Title: Development and Evaluation of the performance of the Polar Organic Chemical Integrative Sampler for Linear Alkylbenzene Sulfonate

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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. Owing to natural disasters and accidents, these LASs have a potential risk to leak into aquatic environments at high concentrations, and thus far, passive sampling methods have not yet been applied in their detection as, being a sorptive compound, they do not easily permeate the membrane of passive samplers. 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 developed 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 developed POCIS device was validated under non-steady-state conditions via both chamber and field tests. The condition in the chamber test replicated the LAS concentration change in rivers contaminated by LAS-leaked accidents. The time-weighted average concentrations of dodecylbenzenesulfonate measured using the improved POCIS agreed well with those obtained via grab sampling within 21% over the sampling period of 14 d in both the chamber and field tests. Therefore, the developed POCIS can be successfully applied in the detection of LASs in LAS-contaminated aquatic environments owing to chemical leak accidents.

Keywords: Passive Sampling, Surfactant, Chemical leak accident, Monitoring.

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Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Availability of data and material

The datasets generated during and/or analyzed during the current study are shown in supplemental materials as tables.

Code availability

Not applicable.

Authors’ contributions

Kazushi. Noro, Yoshinori Yabuki, and Satoshi Nakamura: Conceptualization. Kazushi Noro, Junko Ono, and Yoshinori Yabuki: Investigation. Kazushi Noro: Writing – Original Draft. All authors: Writing – Review & Editing.

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Introduction

Safety measures are necessary to control chemical leaks resulting from disasters and catastrophes in aquatic environments. For example, the Great East Japan Earthquake that occurred in 2011 resulted in a significant leakage of different chemicals into the environment. Therefore, it is necessary to develop monitoring methods, prediction models, and risk assessment strategies with respect to chemical leakages caused by overwhelming disasters (Nakamura et al., 2019).

The polar organic chemical integrative sampler (POCIS), which is a type of passive sampler for aquatic environments, has been suggested as a device for the monitoring of such chemical leaks in aquatic environments (Noro et al. 2019). Such passive sampling provides the time-weighted average (TWA) values of the contaminants present in the aquatic ecosystem without the need for grab sampling. Additionally, the primary advantage of passive sampling is that it is suitable for monitoring the aquatic environment even after an emergency as a complementary monitoring method apart from grab samplings (Noro et al. 2019). For example, it has been suggested that passive sampling methods can be applied to monitor the decrease in the concentration of the chemicals that leak into the aquatic environment after the accident, and in a recent investigation, the concentration spikes corresponding to several hydrophilic chemicals (log K_{ow}: –0.55 to 1.26) were accurately measured using a POCIS device under emergency conditions (Noro et al. 2019). All the parts of POCIS devices, e.g., membranes and absorbents, are easily available; thus, first responders, such as local environmental research institutes, can easily equip POCIS devices with different types of membranes and adsorbents depending on the type of chemical leak accident to be investigated.

The chemicals to be monitored using the POCIS device following an emergency should be decided based on toxicity and abundance, i.e., the potential negative impact of the chemicals (Nakamura et al. 2019). For example, the detection of linear alkylbenzene sulfonates (LASs), which are one of the most widely used chemicals globally and represent a type of surfactant agent, is necessary (Lara-Martín et al. 2005). This is because 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 (Ministry of the Environment of Japan 2017). Therefore, leaked LASs can be hazardous to some aquatic organisms. Even though LASs have low toxicity in humans and other mammals, a review of the aquatic toxicity data on commercially representative LASs revealed that the lowest values of reliable acute $LC_{50}/EC_{50}/ErC_{50}$ for fish, Daphnia Magna, and algae are 1.67, 1.62, and 29.0 mg L^{-1}, respectively (Organisation for Economic Co-operation and Development 2006).

Conventional methods for detecting LASs include the methylene blue active substances method, high-performance liquid chromatography and mass spectrometry (LC-MS) (Lara-Martín et al. 2005), and the use of biosensors (Nakae et al. 1981; Nomura et al. 1998; Lara-Martín et al. 2005). However, passive sampling methods have not yet been applied in the detection of LASs given that they may absorb on membranes, making their permeation to sorbents difficult. In addition, in previous studies, target chemicals of POCIS devices were not chosen based on their abundance, but on their toxicity or measurability using conventional devices (Kaserzon et al. 2012; Noro et al. 2020; Rosen et al. 2018, Yabuki et al. 2018). Therefore, no POCIS device has been developed to monitor LASs, which have relatively low toxicity in aquatic environments.

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

Methods

Materials

To develop the POCIS device for LAS detection, nine candidate sorbents were considered initially, including ENVI-Carb (Supelco, Bellefonte, PA, USA), GC, Active Carbon (both from GL Sciences; Tokyo, Japan), and AC2 (Waters; Milford, MA, USA), which are active carbon-type sorbents, Oasis MAX and Oasis WAX (both from Waters), which are ion-exchange polymer-type sorbents, and Pharma FF, PLS3 (both purchased from GL Sciences), and Oasis HLB (Waters), which are polymer-type sorbents. Table 1 shows the structures and sizes of these sorbents. 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.

Table 1. Candidate sorbents in this study.

Sorbent	Provider	Material	Structure	Size (µm)
Oasis HLB	Waters	Polymer	A copolymer of styrene-divinylbenzene and vinyl pyrrolidone	60
InertSep PLS3	GL Sciences	Polymer	A copolymer of styrene-divinylbenzene and vinyl pyrrolidone	50–70
InertSep PharmaFF	GL Sciences	Polymer	N-containing polar group, styrene-divinylbenzene methacrylate copolymer	45–65
Envi-carb	Supelco (Sigma-Aldrich)	Nonporous Carbon	Graphitic, nonporous carbon	35–117
InertSep Active carbon	GL Sciences	Activated carbon	(No additional information)	104–221
AC2	Waters	Low ash content activated carbon	Low ash content activated carbon	85
Oasis MAX	Waters	Ion-exchange Polymer	Strong anion exchange polymer	30
Oasis WAX	Waters	Ion-exchange Polymer	Weak anion exchange polymer	30
InertSep GC	GL Sciences	Graphite carbon	graphite carbon in a planar structure	37–74

Microporous polyethersulfone (PES) membranes (pore size, 0.1 µm; thickness, 102–158 µm) and hydrophilic polytetrafluoroethylene (PTFE)-type membrane filters (pore size, 0.1 µm; thickness, 35 µm) 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 Wako Pure Chemical Ind. (Osaka, Japan). The sodium 4-dodecylbenzenesulfonate (RING-$^{13}C_6$) methanolic solution (10 mg L^{-1}), which was used as an internal standard, was purchased from Cambridge Isotope Laboratories, Inc. (Tewksbury, MA). 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 (Wako Pure Chemical Ind.) 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 Wako Pure Chemical Ind. (Osaka, Japan).

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 ($C_{10–14}$-LAS), batch experiments were performed followed by the execution of an optimization method for the development of POCIS devices (Noro *et al.* 2020). To conduct the batch experiment, the anionic surfactant mixture solution containing $C_{10–14}$-LAS at a concentration of 1,000 µg 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 μg L^{-1}, 25 μL) after 10 min of the centrifugation process. $C_{10–14}$-LAS concentrations in the supernatant were analyzed using LC-MS/MS. A control experiment was also conducted concurrently.

Recovery experiments

The efficiency of $C_{10–14}$-LAS recovery from the sorbents via extraction using a mixture of acetone:hexane:toluene (30:65:5 in volume ratio) containing 0.3% ammonium was estimated (National Institute for Environmental Studies, 2017). The sorbent loaded with $C_{10–14}$-LAS was prepared in a similar manner as was 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 (National Institute for Environmental Studies, 2017). This was followed by the addition of 25 μL of the IS solution (100 ng 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 (Endo and Matsuura 2018). The membranes were used to separate two solutions in glass cells. A mixed $C_{10–14}$-LAS solution (32 mL, 100 μg L^{-1} each) and a NaCl solution (32 mL, 84 μg L^{-1}) were added to the donor and accepter 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).

LC-MS/MS conditions

The LC-20 system (Shimadzu Corporation, Kyoto, Japan) was used to perform the LC-MS/MS analysis. An InsertSustain C18 column (5 μm, 150 mm × 2.1 mm) (GL Sciences) 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-Quad^{TM} 4500 system, which is a tandem mass spectrometer, equipped with an electrospray ionization mass spectrometer source (AB Sciex Pte. Ltd. MA, 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.

Determination of linear range and sampling rate via static renewal experiments

Static renewal experiments were conducted to determine the sampling rate (R_s) as well as the linear ranges of the developed POCIS device as previously described (Noro et al. 2019, 2020). 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 on either side.

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 (Noro et al. 2019). 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.

$$M=m\times K_{\mathrm{d}}\times C_{\mathrm{w}}\times\left(1-e^{\left(-R_{\mathrm{s}}\times\frac{t}{m\times K_{\mathrm{d}}}\right)}\right)\cdots\ (\mathrm{Eq.1})$$

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

$$t_{\frac{1}{2}}=\ln 2\times m\times\frac{K_{\mathrm{d}}}{R_{\mathrm{s}}}\cdots\ (\mathrm{Eq.}\ 2)$$

Chamber tests

Chamber tests were conducted as previously described (Noro et al. 2019). 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 (Nishioka et al. 2019; Noro et al. 2019).

A stainless-steel tank containing tap water (volume, 27 L; flow rate, 9 cm s^{-1}) was used as the test chamber. The developed 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 C_{12}-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 C_{12}-LAS in the chamber should be at 1 mg L^{-1}, which is below the critical micellar concentration of 1.1 mg L^{-1} (International Programme on Chemical Safety, 1996). 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 C_{12}-LAS in the chamber decreased by half every day from the start of the second day. In short, the half-life period of the C_{12}-LAS concentration was 1 d. The water samples (1 mL) that were collected several times to check the C_{12}-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.

Field test

A field test was conducted at the Ishikawa River in southern Osaka, Japan. The basin area (222 km^2) and agricultural area (10 km^2) of the river were reported in a previous study (Yabuki et al. 2018). 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 developed 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. Additionally, 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.

R_s was estimated under 1500 rpm (18 cm s^{-1}) (see *Determination of linear range and sampling rate by static renewal experiments*), which was the same stirring condition that was employed in previous studies (Noro et al. 2019, 2020). Reportedly, R_s is basically constant, above the flow rate at 6 cm s^{-1} (Toteu Djomte et al. 2018). Therefore, in this study, it was reasonable to apply this determined R_s based on a static renewal experiment in the field test.

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 are shown in Fig. 1. The $C_{10–14}$-LAS was sorbed effectively onto two of the active carbon-type sorbents and one of the ion-exchange polymeric sorbents. (Fig. 1, Tables S2 and S3). However, the polymeric sorbents showed a weaker sorption performance. The log K_d values of the sorbents were determined as 5.9 (C_{12}) to >7 (C_{10}, C_{11}, C_{14}-LAS) for AC, 5.8 (C_{12}-LAS) to > 7 (C_{10}-LAS) for AC2, and 6.0 (C_{12}-LAS) to 6.9 (C_{10}-LAS) for Oasis WAX (Fig. 1 and Table S4). Thus, these three most performant sorbents (AC, AC2, and Oasis WAX) were selected as candidate sorbents for the recovery experiment.

The recovery test was conducted using AC, AC2, and Oasis WAX, which showed the best performances as candidate sorbents from the sorption experiments. The results of the recovery experiments showed that a $C_{10–14}$-LAS recovery rate of 78–104% when Oasis WAX was used as the sorbent, while the recovery rate was only 24–42% when AC and AC2 were used (Table S5). These results are consistent with the observation described above that AC and AC2 have stronger sorption toward $C_{10–14}$-LAS than Oasis WAX. Therefore, in this study, Oasis WAX, which showed strong sorption and high recovery efficiency, was selected as the best sorbent for the developed POCIS device.

Permeation experiments

With the PTFE membrane, the concentrations of C_{10}-LAS, C_{11}-LAS, and C_{12}-LAS reached equilibria rapidly (Fig. 2, Table S6). Further, the results corresponding to C_{13}-LAS and C_{14}-LAS showed that the PTFE filter absorbed longer-chain LAS only slightly (Fig. 2). The results corresponding to C_{10}-LAS and C_{11}-LAS in relation to the PES membrane were similar to those obtained using the PTFE membrane. Additionally, the equilibrium concentrations of C_{12}-LAS, C_{13}-LAS, and C_{14}-LAS in the accepter cell with the PES membranes installed were lower than those in the cell with the PTFE membranes installed, ranging from 50% (C_{12}-LAS) to 88% (C_{14}-LAS). These observations indicate that these longer-chain LASs were strongly absorbed onto the PES membrane (Fig. 2). 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 accepter 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. 5, Endo and Matsuura 2018), and it was observed that the fitted first-order rate constants of C_{11}-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 mm); these results agree with those reported in previous studies (Endo and Matsuura

2018, Noro et al. 2020). In summary, the 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 lagging.

Table 2. 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

[a] sodium decylbenzenesulfonate

[b] sodium undecylbenzenesulfonate

[c] sodium dodecylbenzenesulfonate

[d] sodium tridecylbenzenesulfonate

[e] sodium tetradecylbenzenesulfonate

Sampling rates and linear ranges

Oasis WAX was selected as the sorbent for the developed POCIS device meant for LAS monitoring. Therefore, the static renewal experiment was conducted using the developed 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. 3 and Tables 2, S7, and S8.

The R_s values and linear ranges of the LASs corresponding to the PTFE POCIS device were estimated using the model shown in Eq. 1 based on the K_d values obtained following the sorption experiment (Table S3, Fig. 1). 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), 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 POCIS device rapidly increased within the first seven days, after which the uptake rates decreased gradually. Therefore, it is possible that the developed 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 reaches the saturation.

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

Evaluation of the POCIS using the chamber test

The POCIS device was tested in a chamber in which non-steady-state conditions were replicated, with the peak C_{12}-LAS at 1,000 $\mu g\ L^{-1}$. The results obtained are shown in Fig. 4 and Tables S9, S10. Further, the average concentration of C_{12}-LAS in the chamber, which is a theoretical value that represents the POCIS-measured value, was calculated alongside the POCIS sampling.

The developed POCIS device captured the change in the concentration of C_{12}-LAS effectively (Fig. 4(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. 4(B)), and the differences between the POCIS-measured values and the TWA values were within 25% (Fig. 4(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 POCIS device within short sampling periods as shown in *Sampling rates and linear ranges* and Fig. 3.

Assuming a chemical leak accident, these results indicate that the developed POCIS device effectively captured changes in the concentration of C_{12}-LAS. Therefore, it would be suitable for application in monitoring LAS 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 $\mu g\ L^{-1}$ (Noro et al. 2019). Thus, it is necessary to optimize the POCIS device so that it can be applied in the detection of LAS at high concentrations.

Field test

The results of the field test are shown in Table 3 and Figs. 5 and 6. The LAS concentrations obtained based on the grab samples ranged from 118 (C_{13}-LAS, 17th June) to 1.66×10^3 (C_{11}-LAS, 8th June) ng L^{-1} (Fig. 5), and the mean concentrations of LAS in the grab samples (C_{mean}; ng L^{-1}) were 393 (C_{10}-LAS), 859 (C_{11}-LAS), 645 (C_{12}-LAS), and 274 (C_{13}-LAS) ng L^{-1} (Table 3, Fig. 5), 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} (Ministry of the Environment, Japan 2018). Thus, the measured values obtained in this study are comparable with those reported in literature (Ministry of the Environment, Japan 2018). In addition, the POCIS-measured values calculated using Eq. 1 were 375 ± 83 (C_{10}-LAS), 713 ± 185 (C_{11}-LAS), 673 ± 167 (C_{12}-LAS), and 467 ± 144 (C_{13}-LAS) ng L^{-1} (Table 3, Fig. 5). Even though the presence of C_{14}-LAS was not detected in the grab samples, LAS measurements using the developed 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. 6). 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. 6). 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 developed POCIS effectively captured LAS concentrations in the natural condition.

Table 3. 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 = 1 σ

[a] sodium decylbenzenesulfonate

[b] sodium undecylbenzenesulfonate

[c] sodium dodecylbenzenesulfonate

[d] sodium tridecylbenzenesulfonate

[e] sodium tetradecylbenzenesulfonate

Conclusions

The developed 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, chamber experiments showed that this optimized PTFE POCIS device responded sufficiently to a concentration spike under high concentration condition (~1 mg L^{-1}) and also showed sensitivity under low LAS concentration conditions (~1 μg L^{-1}) as evidenced by the results of the field test. 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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Figures

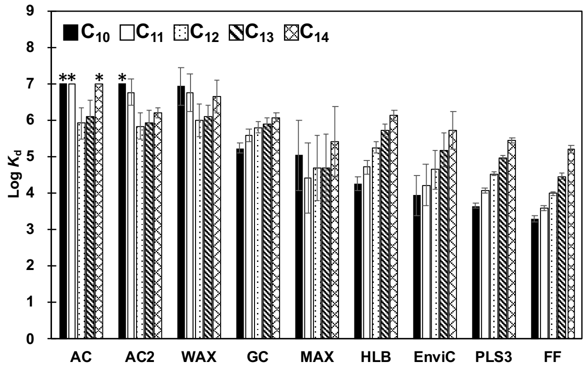

Fig. 1. Log of the apparent sorption coefficient (K_d; L kg^{-1}) values calculated based on the results of the sorption experiments. The target chemicals were sodium decylbenzenesulfonate (C_{10}), sodium undecylbenzenesulfonate (C_{11}), sodium dodecylbenzenesulfonate (C_{12}), sodium tridecylbenzenesulfonate (C_{13}), and sodium tetradecylbenzenesulfonate (C_{14}). The initial concentration of each analyte was 1,000 µg L^{-1}. The weight of the sorbents was 10 mg, and the volume of the solution was 10 mL. The error bars show 1 σ ($n = 3$).

AC: InertSep Active Carbon (GL Sciences), AC2: AC2 (Waters), WAX: Oasis WAX (Waters), GC: InertSep GC (GL Sciences), MAX: Oasis MAX (Waters), HLB: Oasis HLB (Waters), EnviC: Envi-carb (Supelco), PLS3: InertSep PLS3 (GL Sciences), FF: InertSep PharmaFF (GL Sciences). * and ** indicate log $K_d > 7$.

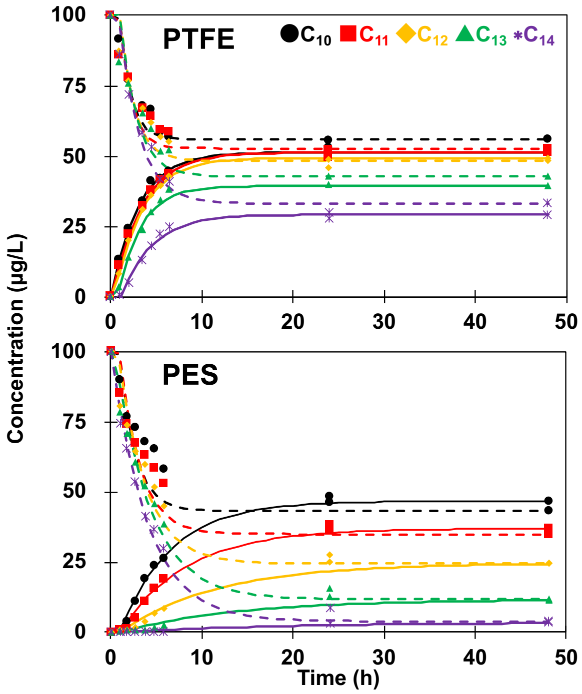

Fig. 2. Permeation experiments with polytetrafluoroethylene (PTFE) and polyethersulfone (PES) membrane filters. The target chemicals were sodium decylbenzenesulfonate (C_{10}), sodium undecylbenzenesulfonate (C_{11}), sodium dodecylbenzenesulfonate (C_{12}), sodium tridecylbenzenesulfonate (C_{13}), and sodium tetradecylbenzenesulfonate (C_{14}). The lines indicate the first-order model fit (Eq. 5, Endo and Matuura, 2018). The solid lines and dashed lines indicate the results of the donner cell and the accepter cell, respectively.

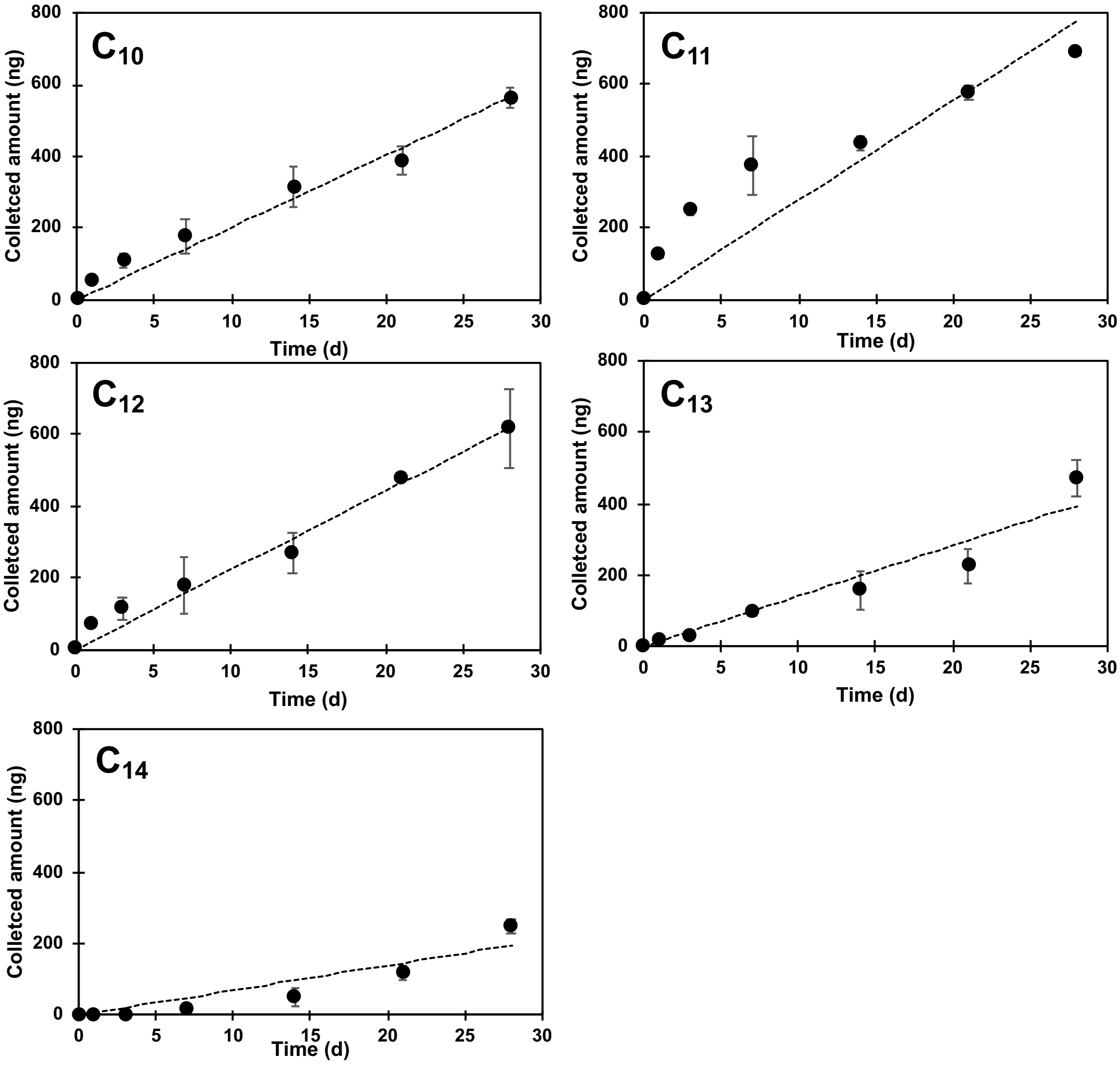

Fig. 3. Amounts of linear alkylbenzene sulfonates accumulated in the polar organic chemical integrative sampler. The target chemicals were sodium decylbenzenesulfonate (C_{10}), sodium undecylbenzenesulfonate (C_{11}), sodium dodecylbenzenesulfonate (C_{12}), sodium tridecylbenzenesulfonate (C_{13}), 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$\boldsymbol{\sigma}$ (n = 3), and the dotted line indicates model fitting (Eq. 1) with the K_d values based on the sorption experiments.

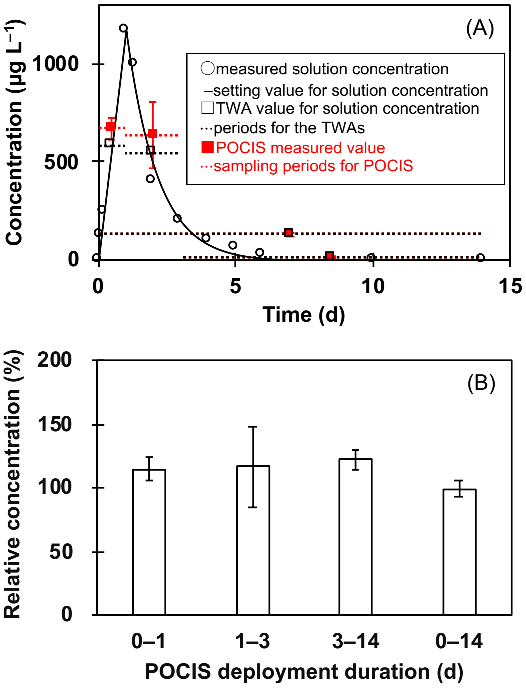

Fig. 4 Comparison of polar organic chemical integrative sampler (POCIS)-measured values with time-weighted average (TWA) values based on the concentrations of sodium dodecylbenzenesulfonate in the aqueous solution. (A) Time series of the chamber experiment. The vertical error bar shows 1σ (n = 3). (B) Ratio of POCIS-measured values to TWA values. The vertical error bar shows 1σ (n = 3).

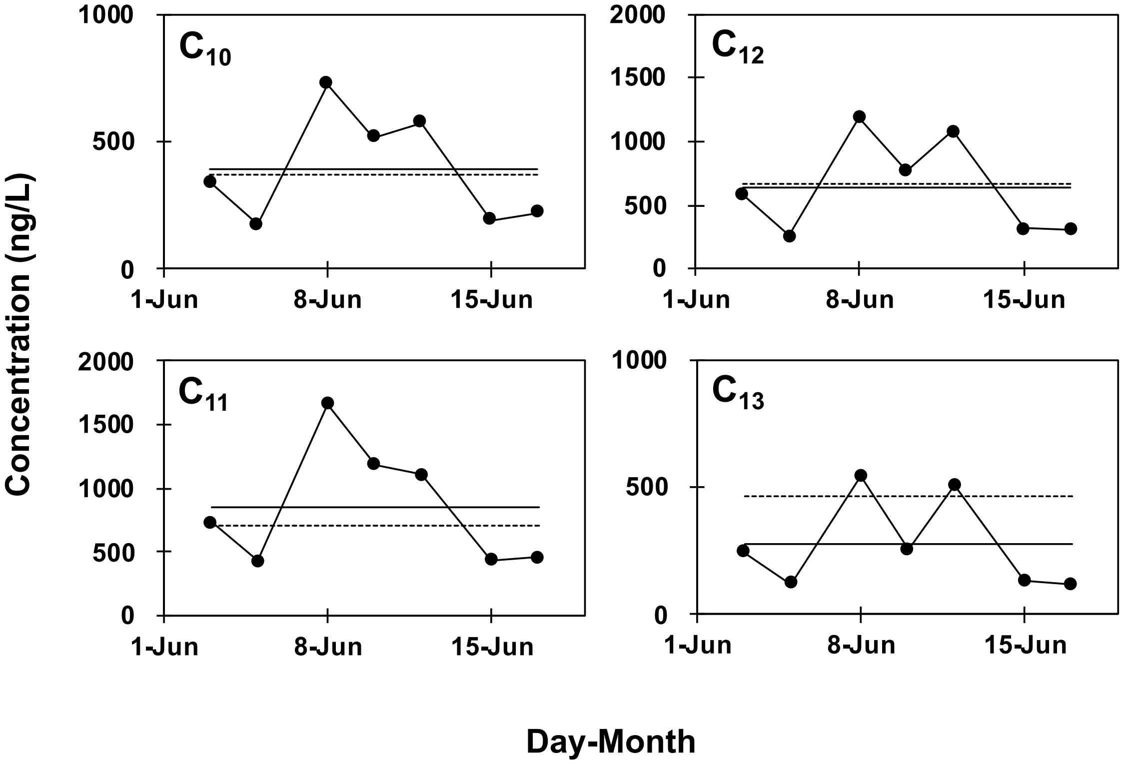

Fig. 5. Results of field test conducted at the Ishikawa River for sodium decylbenzenesulfonate (C_{10}), sodium undecylbenzenesulfonate (C_{11}), sodium dodecylbenzenesulfonate (C_{12}), and sodium tridecylbenzenesulfonate (C_{13}). The closed circles show the concentration measured via grab samplings. 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.

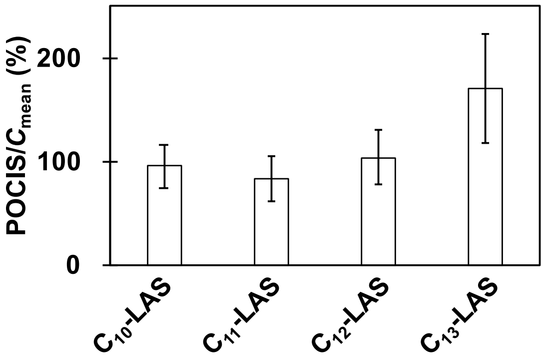

Fig. 6. Ratio the POCIS-measured values to the mean values corresponding to the grab samples (C_{mean}) based on the field test. The detected chemicals were sodium decylbenzenesulfonate (C_{10}-LAS), sodium undecylbenzenesulfonate (C_{11}-LAS), sodium dodecylbenzenesulfonate (C_{12}-LAS), and sodium 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).