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A low-tech, low-cost passive sampler for the long-term monitoring of phosphate loads in rivers and streams

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The concentration of dissolved reactive phosphorus (DRP) in rivers can change intermittently within minutes depending on the weather and water discharge (Q), or activities in the watershed. Accordingly, accurate estimation of the annual DRP load requires frequent sampling or even continuous monitoring, which is laborious and cost-intensive. We present the design and laboratory evaluation of a new, robust, low-cost, low-tech device based on passive samplers (P-traps). The traps use Fe-(oxy)hydroxide coated quartz sand as an adsorbent enclosed in a vertical grid of individual cells separated from the river water by filter membranes. They are inexpensive, easy to handle, resistant to repeated desiccation and immersion and exposable for several months. They permit estimation of discharge dependant time weighted average DRP concentrations (C – Q relationships) and annual P loads of rivers characterized by highly variable DRP concentrations with a relative accuracy of $\pm 3\%$.

Introduction

The long-term monitoring of phosphorus loads transported by rivers and streams to detect *e.g.*, pollution hot spots, evaluate the effectiveness of altered farming practices or other measures in their catchments is extremely laborious and expensive because quickly changing dissolved phosphorus concentrations $[\text{DRP}](t)$ and water discharge rates $Q(t)$ call for a survey at a high temporal resolution (*e.g.* Gächter *et al.*¹).

Depending on its sources, riverine $[\text{DRP}]$ fluctuates diurnally as well as seasonally, and in addition depends on water discharge Q (*e.g.* Reinhardt *et al.*,² Paccini *et al.*,³ Müller *et al.*⁴). As within a given period of time Δt , the P load ($L_{\Delta t}$) transported by the river equals

$$L_{\Delta t} = \int_{t_1}^{t_2} Q(t) \times [\text{DRP}](t) dt, \quad (1)$$

an accurate measurement of $L_{\Delta t}$ requires continuous monitoring of both, $Q(t)$ and $[\text{DRP}](t)$. Discharge Q and water level H are related by a site-specific function $Q(H)$. Thus, after establishing $Q(H)$, $Q(t)$ can easily be derived from continuously monitored $H(t)$ gauging.

However, no simple method is available for continuously surveying the ambient $\text{DRP}(t)$ concentrations at present. Although, flow injection analysis (FIA) offers the possibility of automatic $[\text{DRP}]$ measurements at a high frequency^{1,5} the facility depends on electricity supply, samples require filtration and maintenance is sophisticated with frequent inspections necessary. Chemical sensors such as those applied for the monitoring of NO_3^- , NH_4^+ and pH in a small stream with a temporal resolution of 12 min⁶ are under development but still lack the specifications needed for field application in surface waters (*e.g.* Wygladacz *et al.*⁷). It is thus a common practice in long-term monitoring to

establish $[\text{DRP}]$ – Q relationships from occasional measurements of water discharge and chemical analyses, and to interpolate intermediate DRP concentrations from continuously monitored $Q(t)$ values.⁸ However, the $[\text{DRP}]$ – Q function based on random sampling is often scattered as apart from Q , $[\text{DRP}]$ may depend on many additional factors.⁸ Therefore, our aim was to develop an array of passive samplers that

- (1) continuously samples time weighted average DRP concentrations $[\text{DRP}_{\text{TWA}}]$ at predefined discharge rates Q ,
- (2) is easy to handle,
- (3) needs a minimum of maintenance, and can be exposed for up to several months.

In principle, a number of passive samplers are exposed at various levels H corresponding to various water discharge rates. They trap DRP in cavities filled with Fe-(oxy)hydroxide coated glass beads separated from the aquatic environment by a filter membrane whenever the membrane is immersed. Hence, the trapped phosphorus (P) is proportional to the $[\text{DRP}_{\text{TWA}}]$ that each individual trap experienced during its immersion period T_{immers} . T_{immers} can be obtained from a gauge recording water level H as a function of time.

Material and methods

Principle of the method

At the sampling site a passive sampler (Fig. 1) monitoring DRP and an instrument monitoring the water level H are installed. Whereas the gauge continuously registers $H(t)$, the cells of the passive sampler adsorb DRP only when immersed. Variation of $H(t)$ and fixed vertical positioning of samplers define their individual T_{immers} . The amount of adsorbed DRP (DRP_{ads}) depends linearly on the product of $[\text{DRP}_{\text{TWA}}]$ and T_{immers} . Hence, $[\text{DRP}_{\text{TWA}}]$ derives from

$$[\text{DRP}_{\text{TWA}}] = \frac{k \times \text{DRP}_{\text{ads}}}{T_{\text{immers}}} \quad (2)$$

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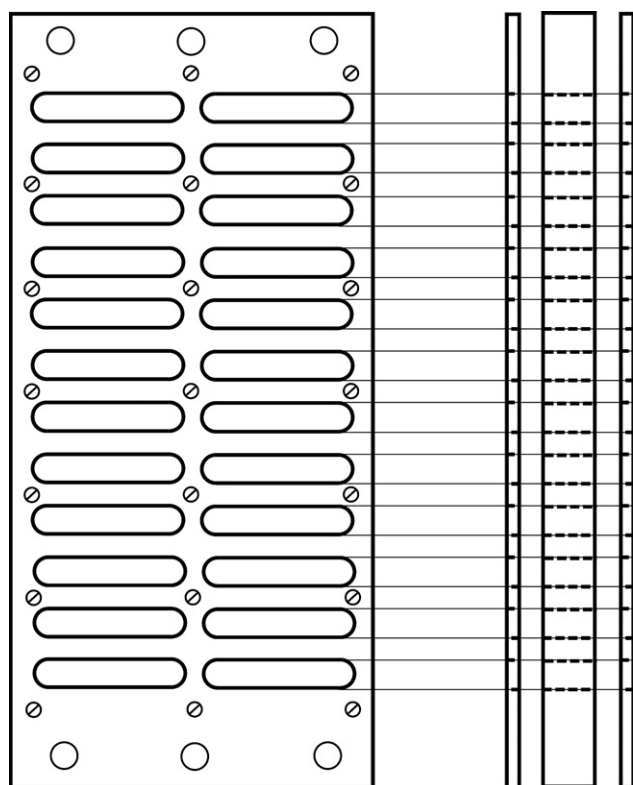


Fig. 1 Design of an acrylic phosphate dialysis plate. A sheet of filter membrane is shut between the outer lids and the main body of the P-peeper. The device is mounted vertically on a holder anchored in the riverbed, together with a facility to continuously record the water level such as *e.g.* a pressure sensor.

k is a calibration factor depending on the area and quality of the membrane. It needs preceding one-time evaluation in the lab. The reciprocal value of k is often called the sampling rate R_s [$L\ d^{-1}$]. Plotting $[DRP_{TWA}]_i$ versus the corresponding Q_i yields

$$[DRP_{TWA}] = f(Q) \quad (3)$$

and inserting eqn (3) in eqn (1) results in

$$L_{\Delta t} = \int_{t_1}^{t_2} Q(t) \times f(Q)(t) dt, \quad (4)$$

permitting the estimation of the DRP load $L_{\Delta t}$ as a function of the continuously monitored water discharge $Q(t)$.

Preparation of Fe-(oxy)hydroxide coated quartz sand

400 g of quartz sand (particle size 0.2–0.8 mm, Merck no. 1.07536) was soaked in 1 M HCl overnight, rinsed five times with nanopure water and added to a solution of 80 g $Fe(NO_3)_3 \cdot 9H_2O$ (Fluka purum p.a. no. 44952). Then 600 ml of 1 M NaOH were slowly added to the stirred quartz suspension with a peristaltic pump. Finally, the pH was adjusted to 7 and the precipitate and quartz were allowed to settle. After decanting the supernatant water, the slurry was dried at 50 °C and homogenized.

Design and preparation of DRP traps

Modifying the general design of the diffusion plates for sediment porewater sampling introduced by Hesslein,⁹ slots with an open surface area of 8.28 cm² were drilled into a 1 cm thick acrylic glass plate as shown in Fig. 1. One side of the plate was covered with a cellulose acetate filter membrane with 0.45 µm pore size (Whatman Schleicher & Schuell, OE 67, no. 10 404 012). The slots were then filled with the Fe-(oxy)hydroxide coated quartz sand and covered with a second cellulose acetate filter membrane.

Experimental design

Four series (A, B, C, D) of passive samplers with four slots each (subsequently termed A₁, A₂, A₃, A₄ *etc.*), were exposed to variable [DRP] in a stirred 70 L tank at room temperature during various time intervals indicated in Fig. 2. The four slots (1–4) used in each of the four exposure experiments (A–D) rendered quadruplicates and corresponding standard deviations. Evaporation, DRP uptake and release by growing and decaying algae and bacteria were deliberately not prevented and ambient [DRP] was measured at about daily intervals with the molybdenum blue method according to EN ISO 6878:2004 (DEW¹⁰).

Sampling and photometric analysis of adsorbed DRP

After exposure, the P-traps were dried at 50 °C. The membranes were cut and the coated quartz sand of the individual slots quantitatively transferred into Erlenmeyer flasks, soaked with 10 ml of concentrated HCl (Riedel-de-Haen, 37% puriss. no. 07102) and stirred on a heating plate at 120 °C for 15 min. Then the acid supernatant was carefully decanted into a 50 ml volumetric flask, without transferring quartz. The quartz sand was washed several times with small amounts of nanopure water and the resulting solutions were also decanted into the volumetric flask. After cooling, the volume was adjusted with nanopure water to 50 ml and the sample vigorously mixed.

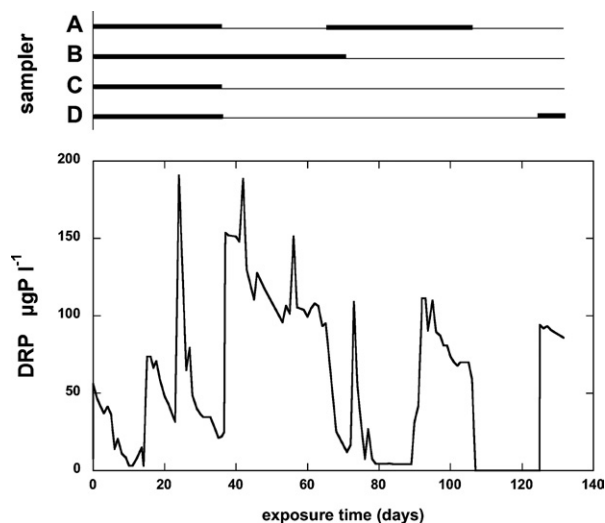


Fig. 2 Variation of DRP concentration in the exposure tank during 133 day, and schematic representation of exposition time periods (T_{immers}) of samplers A to D.

After settling of possibly included quartz particles, 2 ml aliquots of the clear solution were transferred into 100 ml volumetric flasks and adjusted to approx. 70 g with nanopure water. After adding 1 ml ascorbic acid (10%, Fluka puriss. p.a. no. 95210), 2 ml molybdenum tungstate reagent (see below) and 2 drops of SnCl_2 the solution was stirred for 1 h on a magnetic stirring plate at room temperature before adding 10 ml 1-hexanol (Fluka purum no. 52840) and stirring continued for 1 additional hour. The 1-hexanol phase was then carefully separated with a Pasteur pipette avoiding any contamination with water and absorption was measured at 720 nm in a 1 cm photometric cell. The method is derived from EN ISO 6878:2004 (DEW¹⁰). The calibration curve for the extraction analysis was produced from blanks (2 ml of acidic solutions obtained from coated quartz sand not exposed to DRP) that were stocked with appropriate amounts of P and treated as described above.

The molybdenum tungstate reagent was prepared by dissolving 20 g ammonium heptamolybdate tetrahydrate (Fluka puriss p.a. no. 09880) and 0.4 g sodium tungsten dihydrate (Fluka puriss p.a. no. 72070) in approx. 200 ml of nanopure water under heating. After cooling, 700 ml of 50% sulfuric acid (1 : 1 with nanopure water) were added and the solution completed to 1000 ml with nanopure water in a volumetric flask. The SnCl_2 reagent was prepared by dissolution of 4.0 g SnCl_2 (Fluka purum p.a. no. 96501) in 100 ml glycerine under heating (Fluka puriss p.a. no. 49770). The P-stock solution consisted of 4.394 g KH_2PO_4 dissolved in 1 l of nanopure water resulting in a solution of 1.000 g P L^{-1} .

Results and discussion

As Fig. 2 shows, DRP concentrations in the aquarium varied dynamically by nearly two orders of magnitude within a time period of 133 days. Individual T_{immers} periods of samplers A, B, C and D were 75.6, 67.7, 36.7 and 43.7 days, respectively, and they experienced $[\text{DRP}_{\text{TWA}}]$ of 42.3 $\mu\text{g L}^{-1}$, 75.2 $\mu\text{g L}^{-1}$, 38.4 $\mu\text{g L}^{-1}$ and 46.7 $\mu\text{g L}^{-1}$.

Relating DRP_{ads} to the sampler exposure ($[\text{DRP}_{\text{TWA}}] \times T_{\text{immers}}$), Fig. 3 demonstrates a very close proportionality

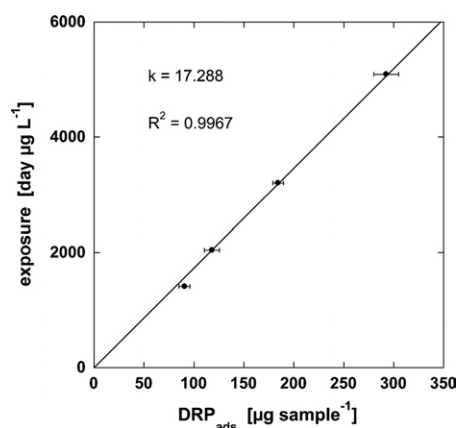


Fig. 3 Measured amounts of phosphate adsorbed in samplers A to D during their exposition in the tank. The slope of the linear regression is the calibration constant k .

between the two variables. The slope ($\partial\text{exposure}/\partial\text{DRP}_{\text{ads}}$) has the dimension [d L^{-1}] and corresponds to the calibration constant k in eqn (2).

In unexposed passive samplers we determined an average apparent base load of 7.6 $\mu\text{g P}$. This originates from the contamination of the $\text{Fe}(\text{NO}_3)_2$ salt and the glass beads with phosphate. As the results presented in Fig. 3 are corrected for this contamination the linear regression is forced through the origin.

Applying the determined proportionality factor ($k = 17.288 \text{ d L}^{-1}$) to the replicate results of DRP_{ads} in the samplers $A_{1,2,3,4}$ to $D_{1,2,3,4}$ we estimated average ambient $[\text{DRP}_{\text{TWA}}]$ according to eqn (2) and the standard deviations within each series as 42.1 ± 1.2 ($n = 8$), 74.7 ± 3.2 ($n = 6$), 42.7 ± 2.5 ($n = 8$) and 46.7 ± 2.9 ($n = 8$), respectively. Comparison with the measured ambient $[\text{DRP}_{\text{TWA}}]$ (see above) demonstrates the excellent ability of passive samplers to accurately assess ambient $[\text{DRP}_{\text{TWA}}]$ in even highly dynamic systems over periods of up to several months. On average, 'true' $[\text{DRP}_{\text{TWA}}]$ (determined by chemical analysis of the tank water) and values estimated from the DRP_{ads} collected by the sampler deviated by only $\pm 3.1\%$.

As shown in Fig. 3, the sampler adsorbed DRP in proportion to its ambient concentration up to an exposure of at least 5000 day $\mu\text{g L}^{-1}$. On the other hand, for analytical reasons about 50 μg of DRP need to be accumulated to clearly exceed the background P (7.6 $\mu\text{g P}$) of the adsorbent. This fixes the lower limit of the samplers' operating capacity at about 1000 day $\mu\text{g L}^{-1}$. Thus, at an elevated average ambient DRP concentration of 50 $\mu\text{g L}^{-1}$ the capacity of the described sampler suffices for at least 100 days, whereas at 1 $\mu\text{g L}^{-1}$, T_{immers} should reach about 50 days. If required, doubling the length of the horizontally exposed slots and halving the thickness of the acrylic glass plate would double the samplers' sensitivity.

As a further development of the device described earlier by Müller *et al.*,⁴ the new design using Fe-(oxy)hydroxide coated quartz sand as a DRP-adsorbent is more versatile and facilitates the vertical positioning of an array of sorption units as slots in an acrylic plate in order to cover a range of water levels. Moreover, the device is highly resistant to repeated cycles of complete dryness followed by inundation because the sand filling mechanically supports the membranes and capillary forces ensure the entire and fast re-wetting of the adsorbent even after complete desiccation. Gravimetric tests showed that after re-immersion, dry samplers regained more than 99% of the water lost during drying within less than 30 min. Furthermore, we suggest positioning the sampler flow parallel with the narrow side upstream to minimize resistance to the flow, thus exposing both collecting membranes to similar turbulence. As the diffusion of ions across the membrane is controlled by the porosity and the thickness of the membrane rather than a diffusive boundary layer at the membrane surface, we expect the flux of phosphate to the sorbent not to depend strongly on river flow velocity.

As this method is independent of electrical power, it does not require nanopure water for periodical rinsing nor a sophisticated pumping system, nor frequent inspection. It permits accurate monitoring of DRP loads of remote rivers at a low-cost.

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