

A low cost method to estimate dissolved reactive phosphorus loads of rivers and streams

Beat Müller,^{*a} Arno Stöckli,^b Ruth Stierli,^a Ernst Butscher^c and René Gächter^a

Received 11th September 2006, Accepted 30th October 2006

First published as an Advance Article on the web 21st November 2006

DOI: 10.1039/b613153k

Concentration of dissolved reactive phosphorus ([DRP]) in rivers changes periodically (daily, weekly, seasonally) and is dependant on the weather and discharge Q . Accordingly, accurate estimation of the annual DRP load requires intensive sampling if not even continuous monitoring, which is laborious and expensive. We present a new, elaborated low cost technique based on passive samplers (P-traps), describing their design and chemical analysis. P-traps use iron(oxy)hydroxide as a sorbent, are inexpensive, easy to handle, and can be exposed for several months. We compare average DRP concentrations obtained from spot samples and P-traps and discuss the applicability and accuracy of the suggested method to measure annual P loads of rivers characterized by highly variable DRP concentrations.

Introduction

In rivers dissolved reactive phosphorus (DRP) loads originate from various sources, *e.g.*, wastewater treatment plant effluents, elution from soils or avulsion by occasional overland runoff. Consequently, DRP concentrations ([DRP]) fluctuate temporally (diurnally, seasonally) (Reinhardt *et al.*,¹ Pacini *et al.*²) and are strongly dependent on flow and weather conditions (Gächter *et al.*^{3,4}). As the flux of phosphate through a river ($L_{\Delta t}$), *i.e.*, the P load transported in the time period t_1 to t_2 , equals

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

Accordingly, a high variability in DRP concentration and Q demand high sampling frequency of both $Q(t)$ and $[\text{DRP}](t)$ to obtain accurate load estimates. $Q(t)$ may be recorded rather easily, as a site specific function of the water level H and flow injection analysis (FIA) permits quasi-continuous DRP concentration measurements (Gächter *et al.*,³ Berg⁵). However, the FIA technique requires filtration of the river water, demands frequent (at least every other day, and after floods) inspection and therefore is cost-intensive. Flow cells with ion-selective electrodes exist for nitrate, ammonium and other parameters (Müller *et al.*⁶), but not for phosphate. Provided a broad $Q/[\text{DRP}]$ database is available, [DRP] might be expressed as a stochastic function of Q . In this case $L_{\Delta t}$ can be expressed as a function of $Q(t)$, which can be recorded easily on-line as mentioned above. Moosmann *et al.*⁷ discussed

a variety of such [DRP] *versus* (Q) relationships that have been parameterized by least square fitting of selected equations to observed [DRP]/ Q data pairs. They showed that the accuracy of an estimated annual DRP load increased when the number of collected data pairs increased. However, in some cases the estimated annual load still deviated from the true value by up to 30% even when more than 50 data pairs were considered.

In this study we present a new, simple, easy to handle, low maintenance, and low cost method for the estimation of DRP loads in streams and rivers. It is based on (1) continuous recording of the water level (discharge) and (2) passive samplers exposed at various levels above the river bed, integrating the DRP concentration when immersed during time periods of weeks to months. Since this method does not require filtration, maintenance can be limited to about one inspection per week. Like the DGT technique (Zhang *et al.*⁸), the presented passive samplers capitalize on the affinity of dissolved HPO_4^{2-} ions with Fe-(oxy)hydroxide surfaces (Sigg and Stumm⁹).

Materials and methods

Synthesis of Fe-(oxy)hydroxide suspension

600 ml 1 M NaOH (0.6 mol, Riedel-de-Haen, Fixanal no. 38215) were slowly added to a stirred solution of 80.8 g (0.2 mol) $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Fluka purum p.a. no. 44952) with a peristaltic pump according to Zhang *et al.*⁸ The pH was then adjusted to approx. 7 and the precipitate was allowed to settle. The overlying solution was decanted and the precipitate washed three times with nanopure water and adjusted to a final volume of 1000 ml. Due to aging of the Fe-(oxy)hydroxide, the pH decreased within a few days thus preventing coagulation and settling of the particles due to their positive surface charges. pH was then again adjusted to approx. 7 with NaOH.

The Fe-(oxy)hydroxide was contaminated with 5×10^{-7} mol P g^{-1} $\text{Fe}(\text{OH})_3$ (blank value). Its maximum adsorption capacity for phosphate (6.2×10^{-4} mol P g^{-1} $\text{Fe}(\text{OH})_3$) was

^a Swiss Federal Institute for Environmental Science and Technology, Eawag, CH-6047 Kastanienbaum, Switzerland. E-mail: beat.mueller@eawag.ch; Fax: + +41 41 349 21 68; Tel: + +41 41 349 21 49

^b Department of Construction, Traffic and Environment, Entfeldenstrasse 22, CH-5001 Aarau, Switzerland

^c Office of Environment and Energy (uwe), Libellenrain 15, PO Box 3439, CH-6002 Luzern, Switzerland

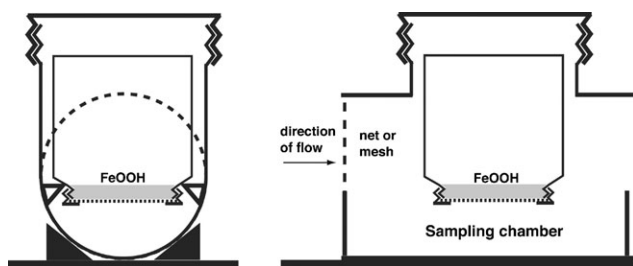


Fig. 1 Schematic representation of a DRP sampler in a casing made of PVC tubing mounted on a metal plate. A coarse mesh protected the P-trap from drifting debris. In the inverted bottle the FeOOH precipitate settled to the membrane, closing the bottle. If the water level in the river exceeds H, the sampling chamber is continuously flushed with river water. Periodical flushing of the sampling chamber with distilled water (not shown in the sketch) prevents P sampling and drying out of the membrane when the river water level is below H.

determined by titrating suspensions of Fe-(oxy)hydroxide with phosphate and analyzing the Langmuir isotherm (Müller *et al.*¹⁰).

Preparation of P-traps

Square powder bottles of transparent PVC with a 200 ml volume and large opening (Semadeni AG, Switzerland, no. 0671) were used with holes of 41 mm diameter drilled in the lids. 20 ml of the vigorously stirred Fe-(oxy)hydroxide suspension was transferred to each bottle, which was then filled to the rim with nanopure water. Either a cellulose acetate membrane filter of 47 mm diameter with 0.45 µm pore size (Whatman, OE 67) or a Nuclepore polycarbonate track-edged membrane filter of 5.0 µm pore size (Whatman, no. 111113) was laid on the water, allowed to adhere and screwed tight with the lid avoiding the entrapment of air bubbles. The bottle was then exposed to the sample solution on upside-down position with the Fe-(oxy)hydroxide settled on the inside of the filter membrane (Fig. 1). Cellulose acetate filters are prone to degradation by microbes, damage by snails or erosion *etc.* when exposed for several months. Nuclepore filter membranes are much better suited for long-term exposition.

Photometric analysis of phosphate from P-traps

After exposition, the P-traps were retrieved and the suspension was allowed to settle to the bottom of the bottles. About 150 ml of the clear, overlying water was decanted and the suspension quantitatively transferred to a 100 ml volumetric flask. 10 ml HCl conc. (12 M, purum p.a. Fluka no. 84426) was added and the precipitate dissolved while stirring and heating to 100 °C. The flasks with the cooled clear brown solution were then replenished to the mark with nanopure water.

An increment of the acidic sample (usually 7 ml or 10 ml, max. 70 ml) was transferred to an Erlenmeyer flask and—if less than 70 ml—filled up to 70 ml with 1.2 M HCl. Standards were prepared in 1.2 M HCl solution. The photometric determination of [DRP] with the ammonium molybdate method involving solvent extraction with hexanol was performed according to DEV.¹¹ In short, 1 ml of ascorbic acid (10%, Fluka puriss. p.a. no. 95210) and 2 ml molybdenum tungstate

reagent (see below) were added to standards and samples. After 60 min of stirring at room temperature, 15 ml of 1-hexanol (Fluka purum no. 52840) were added and extraction continued while stirring for another 60 min. The organic phase was then carefully separated with a pipette and absorption measured at 720 nm in a 1 cm cuvette. The dynamic range used by the method (the range of the calibration curve) was 0–100 µg P l⁻¹. The mean slope calculated from 16 calibration curves was 4.9 ± 0.64 absorption units µg⁻¹ of phosphate, with correlations of *R* > 0.99.

The molybdenum tungstate reagent was prepared by dissolving 20 g ammonium heptamolybdate tetrahydrate (Fluka puriss p.a. no. 09880) and 0.4 g sodium tungstate 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 water) were added and the solution completed to 1000 ml with nanopure water in a volumetric flask.

A P-stock solution was prepared by dissolving 4.394 g KH₂PO₄ in 1 l of nanopure water resulting in a solution of 1.000 g P l⁻¹.

Calibration of P-traps

Concentration-dependent. Eight plastic buckets were filled with 10 l of deionized water and 0 ml–10 ml of P-stock solution were added. The solutions were equilibrated in a climatic chamber at 20 °C in the dark under constant stirring. P-traps were then exposed in duplicates for each membrane type, (*i.e.*, cellulose acetate and nuclepore membrane), for approx. 3 days. Data are presented in Fig. 2.

Time-dependent. 100 ml of the P stock solution was added to 100 l of deionized water in a PVC tank in a dark climate chamber at 8 °C and stirred for two days. The solution was sampled to determine the initial P concentration. 14 P-traps

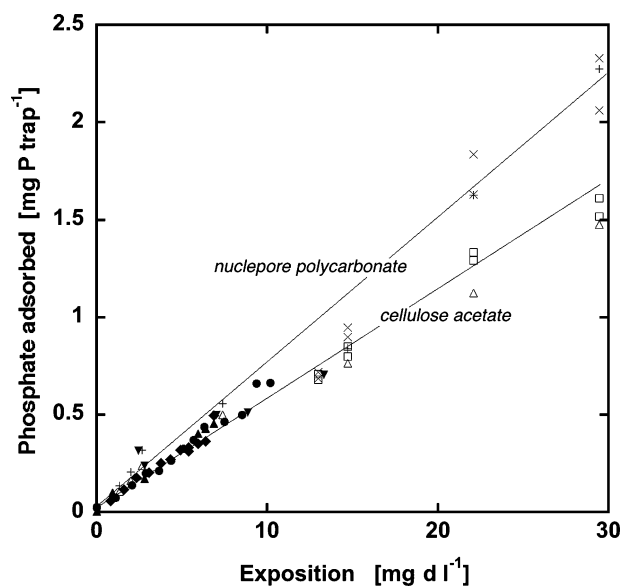


Fig. 2 Time- and concentration-proportional DRP uptake by P-traps with cellulose acetate membrane filters (0.45 µm pore size) (shapes) and nuclepore polycarbonate filter membranes (5 µm pore size) (crosses). The different shapes indicate results from different experiment batches.

were exposed in the tank and retrieved one after the other within 15 to 21 days and stored at 5 °C until analysis. The tank water was sampled every time P-traps were removed since the P concentration in the tank decreased due to the uptake of P by the traps. The mean exposure concentration for each trap was calculated by linear interpolation from the periodic determination of P concentrations in the tank. After retrieval of the last trap the P content of the Fe-(oxy)hydroxide was determined according to the above protocol. These experiments resulted in calibration constants K of 0.061 and 0.077 l d⁻¹ for cellulose acetate and nuclepore filter membranes, respectively (Fig. 2). The linear regression analysis of the results gained from both time and concentration-dependent experiments yielded calibration constants of 0.060 for membrane filters and 0.079 l d⁻¹ for nuclepore filters (Fig. 2).

Field sites. The Kleine Aa and the Lippenrütibach (L) are tributaries to Lake Sempach. Pastures receiving large amounts of manure due to intense pig farming dominate their catchments. Their annual runoffs are 5.6×10^6 m³ yr⁻¹ and 1.5×10^6 m³ yr⁻¹, respectively. The Meisterschwander Dorfbach (MD) is a tributary to Lake Hallwil, another lake in the Swiss Plateau. Cultivation is dominated by agriculture rather than intensive animal husbandry. Its annual runoff is 4.1×10^6 m³ yr⁻¹. Furthermore, two drainage pipes (M8 and S1) were sampled in the catchment of Lake Hallwil. M8 had water running permanently, whereas in case of S1 it ran only during wet periods.

On line monitoring of DRP with flow injection analysis (FIA). Trailers parked at the shore of the creeks Kleine Aa and Lippenrütibach contained the analytical facilities for flow injection analysis previously described in Gächter *et al.*³ In short, water was continuously pumped (about 1 l s⁻¹) from the creeks into an overflowing bucket in a first cycle. In a second cycle, the water was filtered on-line through a glass fiber filter and a 0.45 µm cellulose acetate filter (about 1 ml s⁻¹). In the third cycle, the filtered water was mixed with molybdenum tungstate reagent and ascorbic acid, and pumped in a continuous stream through a photometric cell. Additionally, individual spot samples were collected from the creeks, filtered with 0.45 µm cellulose acetate membranes and analyzed in the lab according to a standard photometric method (DEV¹¹).

Results and discussion

Fig. 3 compares average DRP concentrations determined using passive samplers exposed for several weeks to values obtained from occasional spot samples and FIA readings. Because DRP concentrations in drainage pipes and rivers may change by an order of magnitude within hours—depending on discharge (Fig. 4) and/or time of day (Lazzarotto *et al.*¹²—low frequency random spot sampling misses part of such fluctuations. The large vertical error bars indicate the concentration range determined from individual samples. Thus, depending on whether a majority of samples are taken at high or low discharges, the average DRP concentration will be over- or underestimated, respectively. Passive samplers, however, register the total variability of DRP concentrations irrespective of its frequency and amplitude. In spite of this

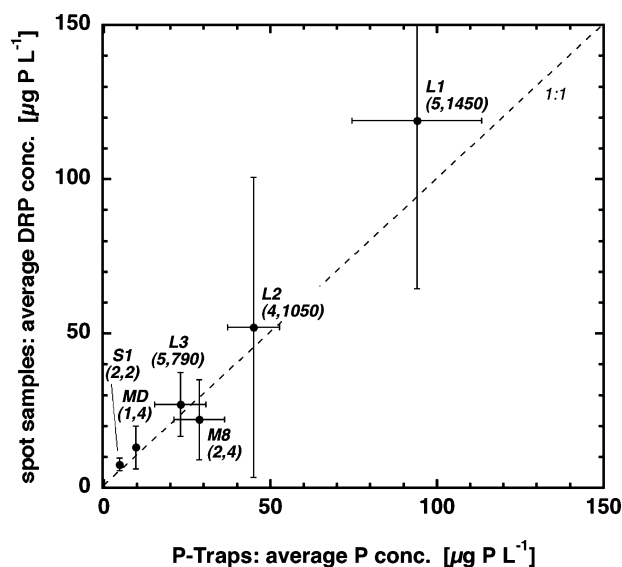


Fig. 3 Comparison of average DRP concentrations determined in four environments (MD, M8, S1 and L) estimated from passive samplers and from averages of spot samples. Error bars indicate standard deviations. Numbers in parentheses state the number of P-trap replicates, and the number of spot samples analyzed. Locations were: MD (Meisterschwander Dorfbach, 7 Sep 01–13 Dec 01); M8 (drainage pipe, 7 Sep 01–13 Dec 01); S1 (drainage pipe, 7 Sep 01–13 Dec 01); L1 (Lippenrütibach, 11 Sep 05–30 Sep 05); L2 (Lippenrütibach, 30 Sep 05–13 Nov 05); L3 (Lippenrütibach, 13 Nov 05–17 Dec 05).

methodological difference and in spite of the flow variability that the various P-traps experienced, the two approaches generated very similar results, indicating that flow velocity had relatively little effect on P-trap performance. Of course, due to incomplete water mixing resulting in concentration heterogeneities within a river and/or analytical inaccuracy, the passive sampler technique is also not error-free. However, as indicated by the smaller horizontal error bars, P-trap based average DRP concentrations seem to be more reliable than values determined as averages of a few randomly collected

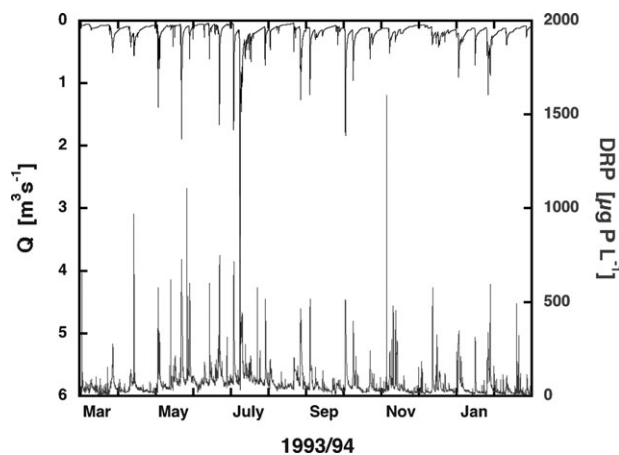


Fig. 4 Variability of discharge (inversely plotted on top of the figure) and DRP concentration in the river Kleine Aa according to Gächter *et al.*³

samples. To further increase its reliability, we recommend exposing and analyzing some replicate P-traps.

For statistical reasons the accuracy of an average concentration increases with the number of analyzed spot samples. However, sampling and chemical analyses are manpower-intensive and costly. Even if these procedures can be automated in principal, sophisticated analyzers need frequent control and maintenance (Berg;⁵ Gächter *et al.*,⁴ Kuban *et al.*¹³). In comparison, the described P-trap technique integrates the ambient DRP concentration continuously and requires neither filtration, nor maintenance. It is thus a highly potent and cost-effective method to evaluate average DRP concentrations with relatively high accuracy even in rivers with highly variable DRP concentrations.

Passive samplers integrate DRP concentrations proportionally to time, but not to discharge. However, as in rivers DRP concentrations are often positively related to water discharge Q , a significant fraction of the annual DRP load L enters the lake during only a few days with high floods (Pacini *et al.*,² Gächter *et al.*,³ Moosmann *et al.*⁷). In such cases the annual load L may be substantially underestimated if expressed simply as the product of the annual average concentration ([DRP]) and the total annual discharge. This is easily demonstrated by modeling a large dataset obtained from the Kleine Aa in which [DRP] and Q were monitored at 35 minute intervals during 1996 (Fig. 4). The roughly 15000 spot sample pairs yielded an annual DRP load of 786 kg yr⁻¹ compared to only 399 kg yr⁻¹ if estimated as a simple product of the average concentration (71.1 mg m⁻³) times the total annual discharge (5613 226 m³ yr⁻¹). Since both the [DRP] and the water level H increase with increasing discharge Q , the exposition of an array of P-traps at various water levels H allows the measurement of the average DRP concentrations of individual, predefined discharge classes and, hence, better accuracy of the estimated DRP load (eqn (2)).

We used the measurements of the Kleine Aa presented in Fig. 4 to model the accuracy which can be attained by applying three passive samplers at different vertical levels. A relationship between water level H and discharge Q was described by empirical equations containing polynomials of the 3rd power. The dataset was sectioned into three groups where each group yielded the total length of periods Δt_i during which the discharge Q was within the ranges ($i = 1, 2, 3$) specified in Table 1, as well as the corresponding average concentrations (DRP₁, DRP₂, DRP₃) and discharge values (Q_1 , Q_2 , Q_3). Approximating the annual DRP load L_{approx} with three P-traps according to

$$L_{\text{approx}} = \sum_{i=1}^3 Q_i \times \text{DRP}_i \times \Delta t_i \quad (2)$$

resulted in an annual load L_{approx} of 688 kg compared to the true load L_{true} of 786 kg

$$L_{\text{true}} = \sum_{i=1}^{15017} Q_i \times \text{DRP}_i \times \Delta t \quad (3)$$

based on 15017 chemical analyses and Δt equaling 35 minutes. Comparison of L_{approx} and L_{true} values indicates that the annual DRP load of a river can be estimated with reasonable accuracy with very low analytical effort if a few passive samplers are intelligently exposed. Assuming a calibration constant K of 0.077 l d⁻¹, the samplers exposed at the levels H_1 , H_2 and H_3 for $Q > 0 \text{ m}^3 \text{ s}^{-1}$, $Q > 0.3 \text{ m}^3 \text{ s}^{-1}$ and $Q > 0.6 \text{ m}^3 \text{ s}^{-1}$, respectively, would have accumulated 2012 µg DRP, 593 µg DRP and 257 µg DRP. As the samplers collect DRP in proportion to exposure time and concentration up to at least 2250 µg trap⁻¹ (Fig. 1), they theoretically could have been exposed for up to one year and still produce reliable results in this river. However, we do not recommend such long exposition periods since the risk of sample loss (vandalism, damage or fouling) increases with increasing exposure time.

Samplers—especially the cellulose membranes—are delicate and may be harmed by harsh currents and drifting objects like sand, stones, wood and other debris during storm flow conditions. We therefore suggest protection against mechanical stress. It proved convenient to expose traps in holders of the type shown in Fig. 1. The ground plate can be designed in a suitable way to anchor the trap on the stream bottom. To minimize the risk of a possible data loss we suggest exposing replicate samplers and inspecting them regularly. Furthermore, in case the samplers are installed at various heights where some of them are not permanently immersed in the water, samplers are prone to drying out which causes damaging of the membranes. Periodic refilling of the sampling chamber underneath the membrane with distilled water, *e.g.* accomplished by a peristaltic pump, can prevent this.

Why didn't we follow the normal procedure for DGT-like samplers, and encapsulate the Fe salts in a gel as suggested by Zhang *et al.*?⁸ Since the diffusive boundary layer above the filter membrane is likely to be thin in turbulent riverine environments and hence its extent does not strongly depend on discharge, the Fe-(oxy)hydroxide was not separated from the membrane by a diffusive gel as in the DGT technique. This minimizes the lag time between variations in [DRP] and P adsorption to the Fe-(oxy)hydroxide. Furthermore, DGT samplers accumulated only 7 µg P if exposed to 0.5 mg l⁻¹ day (Fig. 6 in Zhang *et al.*⁸) compared to about 35 µg P adsorbed by passive samplers (Fig. 2). In addition, the linear adsorption maximum was reached at an exposure of 0.5 mg l⁻¹ day compared to 30 mg l⁻¹ day for the P traps. In conclusion,

Table 1 Discharge classes, length of time during which discharge was within the defined limits, average DRP concentration and average water discharge within the classes, DRP load (eqn (2)) and amounts (A) of DRP adsorbed by the traps ($A = 0.077 \times C_3 \times C_4$, according to Fig. 2)

Discharge class	Discharge/m ³ s ⁻¹	Exposition time/d	Average conc./mg m ⁻³	Average discharge/m ³ d ⁻¹	DRP load/kg yr ⁻¹	DRP ads./µg trap ⁻¹
1	0.0 < Q < 0.3	330	55.9	11 901	219	1419
2	0.3 < Q < 0.6	27	161.8	33 918	148	336
3	0.6 < Q < Q_{max}	8	417.2	96 163	321	257

we recommend applying P traps instead of the DGT samplers in riverine environments, because they are five times more sensitive and tolerate a sixty-fold longer exposure time.

Acknowledgements

We thank Tess Edmonds, Tom Gonser and two anonymous referees for their valuable suggestions, which helped considerably clarifying our thoughts and strengthen the manuscript.

References

- 1 M. Reinhardt, R. Gächter, B. Wehrli and B. Müller, *J. Environ. Qual.*, 2005, **34**, 1251.
- 2 N. Pacini, J. Zobrist, A. Ammann and R. Gächter, *Chimia*, 1997, **51**, 929.
- 3 R. Gächter, C. Stamm, U. Kunze and J. Blum, *Agrarforsch.*, 1996, **3**, 329.
- 4 R. Gächter, J. M. Ngatiah and C. Stamm, *Environ. Sci. Technol.*, 1998, **32**, 1865.
- 5 M. Berg, *Gas, Wasser, Abwasser*, 1991, **12**, 822.
- 6 B. Müller, M. Reinhardt and R. Gächter, *J. Environ. Monit.*, 2003, **5**, 808.
- 7 L. Moosmann, B. Müller, R. Gächter, A. Wüest, E. Butscher and P. Herzog, *Water Resour. Res.*, 2005, **41**(1), W01020.
- 8 H. Zhang, W. Davison, R. Gadi and T. Kobayashi, *Anal. Chim. Acta*, 1998, **370**, 29.
- 9 L. Sigg and W. Stumm, *Colloids Surf.*, 1981, **2**, 101.
- 10 B. Müller, R. Stierli and A. Wüest, *Water Resour. Res.*, 2006, **42**(10), W10414.
- 11 *Deutsche Einheitsverfahren zur Wasseruntersuchung (DEV)*, Wiley-VCH, Weinheim, 1996, vol. 2.
- 12 P. Lazzarotto, V. Prasuhn, E. Butscher, C. Crespi, H. Flühler and C. Stamm, *J. Hydrol.*, 2005, **304**, 139.
- 13 P. Kuban, M. Reinhardt, B. Müller and P. C. Hauser, *J. Environ. Monit.*, 2004, **6**, 169.