Innovative receiving phase for Chemcatcher® passive sampler for phosphorus in the water environment: Calibration of sampling rate by water temperature and pH

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Abstract

Passive sampling is a technique for monitoring orthophosphate (PO_4-P) in the water environment. Compared with traditional grab sampling followed by PO_4-P quantification, kinetic-type passive samplers such as Chemcatcher® express representative concentrations of PO_4-P as time-weighted average concentrations (C_{TWA}). They can also potentially evaluate much lower PO_4-P concentrations, but the available receiving phases of Chemcatcher® used for PO_4-P were extremely limited. We developed a new receiving phase, the PSfZS sheet, comprising a zirconium sulfate–surfactant micelle mesostructure and polysulfone matrix. We examined its performance in terms of PO_4-P sorption characteristics, PO_4-P selectivity, and PO_4-P sampling rate (R_s). Its capacity was adequate (12.0 μg-P/cm^2) and selectivity for PO_4-P uptake was good. The R_s for PO_4-P increased with increasing water temperature (8.1–29.1°C) and decreasing pH (4.1–9.7) in a laboratory calibration, and ranged from 5.27×10^{-2} L/d to 1.66×10^{-1} L/d. We placed the samplers in a municipal wastewater treatment plant, a shallow eutrophic lake, and an oligotrophic caldera lake. The R_s in the deployment sites was calibrated by monitored water temperature and pH. The estimated C_{TWA} of PO_4-P in the municipal wastewater treatment plant was similar to the averaged concentration of soluble reactive phosphorus determined by multiple grab

samplings. In the lake deployments, we found that the new sampler can quantify C_{TWA} values of PO_4-P below 10 μg/L, and thus it provides more technical monitoring options and contributes to the conservation and management of the water environment.

Keywords: Orthophosphate; Soluble reactive phosphorus; Passive sampling; Sorption; Zirconium; Eutrophication

1. Introduction

Excess loading of nutrients into closed water bodies causes eutrophication, one of the world's most common and serious environmental issues (Le Moal *et al.*, 2019). Eutrophication can lead to algal blooms that further deplete dissolved oxygen, increase biodiversity loss, and introduce problems for water use. In addition, recent climate change is expected to increase eutrophication risks in rivers and lakes (Charlton *et al.*, 2018; Chen *et al.*, 2020; Robertson *et al.*, 2016). Phosphorus (P) plays an important role in eutrophication because it is generally the nutrient that limits primary production (Liang *et al.*, 2020). Among the various forms of P, orthophosphate (PO_4-P) is the most bioavailable and is rapidly absorbed by algae (Reynolds and Davies, 2001). Therefore, accurate

46 monitoring of PO_4-P concentrations in lakes, rivers, and at point sources (e.g., wastewater
47 treatment plants) is necessary to support conservation and management of water bodies.
48
49 Monitoring of PO_4-P concentration is often performed by traditional grab sampling
50 followed by sample filtration and PO_4-P quantification. There are two problems with this
51 general process. One is the sensitivities of molybdenum blue absorption spectroscopy and
52 ion chromatography, which are widely used to determine PO_4-P concentrations. The limit of
53 quantification (LOQ) of these analytical methods is above 10 μg-P/L (APHA, 2012).
54 Therefore, determining lower PO_4-P concentration, which is necessary for the adequate
55 management of natural water bodies, is difficult. Inductively coupled plasma mass
56 spectrometry (ICP-MS) can determine such low P concentrations below 10 μg-P/L.
57 However, the form of P determined by ICP-MS analysis is the total P in the sample, and not
58 the PO_4-P form. Although high-performance liquid chromatography (HPLC) coupled with
59 ICP-MS (HPLC-ICP-MS) or solid-phase extraction can determine low concentrations of
60 PO_4-P (Ma *et al*., 2017; Venkatesan *et al.*, 2018), they are very costly. The other difficulty
61 in the general process is that it is unclear whether representative PO_4-P concentration data
62 are obtained. Grab sampling followed by PO_4-P quantification only provides “snapshots” of

63 PO_4-P concentrations at a certain sampling time. Concentrations of PO_4-P can fluctuate
64 over time owing to physicochemical and biological processes in the water environment
65 (Amano *et al.*, 2010; Rixon *et al.*, 2020). Frequent grab sampling and installation of an
66 autosampler may be viable options to obtain representative concentration data (Fones *et al.*,
67 2020), but they are costly and time consuming.
68
69 Passive sampling can solve these two problems. The passive sampling technique is based
70 on diffusion followed by sorption of the dissolved analyte from bulk water to the receiving
71 phase of a passive sampler (Kot-Wasik *et al.*, 2007; Vrana *et al.*, 2005). The dissolved
72 analyte passes through a diffusion-limiting membrane, and it gradually accumulates in the
73 receiving phase during sampler deployment in the water environment. After sampler
74 deployment, a concentrated solution of the analyte can be obtained by eluting the analyte
75 from the receiving phase. Passive sampling has been successfully applied for monitoring
76 compounds that exist at low concentration levels in the water environment. Passive
77 samplers can therefore be effective tools for obtaining a representative concentration of
78 PO_4-P present at low concentration levels.
79

Passive samplers can be divided into two types: kinetic or equilibrium (Vrana *et al.*, 2005). Kinetic samplers are suitable for monitoring PO_4-P at low concentrations because they provide time-weighted average concentrations (C_{TWA}), which reflect fluctuation of the analyte concentration during sampler deployment. Kinetic samplers such as Chemcatcher®, diffusive gradients in thin films (DGT), and polar organic chemical integrative samplers (POCIS) are generally used in the kinetic regime of analyte accumulation during field deployment (Charriau *et al.*, 2016; Davison and Zhang, 2012; Harman *et al*., 2012). Among these kinetic passive samplers, DGT for PO_4-P has been developed and is widely used in environmental studies (Ding *et al*., 2010, 2011, and 2016; Panther *et al.*, 2010; Zhang *et al.*, 1998). In DGT configuration, two different hydrogels (i.e., diffusive gel and binding gel) and a diffusion-limiting membrane are used. Therefore, the configuration and preparation of the sampler are relatively complicated. In addition, such hydrogel-based DGT is difficult to handle and mechanical resistance is weak (Zhang *et al.*, 2018). Compared with DGT-based passive samplers, the Chemcatcher® configuration is simple and it only uses a single diffusion-limiting membrane and receiving phase inside the sampler housing (Kingston *et al*., 2000; Persson *et al.*, 2001). However, application of the Chemcatcher® type of passive sampler for PO_4-P monitoring has rarely been reported. Knutsson *et al.* (2013) reported its

use for phosphate and nitrate by using a Empore™ Anion-SR disk as a receiving phase. However, detailed characteristics of the developed sampler were not evaluated in terms of sampler capacity and selectivity toward PO_4-P. In addition, deployment of the sampler was limited only to a municipal wastewater treatment plant. While three types of binding gels for PO_4-P (ferrihydrite gel, Metsorb® gel, and zirconium oxide gel) have been used for DGT configuration (Ding *et al.*, 2010, 2011 and 2016), only one type of receiving phase for PO_4-P has been reported for Chemcatcher® configuration. Development of a new receiving phase for PO_4-P used with the Chemcatcher® configuration, and detailed assessment of the performance of the Chemcatcher® passive sampler for PO_4-P, will thus facilitate passive PO_4-P sampling.

We previously developed a sorbent for PO_4-P known as zirconium sulfate–surfactant micelle mesostructure (ZS) (Pitakteeratham *et al.*, 2013). This sorbent has a regular array of surfactant micelles and contains hydrogen sulfate ions (HSO_4^-) in its wall. ZSs can sorb PO_4-P in water via an ion-exchange process with high selectivity and high sorption capacity (114 mg P/g-ZS). In this study, a novel receiving phase for PO_4-P was developed by embedding ZS in a polysulfone (PSf) matrix. This allowed us to set up a Chemcatcher®-

114 based passive sampler for PO_4-P by using the newly developed receiving phase. We
115 investigated the orthophosphate sorption characteristics, PO_4-P selectivity, and PO_4-P
116 sampling rate of the passive sampler. Its performance was also assessed in field
117 applications. The C_{TWA} of PO_4-P was estimated at a municipal wastewater treatment plant,
118 in a shallow eutrophic lake, and in an oligotrophic caldera lake.
119
120 **2. Materials and Methods**
121 *2.1 Preparation of receiving phase for PO_4-P and configuration of passive sampler*
122 Chemicals were purchased from Fujifilm Wako Pure Chemical Corporation (Osaka, Japan),
123 Kanto Chemical Co., Inc. (Tokyo, Japan), and Sigma-Aldrich Japan K.K. (Tokyo, Japan)
124 and used without further purification. ZS was prepared as previously described
125 (Pitakteeratham *et al.*, 2013; see Supplementary materials). Synthesized ZS powder was
126 passed through a 63-μm testing sieve prior to use. A ZS-embedded PSf sheet (PSfZS sheet)
127 was prepared as previously described, with some modifications, and used as the receiving
128 phase for PO_4-P (Furuya *et al*., 2017). The polymer solution was prepared by dissolving
129 polysulfone (PSf), polyvinylpyrrolidone (PVP), and ZS in *N*-methyl-2-pyrrolidone (NMP),
130 and the PSfZS sheets were prepared by a non-solvent induced phase separation process.

131 Polyvinylpyrrolidone (3.40 g, MW−40,000 g/mol) and *N*-methyl-2-pyrrolidone (14.25 g)
132 were added to a test tube and heated to 135°C with an aluminum block heater, after which
133 PSf (3.40 g, MW−35,000 g/mol) was added in small increments. The polysulfone was
134 completely dissolved in NMP by stirring with a glass rod. The solution was subsequently
135 cooled to 90°C. Then, 1.70 g of ZS was added and dispersed in the mixture, after which
136 dissolved air was removed under vacuum. Approximately 9g of the mixture was dropped
137 onto a glass plate and spread to a 200-μm thickness using a film applicator (Elcometer
138 3545; Elcometer Ltd, Manchester, UK). The glass plate was then immersed in Milli-Q
139 water (18.25 MΩ cm, 40°C) to cause non-solvent induced phase separation. The PSfZS
140 sheet was then peeled from the glass plate and put into Milli-Q water for 1 day. Next, the
141 membrane sheet was soaked in a 500 mg/L NaClO solution at 70°C for 2 h to remove
142 residual PVP. The sheet was then transferred to 50°C Milli-Q water and soaked for 2 h.
143 Finally, the prepared PSfZS sheet was cut into a circle with a diameter of 47 mm and
144 preserved in Milli-Q water prior to use.
145
146 A passive sampler comprises a PSfZS sheet, a diffusion-limiting membrane, and a sampler
147 housing (Fig. S1). A polyethersulfone (PES) membrane (Supor®100; Pall Corporation, Port

148 Washington, NY, USA) was used as a diffusion-limiting membrane. The diameter, pore
149 size, and thickness of the PES membrane were 47 mm, 0.1 μm, and 132 μm, respectively. A
150 Chemcatcher® (T.E Laboratories Ltd, Tullow, Ireland) was used as a sampler housing.
151 Prepared passive samplers were stored in Milli-Q water.
152
153 *2.2 Kinetics and isotherm studies on PO_4-P sorption*
154 Batch sorption experiments were carried out to examine the sorption kinetics and isotherm
155 behaviors of PO_4-P on the PSfZS sheet. A stock solution of PO_4-P was prepared by
156 dissolving KH_2PO_4 in Milli-Q water. In the sorption kinetic experiments, PSfZS sheets
157 (17.3 cm^2) were introduced into vials with 50 mL of PO_4-P solutions (10 mg-P/L, pH 6.1).
158 The vials were shaken continually at 20°C for 48 h using a shaker. During the sorption
159 process, 4 mL of the solution was collected from the vials at preset time intervals. The PO_4-
160 P concentrations in the solution were determined by the molybdenum blue method with a
161 spectrophotometer (V-730; Jasco Corporation, Tokyo, Japan) (Murphy *et al.*, 1962). The
162 limit of detection (LOD, 3σ/slope) and LOQ (10σ/slope) for PO_4-P in the molybdenum
163 blue method were determined based on the standard deviation (σ) of 12 blank solutions.
164 The LOD and LOQ in the molybdenum blue method were 2.27 μg-P/L and 7.57 μg-P/L,

165 respectively (Fig. S2). The sorbed amount of PO_4-P was calculated by Eqn (1):

166 $$q_t = \frac{(C_0 - C_t)V}{S}, \quad (1)$$

167 where q_t is the amount of sorbed PO_4-P (μg-P/cm^2), C_0 is the initial PO_4-P concentration

168 (μg-P/L), C_t is the PO_4-P concentration (μg-P/L) after time t, V is the solution volume (L),

169 and S is the surface area of the PSfZS sheet (cm^2). The equilibrium sorption amounts were

170 analyzed using pseudo-second order kinetics expressed by Eqn (2) (Ho and McKay, 1999):

171 $$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e}, \quad (2)$$

172 where k_2 is the pseudo-second order rate constants (cm^2/(μg-P·h)) and q_e is the equilibrium

173 sorption amount of PO_4-P on the PSfZS sheet (μg-P/cm^2).

174

175 Sorption isotherm experiments were carried out in the batch mode experiments as described

176 above. The initial pH of the PO_4-P solution was adjusted to 7.0 and the vials were shaken

177 continually at 22°C for 24 h. The PO_4-P sorption data were fitted to the Langmuir isotherm

178 model in Eqn (3) (Langmuir, 1981):

179 $$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}, \quad (3)$$

180 where q_{max} is the maximum sorption capacity (μg-P/cm^2) and K_L is the Langmuir isotherm

181 constant.

182

183 *2.3 Selectivity of passive sampler for PO_4-P*

184 Batch sorption experiments in the presence of possible competing anions or natural organic
185 matter (NOM) were conducted to investigate the PO_4-P selectivity of the passive sampler. A
186 stock solution containing five anions (Br^-, Cl^-, F^-, NO_3^-, and SO_4^{2-}; 10 mM each) was
187 prepared by dissolving sodium salts in Milli-Q water. A stock solution of
188 hydrogencarbonate (HCO_3^-; 10 mM) was prepared by dissolving $NaHCO_3$ in Milli-Q
189 water. Suwannee River NOM (RO isolation; 2R101N) was purchased from the
190 International Humic Substances Society and was used as NOM standard. The NOM was
191 dissolved in Milli-Q water, filtered through a 0.45-μm pore size membrane (A045A047A;
192 Toyo Roshi Kaisya, Ltd, Tokyo, Japan), and stored as NOM stock solution (100 mg-C/L).
193 We prepared PO_4-P solutions (0.01 mM) with different concentrations of anions or NOM
194 by mixing and diluting the stock solutions with Milli-Q water. The initial pH of the test
195 solutions was adjusted to 7.0 by adding NaOH (0.1 M). Each passive sampler was placed in
196 a 500 mL glass beaker with the prepared test solution (200 mL). The beakers were covered
197 with cling wrap and then stored at 22°C in an incubator without shaking. Initial
198 concentrations of anions (Br^-, Cl^-, F^-, NO_3^-, and SO_4^{2-}) in the test solutions were

199 determined using an HPLC system (Dionex Integrion; Thermo Fisher Scientific K.K.,
200 Tokyo, Japan) equipped with Dionex IonPac^{TM} AS23 (4 mm × 250 mm) and Dionex
201 IonPac^{TM} CS16 (5 mm × 250 mm) columns. Initial concentrations of dissolved inorganic
202 carbon (DIC) and dissolved organic carbon (DOC) in the test solutions were determined
203 using a total organic carbon analyzer (TOC-V CSH; Shimadzu Corporation, Kyoto, Japan).
204 After the samplers had soaked in the test solutions for 5 days, PO_4-P concentrations were
205 determined, and then the sorbed amount of PO_4-P was calculated. Variations in the amount
206 of sorbed PO_4-P among the samplers (n = 12) were also investigated using the same
207 procedure described above.
208
209 *2.4 Elution of PO_4-P from the sampler*
210 Elution of PO_4-P from PO_4-P-loaded PSfZS sheets was studied. Samplers loaded with PO_4-
211 P were prepared by batch sorption experiments (subsection 2.3). After the samplers had
212 soaked in the PO_4-P solutions for 5 days, PO_4-P concentrations were determined, and then
213 the amount of PO_4-P sorbed was calculated. The PO_4-P-loaded PSfZS sheet was taken from
214 the sampler and was then immersed in a 0.3 M NaOH solution (50 mL or 10 mL) for 24 h
215 at 20°C in an incubator. The maximum phosphorus desorption efficiency from ZS occurs at

values above pH 13.3 (Pitakteeratham *et al.*, 2013), and so 0.3 M NaOH was selected. During the desorption process, 2 mL of the solution was collected 1, 2, 3, 6, 12, and 24 h after the experiment began. After the sample had been diluted at least twofold with Milli-Q water, the PO_4-P concentration was determined. Calculation of the PO_4-P elution efficiency was based on the sorbed and the desorbed amount of PO_4-P.

2.5 Determination of sampling rate for PO_4-P

Flow-through sorption experiments were conducted to obtain the sampling rate of the passive sampler for PO_4-P (Fig. S3). The PO_4-P solution (0.16 mg P/L) was continuously supplied to a tank (10 L) at constant flow rate (4.9 mL/min) using a peristaltic pump. Water temperature (8.1–29.1°C) was controlled using a water jacket and water circulator. The pH (4.1–9.7) was also controlled with a digital pH controller by supplying NaOH solution (0.1 M) into the tank with a peristaltic pump. A pH/temperature data logger (Hobo MX2501; Onset Computer Corporation, Bourne, MA, USA) was placed on the bottom of the tank to record pH and water temperature every 10 min. Each experiment consisted of six passive samplers, where two samplers were taken from the tank at specific time intervals (after 1, 3, and 7 days). The PO_4-P solution in the tank was continuously stirred at 50 rpm with a

233 stirrer. The flow velocity above the sampler surface was 5 cm/s, which was determined by
234 an electromagnetic velocity meter (ACM2-RS; JFE Advantech Co., Ltd, Nishinomiya,
235 Japan). During the experiment, the PO_4-P concentrations in the tank were determined every
236 day. The sorbed amount of PO_4-P on the sampler was determined according to the
237 procedure described in subsection 2.4.
238
239 *2.6 Field deployments of passive sampler*
240 Passive samplers were deployed in an existing full-scale municipal wastewater treatment
241 plant (Soseigawa wastewater treatment plant, Sapporo, Japan) to obtain the C_{TWA} of PO_4-P.
242 A conventional activated sludge process is used in the plant and the treatment capacity is
243 144,000 m^3/d. Effluent from the disinfection basin was continuously supplied to a bucket
244 (10 L) at a flow rate of 4.5 L/min (Fig. S4). Passive samplers and a pH/temperature data
245 logger were put in the bucket and the samplers were deployed for 3 or 7 days (from 7
246 December 2021 to 14 December 2021).
247
248 Passive samplers were also deployed in two lakes: Lake Barato and Lake Kussharo. Lake
249 Barato is an oxbow lake in the suburban areas of Sapporo and Ishikari cities, Hokkaido,

Japan. Lake Barato is shallow and eutrophic (Hafuka *et al.*, 2021), and has a total area, average depth, and total length of 4.67 km^2, 2.8 m, and 20.2 km, respectively. In contrast, Lake Kussharo is an oligotrophic lake in Akan-Mashu National Park, eastern Hokkaido, Japan. It is the largest caldera lake in Japan, and its total area, average depth, maximum depth, and shore length are 79.3 km^2, 28.4 m, 118 m, and 57 km, respectively. Passive samplers and pH/temperature data loggers were put into baskets, which were deployed in the study sites of Lake Barato (+43° 17′ 46.18″, +141° 35′ 42.28″) and Lake Kussharo (+43° 56′ 07.35″, +144° 33′ 93.87″) using buoys (Figs S5 and S6). The water depths of the study sites in Lake Barato and Lake Kussharo were 0.9 m and 1.0 m, respectively. Passive samplers were placed 0.3 m below the water surface and were deployed for 7 days (from 29 June 2021 to 6 July 2021) and a maximum of 50 days (from 6 September 2022 to 26 October 2022) in Lake Barato and Lake Kussharo, respectively. The collected samplers were then placed in Milli-Q water and brought to the laboratory.

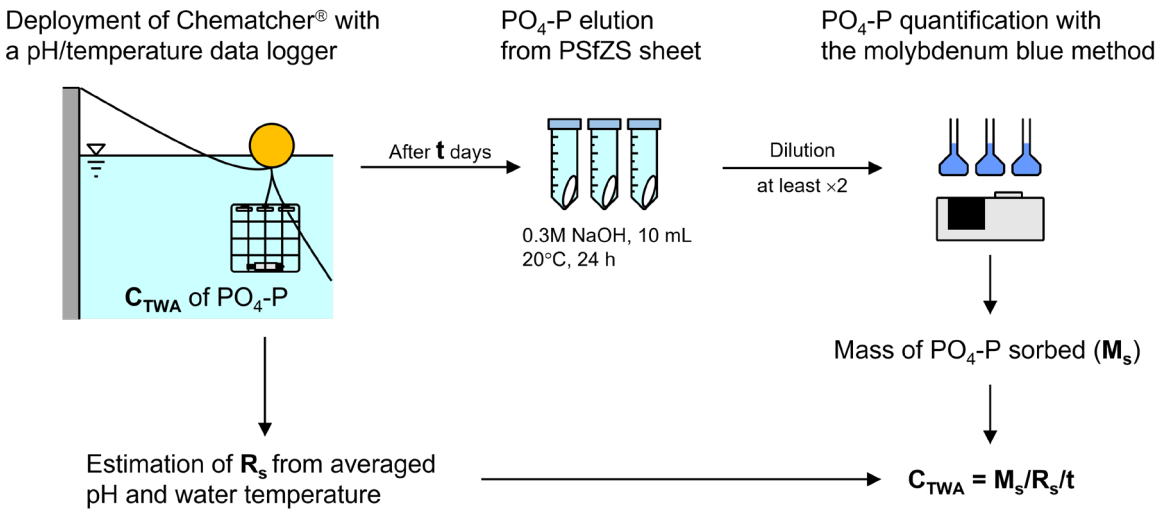
Grab samplings followed by P quantification were also conducted during the sampler deployments in the three study sites. For the samples obtained from Soseigawa wastewater treatment plant and Lake Barato, concentrations of soluble reactive P (SRP) and dissolved P

267 (DP) were determined with the molybdenum blue method after sample pretreatment
268 (Hafuka *et al.*, 2021). Concentrations of DP in Lake Kussharo were determined by ICP-MS
269 because of its low concentrations. The samples were filtered through glass fiber filters with
270 a nominal pore size of 0.7 μm (Whatman™ GF/F, GE Healthcare Life Sciences,
271 Amersham, UK). A 40 mL portion of each filtered sample was digested with concentrated
272 HNO_3 (2 mL) at 105°C for 30 min in a vial on an aluminum block heater. The P
273 concentrations of the digested samples were determined by using ICP-MS (8800 ICP-QQQ;
274 Agilent Technologies, Inc., Santa Clara, CA, USA). The LOD and LOQ in the ICP-MS
275 method were 0.0403 μg-P/L and 0.134 μg-P/L, respectively (Fig. S7).
276
277 After the deployment, PO_4-P was eluted from the PSfZS sheet and the C_{TWA} of PO_4-P was
278 determined by Eqn (4) (Charriau *et al.*, 2016):
279 $$M_s = k_0 \times A \times C_{TWA} \times t = R_s \times C_{TWA} \times t \quad , (4)$$
280 where M_s is the mass of PO_4-P sorbed on the PSfZS sheet (μg-P), k_0 is the overall mass
281 transfer coefficient (10^3 cm/d), A is the surface area of the sampler exposed to bulk water
282 (cm^2), C_{TWA} (μg-P/L) is the time-averaged concentration of PO_4-P, R_s (L/d) is the sampling
283 rate, and t (d) is the deployment time. The surface area of the used sampler (A) is 13.85

284 cm^2. The R_s value was determined by averaged pH and water temperature during the

285 deployment. The estimation procedure for C_{TWA} of PO_4-P is shown in Fig. 1.

286



287

288 **Fig. 1.** Procedure for the estimation of time-weighted average concentrations of PO_4-P in

289 the water environment using the passive sampler and a pH/temperature data logger.

290

291 **3. Results and Discussion**

292 *3.1 Sorption kinetics and isotherm of PSfZS sheet for PO_4-P*

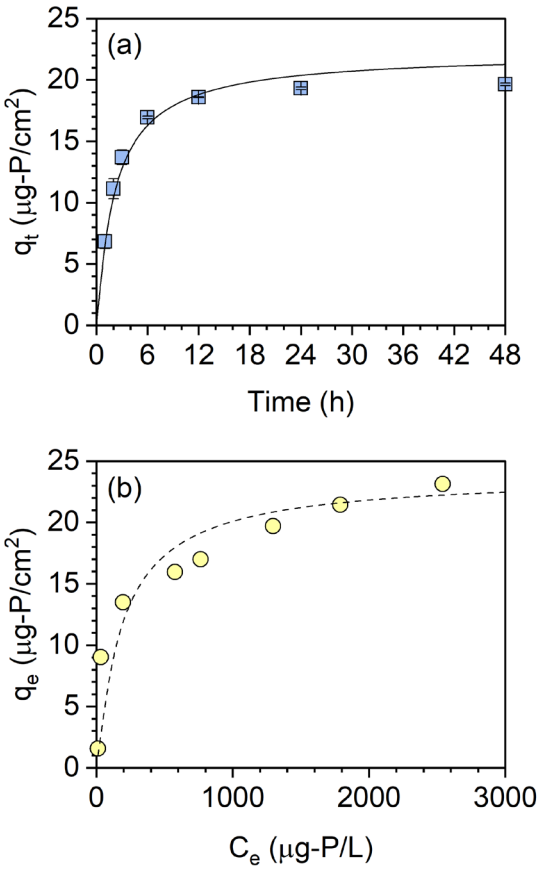
293 The receiving phase used for the PO_4-P passive sampler must have a sufficient capacity for

294 PO_4-P to be taken up rapidly. For this reason we investigated the capacity of the PSfZS

295 sheet for PO_4-P. Figure 2-(a) shows the sorption kinetics of a PSfZS sheet for PO_4-P.

296 Sorption equilibrium was reached in 24 h, and the kinetic parameters were evaluated

297 according to the pseudo-second order equations. The q_e and k_2 were 22.2 μg-P/cm^2 and
298 0.0208 cm^2/μg-P/h, respectively (r^2 = 0.989). Sorption isotherm experiments were
299 performed at pH 7.0 for 24 h (Fig. 2-(b)), which is a sufficient period of time for sorption
300 equilibrium to be reached, according to the kinetic studies. The experimental data were
301 analyzed with the Langmuir isotherm model. The maximum PO_4-P sorption capacities
302 (q_{max}) of the PSfZS sheet were estimated to be 23.9 μg-P/cm^2, and K_L was 0.00532 L/μg-P
303 (r^2 = 0.989). Considering that kinetic-type passive samplers are used in the regime of linear
304 increase in accumulation of analyte, our developed sampler should be used within 12.0 μg-
305 P/cm^2 (i.e., half of the maximum capacity) (Vrana *et al*., 2005). The capacity of this
306 sampler for PO_4-P is comparable to that of DGT using Metsorb® gel and is higher than that
307 of DGT using ferrihydrite, which is the most popular PO_4-P-receiving gel in the DGT
308 techniques (Table S1).
309



310

311 **Fig. 2.** (a) Sorption kinetics and (b) isotherm of PSfZS sheets for PO_4-P. Solid and dotted

312 lines are predictions calculated using the pseudo-second order kinetic model and the

313 Langmuir isotherm model, respectively.

314

315 *3.2 PO_4-P selectivity of passive sampler*

316 To assess the PO_4-P selectivity of the passive sampler, the interfering effects of co-existing

317 anions and NOM were investigated in the batch experiments (Fig. 3). Five co-existing

318 anions (Br^-, Cl^-, F^-, NO_3^-, and SO_4^{2-}) did not influence the amount of PO_4-P sorbed on the
319 passive sampler, even if their concentrations were 300 times higher than that of PO_4-P (Fig.
320 3-(a)). These results indicate that the sampler has high PO_4-P selectivity toward these co-
321 existing anions. Co-existing NOM also did not affect the amount of PO_4-P sorbed (Fig. 3-
322 (b)). Because dissolved organic matter is always present in the water environment, there
323 should be no interference from dissolved organic matter toward PO_4-P uptake by the
324 sampler. In contrast, the amount of PO_4-P sorbed on the passive sampler decreased in the
325 presence of HCO_3^- (Fig. 3-(c)), decreasing by 17% when the co-existing HCO_3^-
326 concentration was 8.0 mg-C/L. This result indicates that HCO_3^- should be considered to be
327 a possible interfering anion for passive PO_4-P sampling. This result agrees with our
328 previous research on ZS sorbent, when we reported that HCO_3^- can be an interfering anion
329 and that it reduces the sorption capacity of ZS for PO_4-P (Pitakteeratham *et al.*, 2013).
330 Variations in the amount of PO_4-P sorbed among passive samplers were also investigated
331 because the receiving phase was our own construction. As a result, the standard deviations
332 of the amount of PO_4-P sorbed among 12 samplers were within 3% (Fig. S8), which
333 indicates that the quality of the newly manufactured receiving phase was uniform and
334 stable.

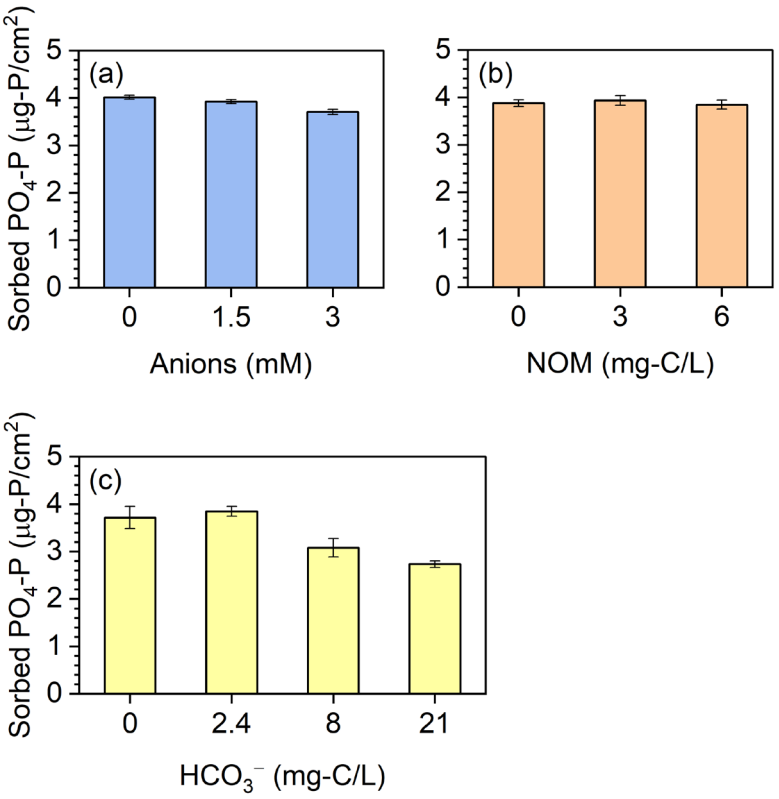
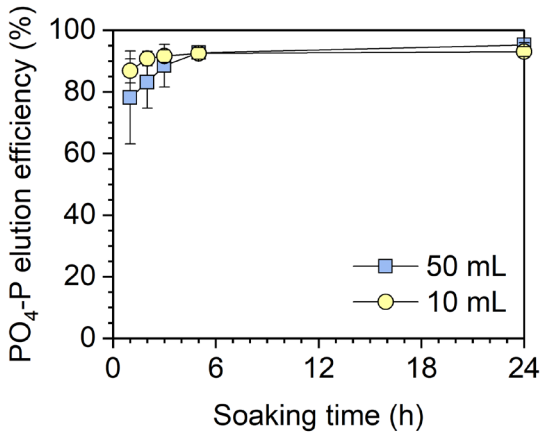


Fig. 3. Amount of PO_4-P sorbed on passive samplers in the batch experiments with co-existing (a) five anions (Br^-, Cl^-, F^-, NO_3^-, and SO_4^{2-}), (b) natural organic matter, and (c) HCO_3^-.

3.3 Elution of PO_4-P from PSfZS sheet

Elution of PO_4-P from the receiving phase (i.e., PSfZS sheet) is necessary to obtain M_s and to estimate C_{TWA}. The elution efficiency of PO_4-P was 78% after the PO_4-P-loaded PSfZS

344 sheets had been soaked for 1 h in 50 mL of 0.3 M NaOH aqueous solution (Fig. 4). The
345 elution efficiency gradually increased and reached 95% after soaking for 24 h. The volume
346 of liquid used in the elution process is important for the later PO_4-P quantification process.
347 Although a sufficient sample volume for PO_4-P quantification needs to be ensured, a
348 limited liquid volume can lead to a more concentrated solution of PO_4-P being obtained.
349 Therefore, the effect of liquid volume of 0.3 M NaOH solution on the PO_4-P elution
350 efficiency was also investigated. The elution efficiency was also as high as 93% when 10
351 mL of 0.3 M NaOH solution was used when soaking for 24 h. The PO_4-P elution
352 efficiencies in this study were as high as those of other PO_4-P passive samplers based on
353 DGT (Table S1). These results show that PO_4-P can be eluted with high efficiency by a
354 simple procedure.
355



356

357 **Fig. 4.** Elution efficiency of PO_4-P from PO_4-P-loaded PSfZS sheets with 0.3 M NaOH

358 aqueous solution.

359

360 *3.4 Effects of water temperature and pH on sampling rate*

361 Calibrating the Chemcatcher® passive sampler (i.e., determining k_0 or R_s) is an essential

362 step for estimating C_{TWA} before field deployments. Calibration is generally performed by

363 exposing samplers to known analyte concentrations under controlled conditions in the

364 laboratory (Charriau *et al.*, 2016). When the sampler is used in the kinetic regime of analyte

365 accumulation and the exposed surface area of the sampler (A) is fixed, the M_s/A increases

366 linearly with deployment time, and Eqn (4) is valid (subsection 2.6). Plots of $M_s/A/C_{TWA}$

367 versus deployment time provide k_0 as the slope value of the plots. Because the M_s on the

368 developed passive sampler can be affected by water temperature and pH (Lissalde *et al.*,

2016), the effects of these parameters on the M_s were investigated in the flow-through PO_4-P sorption experiments, and R_s values were obtained in 11 conditions (Table 1). The accumulated mass of PO_4-P per sampler surface (M_s/A) increased during sampler deployment (Fig. 5). The M_s/A were within half of the maximum capacity of the sampler for PO_4-P (12.0 μg-P/cm^2), which indicates the sampler still had remaining capacity for PO_4-P in these experimental systems. The M_s/A increased as the water temperature rose (Fig. 5-(a)). This result was mainly due to the temperature dependence of the diffusion coefficient of PO_4-P. We observed that the M_s/A increased as pH decreased (Fig. 5-(b)). This result came from preferable sorption of $H_2PO_4^-$ to HPO_4^{2-} by ZS (Furuya *et al*., 2017; Pitakteeratham *et al.*, 2013). Considering the acid dissociation constant values of phosphoric acid (pKa_1 = 2.16, pKa_2 = 7.20, and pKa_3 = 12.35) (Benjamin, 2002), an increase in pH above 7.20 makes the PO_4-P species more negatively charged. Therefore, the increased formation of HPO_4^{2-} decreased the M_s in the passive sampler.

Overall mass transfer coefficients (k_0) of PO_4-P were obtained by plotting $M_s/A/C_{TWA}$ toward deployment time using the data obtained in the flow-through PO_4-P sorption experiments (Fig. S9). The linear relationship between $M_s/A/C_{TWA}$ and deployment time

386 was obtained, and the slope provided the k_0 value. The R_s value was obtained by
387 multiplying the k_0 and sampler surface (A). The R_s ranged from 5.27×10^{-2} L/d to $1.66 \times$
388 10^{-1} L/d depending on water temperature and pH (Table 1). Knutsson *et al.* (2013) reported
389 a sampling rate of 0.83×10^{-1} L/d for PO_4-P under one condition (pH 7.0, 14°C) using the
390 Chemcatcher® based on an Empore™ Anion-SR disk. Compared to their study, the present
391 study performed the sampler calibration in a wide range of water temperatures (8.1–29.1°C)
392 and pH values (4.1–9.7), which can provide more accurate R_s. One advantage of the
393 receiving disk we developed (i.e., the PSfZS sheet) is that there is flexibility in governing
394 the sheet area during the manufacturing process. Therefore, R_s can be enhanced by
395 increasing the sheet area, which is an advantage in determining low concentrations of PO_4-
396 P. Development of a new sampler housing is now under way to achieve this.
397
398 The calibration data (Table 1) suggest that it is important to estimate the k_0 or R_s values in
399 an actual field where the samplers are deployed. Therefore, Eqn (5) was obtained by using a
400 multiple regression analysis with k_0 (10^3 cm/d) as the objective variable and water
401 temperature (°C) and pH as explanatory valuables:
402 $$k_0 = 2.05 \times 10^{-4} \times \text{Water temperature} - 1.29 \times 10^{-3} \times pH + 1.29 \times 10^{-2}. \quad (5)$$

403 Equation (5) can be used to calculate the k_0 value from water temperature and pH in actual

404 water environments. These water temperature and pH values can be obtained by deploying

405 a pH/temperature data logger with passive samplers.

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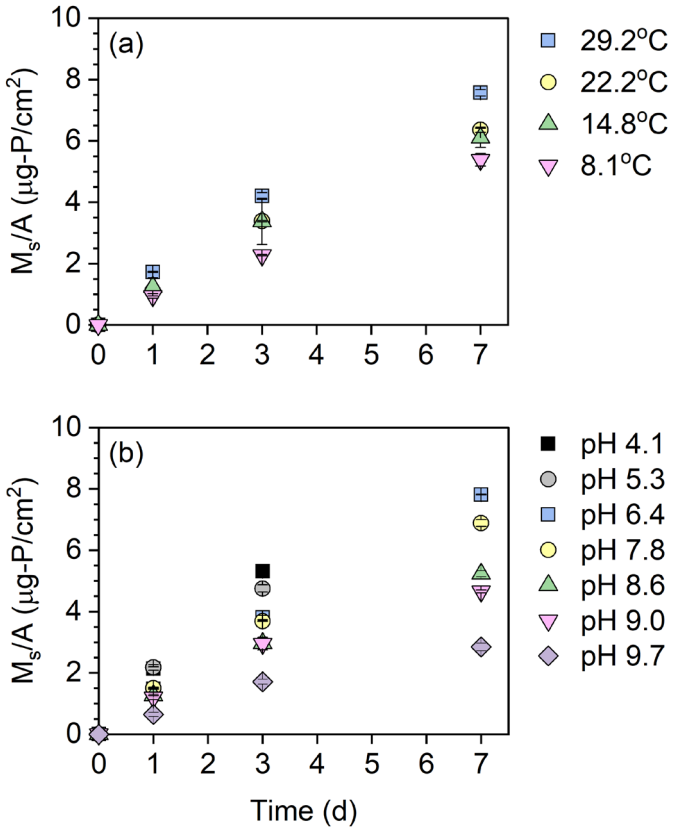


407

408 **Fig. 5.** Effects of (a) water temperature and (b) pH on the accumulated mass of PO_4-P in the

409 passive samplers during calibration in a laboratory. The PO_4-P concentration was kept

410 constant at 0.16 mg-P/L.

411 **Table 1.** Overall mass transfer coefficients and sampling rates of the passive sampler for

412 PO_4-P at different water temperatures (8.1–29.2°C) and pH values (4.1–9.7). The surface

413 area of the sampler exposed to bulk water was 13.85 cm^2.

Water temperature (°C)	pH	k_0 (cm/d)	R_s (L/d)
8.1	7.1	5.12	0.710×10^{-1}
14.8	7.1	7.93	1.10×10^{-1}
22.2	7.3	7.98	1.11×10^{-1}
29.2	7.1	10.1	1.39×10^{-1}
21.8	4.1	12.0	1.66×10^{-1}
22.0	5.3	10.3	1.42×10^{-1}
21.5	6.4	8.84	1.23×10^{-1}
22.2	7.8	7.51	1.04×10^{-1}
22.1	8.6	6.67	0.924×10^{-1}
22.5	9.0	6.65	0.921×10^{-1}
22.1	9.7	3.80	0.527×10^{-1}

414

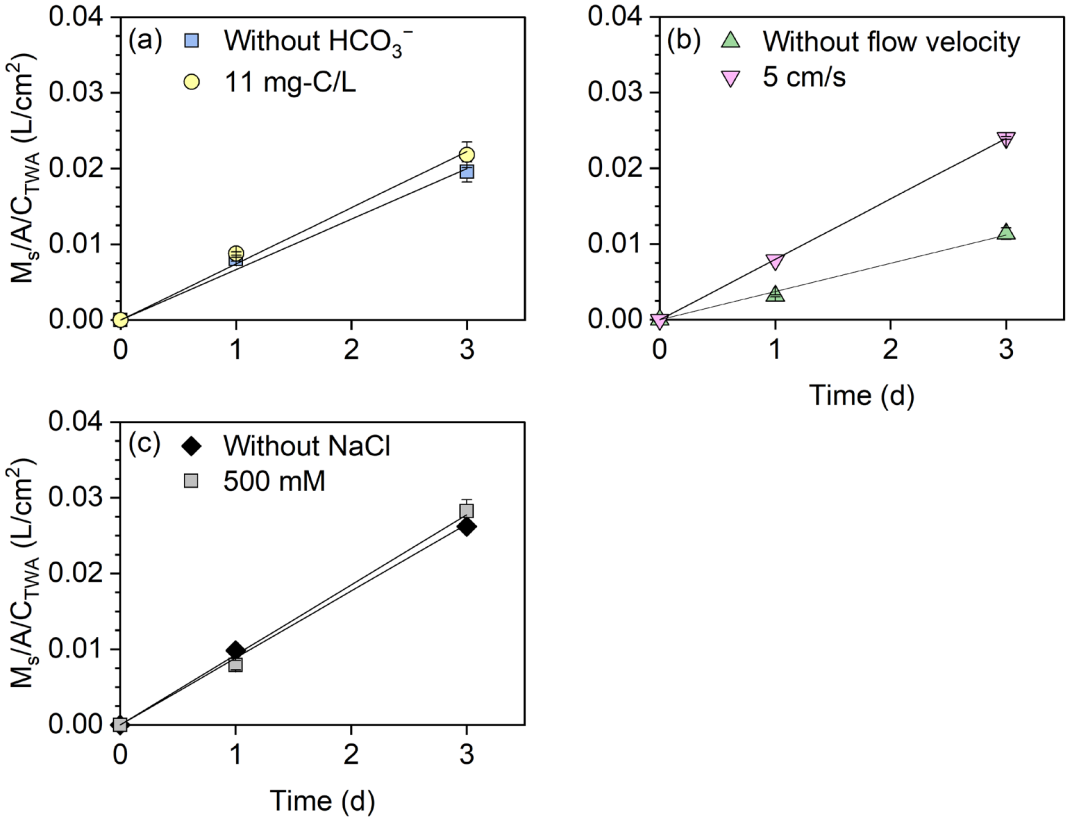
415 Although HCO_3^- reduced the amount of PO_4-P sorbed in the batch experiments (see Fig. 3-

416 (c)), the sampling rate of PO_4-P was not affected by co-existing HCO_3^- (11 mg-C/L) in the

417 flow-through sorption experiment (Fig. 6-(a)). These results indicate that HCO_3^- reduces

418 the sorption capacity of the sampler for PO_4-P but does not reduce the sampling rate for

419 PO_4-P. Water flow velocity affects analyte uptake by passive samplers (not only
420 Chemcatcher® but also POCIS and DGT) (Gimpel *et al*., 2001; Li *et al.*, 2010). Therefore,
421 we investigated the effect of flow velocity on the sampling rate (Fig. 6-(b)). Compared with
422 the R_s value obtained under flow velocity of 5 cm/s (0.111 L/d), the R_s decreased to 0.0517
423 L/d without water flow. Uptake of PO_4-P can be affected by diffusion through the water
424 boundary layer existing on the sampler surface (Endo *et al.*, 2019). A higher flow velocity,
425 however, can provide a higher sampling rate until the thickness of the water boundary layer
426 will be minimal. Moschet *et al.* (2015) reported that flow velocity of 5−80 cm/s did not
427 have an evident effect on the field R_s when using the Chemcatcher® based on an Empore™
428 SDB-RPS disk and PES membrane for polar organic micropollutants. The effect of ionic
429 strength was also investigated because it can affect the diffusion coefficient of the analyte
430 (Aguilar-Martinez *et al.*, 2008). As a result, an ionic strength of 500 mM (NaCl) did not
431 affect the R_s of the passive sampler (Fig. 6-(c)). This result indicates that the developed
432 sampler may be deployed not only in freshwater but also in seawater.
433



434

435 **Fig. 6.** Effects of (a) HCO_3^-, (b) flow velocity, and (c) ionic strength on the sampling rates

436 of the passive sampler for PO_4-P. The PO_4-P concentration was kept constant at 0.16 mg-

437 P/L during the flow-through sorption experiments. Water temperature and pH were kept

438 constant at around 22°C and 7.0, respectively.

439

440 *3.5 Comparison of passive sampling and grab sampling*

441 Passive samplers were deployed in a municipal wastewater treatment plant and two lakes

442 with pH/temperature data loggers to assess the applicability of the sampler for PO_4-P

443 monitoring. Parameters of water quality in the three sites are shown in Tables S2–S4. The
444 "field" R_s values in the deployment sites were calculated by Eqn (5) using averaged water
445 temperature and pH obtained by the pH/temperature data logger (Tables 2 and 3). Water
446 temperature and pH largely fluctuated in all fields during sampler deployments (Fig. S10).
447 Therefore, calculation of the "field" R_s from the obtained water temperature and pH is an
448 excellent way to estimate C_{TWA} more accurately.
449
450 Six passive samplers were deployed in the Soseigawa wastewater treatment plant for 3 or 7
451 days. The grab sampling suggested that the SRP concentration gradually increased from
452 193 μg/L to 329 μg/L until 11 December and then decreased to 78 μg/L (Fig. 7-(a)). Passive
453 samplers provided a C_{TWA} value of 293 μg/L in the 3-day deployment from 7 December to
454 10 December (Table 2), which was very consistent with the averaged concentration in grab
455 sampling (279 μg/L). Passive sampling reflected the decrease in SRP concentration, and a
456 C_{TWA} value of 166 μg/L was obtained in the 7-day deployment. Although the obtained C_{TWA}
457 was lower than the averaged SRP concentration obtained by grab sampling (236 μg/L),
458 samplers still had enough capacity for PO_4-P, and HCO_3^- concentrations were below the
459 interference level (Tables 2 and S2). No apparent biofouling on the sampler surface was

460 observed during sampler deployment in the plant.

461

462 Three samplers were deployed for 7 days in Lake Barato, a shallow eutrophic lake. Soluble
463 reactive P was detected by the molybdenum blue method in grab sampling every day, but its
464 concentrations were below LOQ except for the sample taken on 3 July (Fig. 7-(b)).
465 Evaluating PO_4-P below 10 μg-P/L in grab sampling followed by the molybdenum blue
466 method is difficult because the LOQ of the method is approximately 10 μg-P/L. Compared
467 with grab sampling, passive sampling provided a C_{TWA} value of 3.14 μg-P/L at Lake Barato
468 (Table 2). Considering the SRP concentrations obtained in the grab sampling, the obtained
469 C_{TWA} was considered reasonable. However, minor biofouling was observed after sampler
470 deployment, and so biofouling might slightly affect the R_s. The concentrations of PO_4-P in
471 the eluent (42.5 μg-P/L) were sufficiently high for determination by the molybdenum blue
472 method (Table 2). This result shows the passive samplers successfully accumulated PO_4-P
473 in the receiving phase. Taking into account that R_s ranged from 5.27×10^{-2} to 1.66×10^{-1}
474 L/d (Table 1), the quantification limit of the passive sampling–molybdenum blue method
475 was between 0.172 μg-P/L and 0.542 μg-P/L as C_{TWA} of PO_4-P, when the deployment time
476 was 7 days and the LOQ of the molybdenum blue method was 10 μg-P/L. Therefore, the

477 passive sampler that we have developed is an effective tool for monitoring low PO_4-P
478 concentrations in the water environment. Although the molybdenum blue method was used
479 to determine PO_4-P concentration in the eluents from the samplers in the present study, the
480 combination of the passive sampler and ICP-MS can estimate lower C_{TWA} PO_4-P values.
481
482 Passive samplers were also deployed for three periods in an oligotrophic caldera lake, Lake
483 Kussharo. Because PO_4-P concentrations were low and SRP was not detected by grab
484 sampling followed by the molybdenum blue method, DP concentrations in Lake Kussharo
485 were determined by ICP-MS. The DP concentrations ranged from 0.939 μg-P/L to 3.23 μg-
486 P/L in grab sampling (Fig. 7-(c)). Passive samplers accumulated PO_4-P, and high PO_4-P
487 concentrations (i.e., 138–240 μg-P/L) in the eluent were obtained (Table 3). During sampler
488 deployments from 6 September to 12 October, and from 6 September to 26 October, C_{TWA}
489 values of 0.699 μg-P/L and 0.542 μg-P/L were obtained, respectively. However, these
490 concentrations were lower than the DP concentrations obtained by grab sampling. The
491 samplers probably reached sorption equilibrium during the long-term deployments (i.e.,
492 35.7 days and 49.7 days, respectively), considering the sorption isotherm (see Fig. 2-(b)).
493 Another possible reason for the underestimation of C_{TWA} is that HCO_3^- may occupy the

494 sorption sites of the sampler during long-term deployments. In contrast, a C_{TWA} of 1.22

495 µg/L was obtained in the 14-day deployment from 12 October to 26 October, and this

496 matched the DP concentration provided by grab sampling (see Fig.7-(c)). No apparent

497 biofouling was observed during the three deployment periods in Lake Kussharo.

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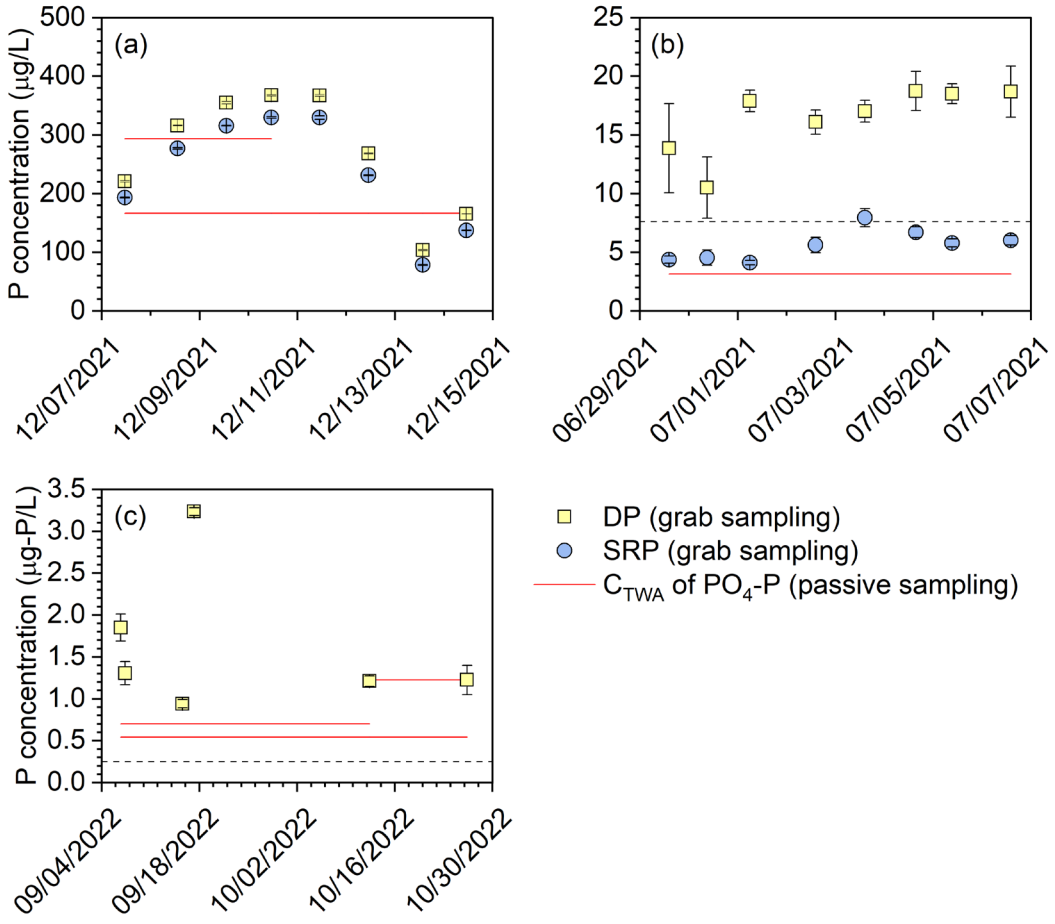

499

500 **Fig. 7.** Comparison of passive sampling and grab sampling in (a) Soseigawa wastewater

501 treatment plant, (b) Lake Barato, and (c) Lake Kussharo. Dashed black lines in panels (b)
502 and (c) represent the limit of quantification values in the molybdenum blue and ICP-MS,
503 respectively. Concentrations of SRP in Lake Kussharo by grab sampling were impossible to
504 determine because its value was so low.

505 **Table 2.** Parameters for calculation of time-weighted average concentrations (C_{TWA}) in Soseigawa wastewater treatment plant and Lake

506 Barato.

	Soseigawa wastewater treatment plant		Lake Barato
Deployment period	12/7/2021–12/10/2021	12/7/2021–12/14/2021	6/29/2021–7/6/2021
Deployment time (d)	3.0	7.0	7.0
Averaged water temperature (°C)	17.6	17.4	22.5
Averaged pH	6.4	6.4	8.2
R_s (L/d)	1.27×10^{-1}	1.26×10^{-1}	0.968×10^{-1}
Liquid volume of NaOH used for PO_4-P elution (mL)	50	50	50
PO_4-P concentration in the eluent (μg-P/L)[a]	2240 ± 96.5	2940 ± 230	42.5 ± 2.2
M_s/A (μg-P/cm^2)	8.07 ± 0.348	10.6 ± 0.825	0.153 ± 0.008
C_{TWA} (μg-P/L)	293 ± 13	166 ± 13	3.14 ± 0.17
Averaged concentration of SRP in grab sampling (μg-P/L)	279 ± 53	236 ± 88	5.64 ± 0.48[b]

507 [a]Determined by the molybdenum blue method.

508 [b]The obtained concentration was above the limit of detection but below the limit of quantification.

509 SRP, soluble reactive phosphorus (P).

510 **Table 3.** Parameters for calculation of time-weighted average concentrations (C_{TWA}) in Lake Kussharo.

	Lake Kussharo		
Deployment period	9/6/2022–10/26/2022	9/6/2022–10/12/2022	10/12/2022–10/26/2022
Deployment time (d)	49.7	35.7	14.0
Averaged water temp. (°C)	17.5	18.6	14.7
Averaged pH	7.9	7.8	7.9
R_s (L/d)	0.888×10^{-1}	0.920×10^{-1}	0.804×10^{-1}
Liquid volume of NaOH used for PO_4-P elution (mL)	10	10	10
PO_4-P concentration in eluent (μg-P/L)[a]	240 ± 14.8	231 ± 42.9	138 ± 4.76
M_s/A(μg-P/cm^2)	0.173 ± 0.0107	0.167 ± 0.0310	0.0992 ± 0.0343
C_{TWA} (μg-P/L)	0.542 ± 0.0334	0.699 ± 0.130	1.22 ± 0.0423
Averaged concentration of DP in grab sampling (μg-P/L)	1.63 ± 0.768	1.71 ± 0.818	1.22

511 [a]Determined by the molybdenum blue method.

512 DP, dissolved phosphorus (P).

513

4. Conclusions

In this study, we developed a new receiving phase for PO_4-P that can be used for the Chemcatcher® passive sampler. A zirconium sulfate–surfactant micelle mesostructure, which was the PO_4-P sorbent, was embedded in a polysulfone matrix and a receiving phase (PSfZS sheet) was prepared by a non-solvent induced phase separation method. The Chemcatcher® passive sampler containing the PSfZS sheet showed sufficient capacity (12.0 μg-P/cm^2) and good selectivity for PO_4-P uptake. Sorbed PO_4-P can be eluted from the sampler with a high efficiency (95%) by a simple protocol. These results indicate that the receiving phase developed has excellent characteristics for passive sampling of PO_4-P. In the laboratory experiments, the R_s for PO_4-P rose with increasing water temperature and decreasing pH, and it ranged from 5.27×10^{-2} L/d to 1.66×10^{-1} L/d. Although co-existing HCO_3^- reduced the sorption capacity of the sampler for PO_4-P, it did not affect the R_s. The passive samplers were then deployed at a municipal wastewater treatment plant, in a shallow eutrophic lake, and in an oligotrophic caldera lake. The R_s calibration method in the deployment sites was established by using the monitored water temperature and pH obtained by the data loggers. The obtained C_{TWA} of PO_4-P at the municipal wastewater treatment plant compared well with the averaged concentration of SRP obtained by grab

sampling. In the two lakes, C_{TWA} values of PO_4-P below 10 μg/L were successfully estimated by deploying the passive sampler. Development of the passive sampler to include the PSfZS sheet will facilitate PO_4-P monitoring in water environments. Development of methods to reduce biofouling, and detailed study of the effects of flow velocity on PO_4-P passive sampling, are needed in future research. Studies to quantify internal loading of phosphorus from lake sediments using the developed passive sampling techniques are now also underway.

Acknowledgments

This work was supported by the Environment Research and Technology Development Fund (JPMEERF20215R03) of the Environmental Restoration and Conservation Agency of Japan, Sapporo City, and by the River Fund of The River Foundation (Grant No. 2020-5311-008 and 2022-5211-036). The authors gratefully acknowledge Akan-Mashu National Park Office, Sapporo Sewerage & Rivers Bureau, Mr Tomoyuki Matamura, and Mr Tatsuya Okuma for water sampling. We thank Edanz (https://jp.edanz.com/ac) for editing a draft of this manuscript.

548

549

550 **Supplementary materials**

551 Supplementary materials are available.

552

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