LAS	^e C ₁₄ -LAS
C_{mean} (ng L ⁻¹)	393	859	645	274	n.d.
POCIS-measured value* (ng L ⁻¹)	375 ± 83	713 ± 185	673 ± 167	467 ± 144	3.6 ± 1.2

C_{mean} : mean value of grab samplings, n.d.: not determined, *: $n = 3$, error = 1σ

^a sodium decylbenzenesulfonate

^b sodium undecylbenzenesulfonate

^c sodium dodecylbenzenesulfonate

^d sodium tridecylbenzenesulfonate

^e sodium tetradecylbenzenesulfonate

Fig. 3 Results of field test conducted at the Ishikawa River for sodium decylbenzenesulfonate (C₁₀), sodium undecylbenzenesulfonate (C₁₁), sodium dodecylbenzenesulfonate (C₁₂), and sodium tridecylbenzenesulfonate (C₁₃). The closed circles show the concentration measured via grab samplings. The lines show the mean values corresponding to the grab samples. The dashed lines show the concentration measured using the polar organic chemical integrative sampler ($n = 3$). The sampling period was June 3–17, 2020 at the Ishikawa River.

monitoring using the POCIS device.

Field test

The results of the field test are shown in **Table 2** and **Figs. 3 and 4**. The LAS concentrations obtained based on the grab samples ranged from 118 (C₁₃-LAS, 17th June) to 1.66×10^3 (C₁₁-LAS, 8th June) ng L⁻¹ (**Fig. 3**), and the mean concentrations of LAS in the grab samples (C_{mean} ; ng L⁻¹) were 393 (C₁₀-LAS), 859 (C₁₁-LAS), 645 (C₁₂-LAS), and 274 (C₁₃-LAS) ng L⁻¹ (**Table 2**, **Fig. 3**), which were all below the lowest environmental LAS concentration criterion (0.02 mg

L⁻¹) in Japan. The Ministry of the Environment in Japan has reported that the measured environmental LAS concentration in Japan within the 2013–2015 period was in the range 0.06–800 µg L⁻¹ [24]. Thus, the measured values obtained in this study are comparable with those reported in literature. The miscellaneous drainage may dominate the LASs concentration in this field because the adoption ratio of the sewer drain was relatively low in the watershed (82.8% (Fujiidera, Osaka)–93.6% (Taishi, Osaka)) [25].

The POCIS-measured values calculated using Eq. 3 were 375 ± 83 (C₁₀-LAS), 713 ± 185 (C₁₁-LAS), 673 ± 167 (C₁₂-

Fig. 4 Ratio the POCIS-measured values to the mean values corresponding to the grab samples (C_{mean}) based on the field test. The detected chemicals were sodium decylbenzenesulfonate (C_{10} -LAS), sodium undecylbenzenesulfonate (C_{11} -LAS), sodium dodecylbenzenesulfonate (C_{12} -LAS), and sodium tridecylbenzenesulfonate (C_{13} -LAS). The sampling period was from June 3–17, 2020 at the Ishikawa River. The vertical error bar shows 1σ ($n = 3$).

LAS), and 467 ± 144 (C_{13} -LAS) ng L^{-1} (Table 2, Fig. 3). Even though the presence of C_{14} -LAS was not detected in the grab samples, LAS measurements using the PTFE POCIS device showed a concentration of 3.6 ± 1.2 ng L^{-1} for C_{14} -LAS. The integration of contaminants is an advantage of the POCIS method compared with grab sampling with respect to the detection of LASs at low concentrations.

The mean LAS concentration values based on the grab sampling were compared with the POCIS-measured values (Fig. 4). The ratio of the POCIS-measured value to the C_{mean} values ranged from 83 ± 22 (C_{11} -LAS) to 171 ± 53 (C_{13} -LAS)% (Fig. 4). The relatively high ratio of the POCIS-measured values to the C_{mean} value of C_{13} -LAS may be due to the integration of the concentration peaks that were not captured by grab sampling. Overall, the PTFE POCIS effectively captured LAS concentrations in the freshwater. A high concentration of anions in the seawater may interfere the absorption of the LASs onto Oasis WAX, which is an ion-exchange sorbent.

Chamber test

The PTFE POCIS device was tested in a chamber in which non-steady-state conditions were replicated, with the peak C_{12} -LAS at $1,000$ $\mu\text{g L}^{-1}$. The results obtained are shown in Fig. 5 and Tables S7, S8. Further, the average concentration of C_{12} -LAS in the chamber, which is a theoretical value that represents the POCIS-measured value, was calculated

Fig. 5 Comparison of polar organic chemical integrative sampler (POCIS)-measured values with time-weighted average (TWA) values based on the concentrations of sodium dodecylbenzenesulfonate (C_{12} -LAS) in the aqueous solution. (A) Time series of the chamber experiment. The vertical error bar shows 1σ ($n = 3$). (B) Ratio of POCIS-measured values to TWA values. The vertical error bar shows 1σ ($n = 3$).

alongside the POCIS sampling.

The PTFE POCIS device captured the change in the concentration of C_{12} -LAS effectively (Fig. 5 (A)). Additionally, the ratio of the POCIS-measured values to the TWA values ranged from 98.9 (sampling period; 0–14 d) to 122% (sampling period; 3–14 d) (Fig. 5 (B)), and the differences between the POCIS-measured values and the TWA values were within 25% (Fig. 5 (B)). The overestimation that characterized the shorter sampling periods (0–1 d and 1–3 d) was possibly due to the relatively rapid uptake of the C_{12} -LAS by the PTFE POCIS device within short sampling periods as shown in Sampling rates and linear ranges and Fig. 2.

Assuming a chemical leak accident, these results indicate that the PTFE POCIS device effectively captured changes in the concentration of C_{12} -LAS. The PTFE membrane had less sorptive properties for the LASs, and the K_d values of Oasis WAX were close among the LASs, implying that the uptake of the LASs should be similar by the PTFE POCIS. In addition, the R_s values for LASs were obtained with sufficient $t_{1/2}$ values (> 28 d), and the PTFE POCIS was successfully

applied in the freshwater. Therefore, the PTFE POCIS would be suitable for application in monitoring LASs in case of an emergency. A commercial HLB-based POCIS device showed sorbent saturation in a chamber test involving neonicotinoid pesticides at a maximum concentration of $1,000 \mu\text{g L}^{-1}$ [3]. Thus, it is necessary to optimize the POCIS device so that it can be applied in the detection of LAS at high concentrations.

Conclusions

The PTFE POCIS showed suitability for the passive sampling of C_{10-14} -LAS owing to its linear range and R_s . This is the first report on the application of the PTFE membrane in a POCIS device to monitor LASs, which cannot be realized using the PES POCIS device. Further, the field tests showed sensitivity under low LAS concentration conditions ($\sim 1 \mu\text{g L}^{-1}$). In addition, the chamber test showed that the PTFE POCIS device responded sufficiently to a concentration spike under high concentration condition ($\sim 1 \text{ mg L}^{-1}$). The field test and the chamber test showed that the PTFE POCIS can be applied for the LASs in the fresh water and for monitoring LASs in chemical leak accidents, respectively. In future studies, it would be necessary to clarify the effects of coexisting chemicals in the natural water environment on the performance of the device. It will also be necessary to clarify the effects of temperature changes and to determine which chemicals might leak into the aquatic environment in case of an accident.

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SUPPLEMENTARY MATERIALS

Supplementary Materials file for this article is available at the link below.

https://www.jstage.jst.go.jp/article/jwet/20/1/20_21-116/supplement/_download/20_21-116_1.pdf

REFERENCES

- [1] Lara-Martín PA, Gómez-Parra A, González-Mazo E: Determination and distribution of alkyl ethoxysulfates and linear alkylbenzene sulfonates in coastal marine sediments from the Bay of Cadiz (southwest of Spain). *Environ. Toxicol. Chem.*, **24**(9), 2196–2202, 2005. PMID:16193746 <https://doi.org/10.1897/04-446R.1>
- [2] Centre for Environmental Information Science: Report of the trade affairs of surfactants. Centre for Environmental Information Science, Tokyo, Japan, 2006. [in Japanese]
- [3] Noro K, Yabuki Y, Banno A, Tawa Y, Nakamura S: Validation of the application of a polar organic chemical integrative sampler (POCIS) in non-steady-state conditions in aquatic environments. *Journal of Water and Environment Technology*, **17**(6), 432–447, 2019. <https://doi.org/10.2965/jwet.19-057>
- [4] OECD high production volume chemicals program (2006): SIDS (screening information data set) initial assessment report 2006, UNEP Publication, Paris, France, 2006.
- [5] Alvarez DA, Petty JD, Huckins JN, Jones-Lepp TL, Getting DT, Goddard JP, Manahan SE: Development of a passive, in situ, integrative sampler for hydrophilic organic contaminants in aquatic environments. *Environ. Toxicol. Chem.*, **23**(7), 1640–1648, 2004. PMID:15230316 <https://doi.org/10.1897/03-603>
- [6] Lissalde S, Mazzella N, Mazellier P: Polar organic chemical integrative samplers for pesticides monitoring: Impacts of field exposure conditions. *Sci. Total Environ.*, **488–489**, 188–196, 2014. PMID:24830931 <https://doi.org/10.1016/j.scitotenv.2014.04.069>
- [7] Thomatou AA, Zacharias I, Hela D, Konstantinou I: Passive sampling of selected pesticides in aquatic environment using polar organic chemical integrative samplers. *Environ. Sci. Pollut. Res. Int.*, **18**(7), 1222–1233, 2011. PMID:21373860 <https://doi.org/10.1007/s11356-010-0436-6>
- [8] Noro K, Endo S, Shikano Y, Banno A, Yabuki Y: Development and calibration of the polar organic chemical integrative sampler (POCIS) for neonicotinoid pesticides. *Environ. Toxicol. Chem.*, **39**(7), 1325–1333, 2020. PMID:32348590 <https://doi.org/10.1002/etc.4729>
- [9] Yabuki Y, Nagai T, Inao K, Ono J, Aiko N, Ohtsuka N, Tanaka H, Tanimori S: Temperature dependence on the pesticide sampling rate of polar organic chemical integrative samplers (POCIS). *Biosci. Biotechnol. Biochem.*, **80**(10), 2069–2075, 2016. PMID:27305429 <https://doi.org/10.1080/09168451.2016.1191329>

- [10] Yabuki Y, Ono J, Nagai T, Inao K, Tanimori S: 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. *J. Pestic. Sci.*, **43**(1), 18–23, 2018. PMID:30363146 <https://doi.org/10.1584/jpestics.D17-063>
- [11] Rosen G, Lotufo GR, George RD, Wild B, Rabalais LK, Morrison S, Belden JB: Field validation of POCIS for monitoring at underwater munitions sites. *Environ. Toxicol. Chem.*, **37**(8), 2257–2267, 2018. PMID:29687474 <https://doi.org/10.1002/etc.4159>
- [12] Noro K, Vermeirssen ELM, Banno A, Ono J, Yabuki Y: Comparative evaluation of the polar organic chemical integrative sampler in two types of validation systems simulating peak concentration events. *Environ. Toxicol. Chem.*, **40**(11), 3010–3018, 2021. PMID:34506633 <https://doi.org/10.1002/etc.5204>
- [13] U.S. Environmental Protection Agency: EPI suite v.3.12, 2012.
- [14] International Programme on Chemical Safety (IPCS): International chemical safety cards. ICSC 1189; Sodium Dodecylbenzenesulphonate, International Labour Organization (ILO), 1997.
- [15] International Programme on Chemical Safety (IPCS): International chemical safety cards. ICSC 1602; C10-13 alkylbenzenesulfonic acid, sodium salt, International Labour Organization (ILO), 2005.
- [16] Nakae A, Tsuji K, Yamanaka M: Determination of alkyl chain distribution of alkylbenzenesulfonates by liquid chromatography. *Anal. Chem.*, **53**(12), 1818–1821, 1981. <https://doi.org/10.1021/ac00235a024>
- [17] Nomura Y, Ikebukuro K, Yokoyama K, Takeuchi T, Arikawa Y, Ohno S, Karube I: Application of a linear alkylbenzene sulfonate biosensor to river water monitoring. *Biosens. Bioelectron.*, **13**(9), 1047–1053, 1998. PMID:9839392 [https://doi.org/10.1016/S0956-5663\(97\)00077-8](https://doi.org/10.1016/S0956-5663(97)00077-8)
- [18] Ministry of the Environment, Japan: Chemicals and environments. Ministry of the Environment, Japan, Tokyo, 2018. [in Japanese]
- [19] Endo S, Matsuura Y: Characterizing sorption and permeation properties of membrane filters used for aquatic integrative passive samplers. *Environ. Sci. Technol.*, **52**(4), 2118–2125, 2018. PMID:29366322 <https://doi.org/10.1021/acs.est.7b05144>
- [20] Djomte VT, Taylor RB, Chen S, Booij K, Chambliss CK: Effects of hydrodynamic conditions and temperature on polar organic chemical integrative sampling rates. *Environ. Toxicol. Chem.*, **37**(9), 2331–2339, 2018. PMID:29978495 <https://doi.org/10.1002/etc.4225>
- [21] Nishioka T, Iwasaki Y, Ishikawa Y, Yamane M, Morita O, Honda H: Validation of AIST-SHANEL model based on spatiotemporally extensive monitoring data of linear alkylbenzene sulfonate in Japan: Toward a better strategy on deriving predicted environmental concentrations. *Integr. Environ. Assess. Manag.*, **15**(5), 750–759, 2019. PMID:31050181 <https://doi.org/10.1002/ieam.4167>
- [22] International Programme on Chemical Safety: Environmental health criteria 169. <http://www.inchem.org/documents/ehc/ehc/ehc169.htm> [accessed on 4 September, 2020]
- [23] Noro K, Yabuki Y, Banno A, Ono J, Nakamura S: Characterization of the permeation properties of membrane filters and sorption properties of sorbents used for polar organic chemical integrative samplers. *ChemRxiv*, 2021. <https://doi.org/10.26434/chemrxiv.14691369.v1>
- [24] Ministry of the Environment, Japan: Public water area – Water quality measurement results, 2018. <http://www.env.go.jp/water/suiiki/> [accessed on 13 May, 2020, in Japanese]
- [25] Osaka Prefectural Government, Japan: The adoption ratio of the sewer drain at the municipal level, 2021. https://www.pref.osaka.lg.jp/gesui_jigyo/tokei/fukuyuh20.html [accessed on 20 October, 2021, in Japanese]