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Quantifying nutrient fluxes in Hyporheic Zones with a new Passive Flux Meter (HPFM)

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Abstract. The hyporheic zone is a hotspot of biogeochemical turnover and nutrient removal in running waters. However, due to methodological constraints, our quantitative knowledge on nutrient fluxes to those reactive zones is still limited.

In groundwater systems passive flux meters, devices which simultaneously detect water and nutrient flows through a screen well in the subsurface, proofed to be valuable tools for ~~load~~ estimates.

Here we present adaptations to this methodology and a smart deployment procedure which allow its use for investigating water and solute fluxes in river sediments. The new hyporheic passive flux meter (HPFM) delivers time integrating values of horizontal hyporheic nutrient fluxes for periods of several days up to weeks. Especially in highly heterogeneous environments like the hyporheic zone, measuring flow and nutrient ~~concentration~~ in a single device is preferable ~~when compared to methods that derive~~ flux estimates from separate measurements of water flows and chemical compounds.

We constructed HPFMs of 50 cm length, separated in 5-7 segments which allowed for vertical resolution of horizontal nutrient and water transport in the range of 10 cm. The results of a seven day long field test, which included simultaneous measurements of oxygen and temperature profiles and manual sampling of pore water, revealed further advantages of the method: While grab sampling of pore water could not account for the high temporal variability of nitrate fluxes in our study reach, HPFMs accumulatively captured reliable values for the complete deployment time. ~~Mass~~ balances showed that more than 50 % of the nitrate entering the hyporheic zone was removed in the assessed area.

Being low in costs and labor effective, many flux meters can be installed in order to capture larger areas of river beds. The extended application of passive flux meters in hyporheic studies has therefore the potential to deliver the urgently needed quantitative data which is required to feed into realistic models and lead to a better understanding of nutrient cycling in the hyporheic zone.

Keywords: hyporheic exchange, nutrient retention, quantitative methods, running waters, stream metabolism

1 Introduction

~~Northern and central European~~ rivers export high loads of nitrogen from inland catchments to the marine environment. The ecological and economic problems caused by eutrophication of coastal and riverine ecosystems systems have been recognized years ago (Artioli et al., 2008;Skogen et al., 2014;Patsch and Radach, 1997). Decades of nutrient studies have unveiled, that rivers cycle rather than only transport nutrients (Seitzinger et al., 2002;Galloway et al., 2003;Garcia-Ruiz et al., 1998a). However, the quantitative dimensions of instream dynamics of nitrogen (N) and other nutrients are still not completely understood (Wollheim et al., 2008;Grant et al., 2014). Even though dissimilatory nitrate reduction to ammonium (DNRA) and subsequent anaerobic ammonium oxidation (anammox) might be of importance in some systems (Smith et al., 2015), in most river systems, nitrate (NO_3^-) removal via denitrification, the anaerobic reduction of NO_3^- to gaseous N_2 is the dominant dissimilatory process which removes N out of the system (Laursen and Seitzinger, 2002;Bernot and Dodds, 2005;Lansdown et al., 2012). Various studies found that in-stream denitrification exclusively happens at “reactive sites” in the hyporheic zone (Duff and Triska, 1990;Rode et al., 2015). The hyporheic zone is defined as the subsurface region of streams and rivers that exchanges water, solutes and particles with the surface (Valett et al., 1993). The occurrence of anaerobic areas, the buffering of variations in flow, temperature or water chemistry, a continuous supply with nitrate and carbon provide a benign habitat for denitrifying microbes (Garcia-Ruiz et al., 1998b;Opdyke et al., 2006;Alexander et al., 2009;Zarnetske et al., 2011a). As a result of much higher residence times hyporheic transient storage was recognized to have a stronger influence on overall removal of NO_3^- and other nutrients like phosphate (P) when compared to surface water storage zones (Basu et al., 2011;Stewart et al., 2011). However, even in nitrogen saturated systems like agriculturally impacted groundwater and streams, denitrification can be limited by NO_3^- availability, because consumption in the hyporheic zone is faster than resupply of solutes (Fischer et al., 2009;Böhlke et al., 2009;O'Connor and Hondzo, 2008;Harvey et al., 2013).

In addition to remove nutrient loadings at larger time scales (e. g. seasonal or annual), intermediate storage disperses the propagation of pollutant spikes which could be harmful for receiving water bodies (Findlay et al., 2011). In stagnant waters, such as lakes, the transport of dissolved nutrients to the sediments is dominantly controlled by diffusion. Therefore, surface water concentrations of nutrients are a good predictor for uptake processes and potential limitations (Dillon and Rigler, 1974;Jones and Bachmann, 1976). In rivers, hydrological processing and physical storage of nutrients were found to be as important or ~~of~~ even ~~higher importance~~ than biological uptake capacity (Covino et al., 2010;Runkel, 2007;Brookshire et al., 2009), because the transport of solutes to reactive sites is determined by advection rather than diffusion (Grant et al., 2014;Wörman et al., 2002). As a result, it is not possible to interpret hyporheic processing rates from surface water observations, if subsurface fluxes and transport velocities are unknown. ~~Nutrient flux (i.e. the product of nutrient concentration and specific discharge) is conclusively a much better metric for hyporheic turnover rates than concentration alone.~~

Several numerical or empirical models demonstrated the complexity of surface – subsurface exchange of water and solutes. Exchange rates could be attributed to surface flow, water level, sediment properties and various other hydrological, chemical and physical factors (Trauth et al., 2015;Boano et al., 2014;Böhlke et al., 2009).

While NO_3^- has been the main focus of hyporheic nutrient studies, in-stream P cycling has recently received increasing interest (Boano et al., 2014;Mulholland et al., 2009). Even though the earliest studies of hyporheic nutrient dynamics focused on P (Mulholland and Webster, 2010;Hall et al., 2009), only very few studies have attempted to directly assess P transport in the hyporheic zone (Boano et al., 2014). Based on the fact that the mobility, transformation and retention of phosphate (PO_4^-) are mainly dependent on redox conditions which are directly coupled with NO_3^- concentrations (Smith et al., 2011;McDaniel et al., 2009;Gabriel et al., 2006) hyporheic transport studies should address NO_3^- and phosphate fluxes simultaneously.

Small changes in stream state or water chemistry ~~variables~~ were found to significantly alter hyporheic zone nutrient processing. Hence quantitative models are fraught with high uncertainties while experimental investigations of nitrate turnover rates in the hyporheic zone are often exclusively of qualitative nature (Grant et al., 2014;Mulholland et al., 1997). As a result, for both, N and P, there is urgent need ~~for quantitative measurements of~~ nutrient flux through the hyporheic zone~~: On one hand,~~ to support ~~the modelled results~~ (Alexander et al., 2009;Boyer et al., 2006;Wagenschein and Rode, 2008), ~~on the other hand,~~ to ~~provide a solid basis for the discussion on~~ the ~~importance~~ of hyporheic processes in whole stream NO_3^- uptake (Fischer et al., 2009). While the importance of subsurface pathways for N-cycling is widely acknowledged (Seitzinger et al., 2006;Zarnetske et al., 2012), there is still disagreement on the amounts of nutrient loadings actually reaching the reactive sites in the subsurface (Fischer et al., 2005;Zarnetske et al., 2011b).

Whil~~st~~ understanding of ~~surface water~~ NO_3^- cycling has ~~remarkably~~ improved in ~~the~~ recent years, benefiting from newly emerging sensors ~~which~~ deliver high resolution time series of nutrient concentrations (Pellerin et al., 2009;Hensley et al., 2014;Rode et al., 2016), ~~equivalent~~ technics ~~are not available for~~ ~~subsurface studies.~~ ~~Here~~, tracer injections and ~~/or manual~~ sampling are ~~still~~ the only approach for ~~observing~~ the fate of NO_3^- and other nutrients (Fischer et al., 2009;Ingendahl et al., 2009;USEP, 2013).

Nutrient uptake measurements based on whole stream tracer injections and mass balances (Böhlke et al., 2009;McKnight et al., 2004) have been used for determining general uptake dynamics on the reach scale, but did not identify the reaction site (hyporheic versus in channel or algal canopies) or specific local uptake processes (Ensign and Doyle, 2006;Ruehl et al., 2007). More important, in-stream measurements do exclusively account for water which is re-infiltrating into the main stem after passage through the hyporheic zone. Under loosing conditions, where most of the surface water nutrient-influx is flowing towards the groundwater, processing rates in the hyporheic zone cannot be observed in the surface water. Likewise, if groundwater is contributing significantly to surface water chemistry, surface water mass balances do not characterize nutrient cycling in the hyporheic zone realistically (Trauth et al., 2014).

Other attempts are based on benthic chamber and incubation experiments (Kessler et al., 2012;Findlay et al., 2011). Those laboratory ~~or~~ mesocosm and flume experiments ~~deliver~~ rates of denitrification potential of the substrates, usually ~~assessed~~ via denitrification enzyme assays (DEA). ~~Nevertheless~~, it ~~was~~ found that ~~the realized~~ denitrification rate ~~is~~ determined by environmental and hydrological conditions rather than by substrate type or denitrification potential (Findlay et al., 2011). Likewise ~~would~~ small scale fluctuations in hyporheic flow and metabolic activity influence the redox conditions and thereby the binding and mobilization of phosphorous. Due to those natural variations and the complexity of environmental conditions, hyporheic transport of nutrients cannot satisfactorily be mimicked in artificial ~~set ups~~ (Cook et al., 2006~~). Hence, those attempts neglect many important hydrological, biophysical and chemical processes that influence the nutrient fate and transport (~~Grant et al., 2014).

Separately measuring exchange rates via hydraulic head differences or tracer injections and pore water nutrient concentrations have often been the methods of choice (Saenger and Zanke, 2009;Alexander et al., 2009). These methods provide valuable insights into the time specific conditions at the target site. However, hyporheic zone processes are highly variable in time and space (Cooke and White, 1987), which can lead to high uncertainties if separated measurements are used to characterize a single parameter (e. g. nutrient flux). Additionally, attempting to characterize larger areas with these methods or account for short term variability is laborious and costly. ~~However, as long as~~ grab sampling is not repeated at high frequencies it ~~can~~ exclusively ~~be interpreted as a~~ snap shot ~~which~~ do~~es~~ not allow a characterization of the system. Conclusively, long-term measurements are required to obtain ~~an~~ integrative mass flux signal.

Measuring solute fluxes through porous media ~~is also aspired~~ in groundwater studies. There, passive flux meters (PFM) have successfully been used to quantify fluxes of dissolved nutrients (Cho et al., 2007) and contaminants (Annable et al., 2005;Verreydt et al., 2013;Hatfield et al., 2004) through screened groundwater monitoring wells. PFMs allow determination of the horizontal water flux through the screened media from the dilution of a resident tracer and to simultaneously capture the amount of transported target solute (nutrient or contaminant) using a permeable sorbent. Observation time can range from days to weeks~~, so that the time averaged solute flux during that defined period can be monitored.~~ A method for quantifying vertical mass flux through sediments (SBPFM) has recently been developed and field testing has been initiated (Layton, 2015)

For the application of PFMs in hyporheic zones, several adaptations are necessary. Most importantly, the flow velocities and the masses of transported solutes are expected to be several orders of magnitude higher in hyporheic zones than in the groundwater. Thus, a suitable sorbent for the target nutrients with ~~appropriately~~ high loading capacity is required. The market of anion absorbing resins, originally manufactured for water purification purposes, is huge and offers a wide range of products with varying characteristics (Annable et al., 2005;Clark et al., 2005). Various criteria, like possible interference of resin compounds with the resident tracer analysis or the hydraulic conductivity of the resin have to be considered depending on the study site and research question.

Additionally, a new deployment and retrieval procedure has to be developed, because contamination with surface water has to be avoided. In hyporheic studies the flux meter should be in direct contact with the surrounding sediments with a minimal manipulation of the natural flow pattern.

Furthermore, PFMs have so far been used in waterbodies which were not subjected to light or high temperatures and where nutrient concentrations were low. Hence, biofouling on the meters was not regarded in previous studies.

In this study we present the modification of the passive flux meter for applications in the hyporheic zone (Hyporheic Passive Flux Meter, HPFM) with the example of N and Pin a nutrient rich 3rd order stream (Holtemme, Germany) with a strong anthropogenic impact gradient (Kamjunke et al., 2013)

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2 Methods

2.1. Construction and materials

The Hyporheic Passive Flux Meters (HPFM) consisted of a nylon ~~sock~~ which was filled with a mixture of a macroporous anion exchange resin as a nutrient absorber and a tracer loaded carrier. In the present study ~~we constructed them in a~~ 50 cm long~~,~~ 5 cm ~~Ø cylindrical form~~. A stainless steel rod in the middle assured the stability of the device (**Figure 1**).

To detect vertical gradients of both nutrient and water fluxes in the hyporheic zone, the HPFM was divided into several segments ~~by~~ rubber washers. Steel tube clamps were used to attach the nylon ~~sock~~ to the steel rod placed in the center of the HPFM. The nylon mesh ~~for the socks~~ was purchased from Hydro-Bios (Hydro-Bios Apparatebau GmbH, Kiel-Holtenau, Germany) and is available in a wide range of ~~mesh~~ size and thicknesses. We used a mesh size of 0.3 mm. A rope was connected to the tube clamp on the upper end of the HPFM in order to facilitate retrieval.

2.1.1. Preparation of activated carbon

Similar to the groundwater PFM, silver impregnated activated carbon (AC) was used as sorbent for the resident tracers. The AC used for the HPFM in this study was provided by the University of Florida, Gainesville and was prepared as reported ~~(~~Annable et al. 2005). By choosing the same manufacture ~~as~~ used in the above mentioned studies, we could rely on physical and chemical characterization and calculated retardation factors for alcohol tracer partitioning ~~behavior which have been established by~~ Hatfield et al. (2004) and Annable et al. (2005).

The magnitude of water flow through the flux meter is unknown in ~~the~~ field applications, ~~therefore~~ multiple resident tracers with a wide range of tracer elution rates were used (Hatfield et al., 2004;Cho et al., 2007). An alcohol tracer mixture for approximately 10 HPFM was prepared by combining 100 mL of methanol, 100 mL of ethanol, 200 mL of isopropanol (IPA), 200 mL of tert-butanol (TBA) and 66 mL of 2, 4-dimethyl-3-pentanol (2,4 DMP) (Cho et al., 2007).

For an aqueous solution of resident alcohol tracers, a standard ratio of 13 mL tracer mixture was transferred to 1 L water in a Teflon sealed container and was then shaken by an automated shaker over a period of several hours. Subsequently, 1.5 L of dry activated carbon was added to the aqueous tracer solution and rotated for 12 hours to homogenize the AC tracer mixture. Following mixing, the AC tracer mixture was stored in a sealed container and refrigerated.

2.1.2. Deployment and retrieval procedure

HPFMs were built, stored and transported in 70 cm long standard polyethylene (PET) tubes (58 x 5.3 SDR 11) purchased from a local hardware store (Handelshof Bitterfeld GmbH, Bitterfeld, Germany). To avoid resident alcohol tracer loss, the transport tubes with the HPFMs were sealed with rubber caps and cooled during storage and transport.

On site, prior to ~~installing~~, the HPFMs were transferred to a stainless steel tube (5.3 cm inner diameter) with a loose steel drive point tip on the lower end. The steel casing and HPFM were driven into the river bed using a 2 kg hammer until the upper end of the HPFM was at the same level as the surface-subsurface interface. The metal casing was retrieved while the HPFM was held in place using a steel rod.

After a specific period of exposure, the HPFM was retrieved by holding the transport tube in place and quickly drawing the HPFM into the tube using the rope fixed to the upper end of the HPFM. The required length of the transport tube, steel drive casing and retrieval rope was determined by the depth of the water level in the stream.

After retrieval, the HPFMs were transported to the laboratory, where they were removed from the transport tube for sampling. Each segment was cut open and the sorbent mixture was recovered, homogenized and a subsample transferred to 40 mL glass vials.

2.2. Analysis and data treatment

2.2.1. Water flux

The AC samples were shipped to the University of Florida for analysis. In the laboratory, the tracer mass in standard AC samples and the tracer mass remaining in the final AC samples were extracted ~~by~~ iso-butyl alcohol (IBA). About 10 g of AC samples were collected into pre-weighed 40 mL vials containing 20 mL IBA. Vials were rotated on a Glas-Col Rotator, set at 20 % rotation speed, for 24 h. Then, subsamples were collected in 2 mL GC vials for alcohol tracer analysis. The samples were analyzed ~~by~~ a GC-FID (Perkin Elmer Autosystem) (Cho et al. (2007).

The relationship between time average specific discharge q through the device and tracer elution is given by ~~the~~ equation (1) (Hatfield et al., 2004)

$$q = \frac{1.67\, r\theta\, (1-M_R)\, R_d}{t} \qquad (1)$$

where r (m) is the radius of the HPFM, θ is the water content in the HPFM (m³ m⁻³), M_R is the relative mass of tracer remaining in the HPFM sorbent, t is the sampling duration and R_d is the retardation factor of the resident tracer on the sorbent.

The retardation factor R_d ~~is a measure for~~ the rate of elution of a particular alcohol from the AC. R_d for the specific set of tracers and AC used in this study had previously been determined by the relationship between tracer mass loss and the cumulative water flow by Hatfield et al. (2004) and Annable et al. (2005) (**table 1**).

2.2.2. Nutrient flux

All values for NO_3^- and PO_4^- in this article are noted as NO_3^--N or PO_4^--P respectively if not indicated otherwise.

NO_3^- and PO_4^- were extracted and analyzed in the laboratory at UFZ in Magdeburg, Germany.

For extraction, 30 mL of 2M KCl was added to 5 g of resin and rotated for 24hours. The solution was then analyzed on a Segmented Flow Analyser Photometer (DR 5000, Hach Lange): NO$_3^-$ -N at 540 nm (precision of 0.042 mg L^{-1})~~,~~ SRP at 880nm (precision 0.003 mg L^{-1}).

The time-averaged advective horizontal nutrient flux can be calculated ~~by the following relationship~~ (Hatfield et al., 2004):

$$J_N = \frac{qM_N}{2\alpha r L t} \qquad (2)$$

Where M_N (kg) is the mass of nutrient adsorbed, L (m) is the length of the vertical thickness of the segment, α (-) is a factor that characterizes the convergence or divergence of flow around the HPFM.

2.3. Laboratory experiments

All experiments ~~described in this paragraph~~ were accomplished on triplicate samples, if not indicated otherwise.

The nutrient sorbent had to meet the following criteria:

a) Have a high loading capacity for NO$_3^-$, PO$_4^-$ and competing anions
b) Be free of compounds which could interfere with the alcohol tracer measurements (e.g. organic substances)
c) Have a low background of NO$_3^-$ and PO$_4^-$

A pre-selection for anion-absorbing resins ~~which were~~ free of organic compounds was made based on information provided by ~~the~~ manufacturers (Purolite®, Lewatit®, Dowex®). Nutrient background was ~~then~~ determined by extracting and analyzing NO$_3^-$ and PO$_4^-$ from 5 g of each pure resin as described above. Extractable background concentrations were ~~then~~ converted to nutrient fluxes using a Darcy flux of 45 mm h^{-1}, ~~an~~ estimate of hyporheic flow velocity ~~based on~~ prior salt tracer tests at the study side. Likewise expected hyporheic nutrient flux was computed from previously examined concentrations in pore water samples and above-mentioned hyporheic flow. The only resin with nutrient background below 5 % of expected concentrations was Purolite® A500 MB Plus (Purolite GmbH, Ratingen, Germany), which had extractable background NO$_3^-$ of 8 µg NO$_3^-$-N g^{-1} wetted resin and 0.08 µg PO$_4^-$-P g^{-1} resin. Purolite® A500 MB Plus was then considered for further testing.

For the determination of the loading capacity, three 5 cm diameter columns were filled to a height of 5 cm with wetted Purolite® A500 MB Plus resin and infiltrated with water collected from the study reach. The columns were covered with tin foil to keep ~~out light~~ and ensure stable temperature. A constant supernatant of 1 cm was kept on all three columns. Water was continuously pumped through the columns at a speed of 20 mL h^{-1}, which also equals the expected Darcy velocity of 45 mm h^{-1}. The draining water was sampled twice a day and analyzed for SRP and NO$_3^-$. Biofilm growth on the resin was assessed by repeating the same experiment in smaller columns and extending it for several days after break-through occurred~~. That way,~~ nutrient consumption by biofilm after the exhaustion of the loading capacity could be monitored. Additionally, samples of resin granules were colored with SybrGreen ($C_{32}H_{37}N_4S^+$) on nucleic acid and examined under a confocal laser scanning microscope, to depict the degree of bacterial fouling on the granular surface.

~~Concurrent to the resin,~~ AC was tested for background nutrients by extraction with 30 ml KCL per 5 g AC.

The activated carbon contained 0.01 mg PO_4^--P g^{-1}AC and 0.08 mg NO_3^--N g^{-1} AC, which amounts up to 75 % of the expected concentration for nitrate and 320 % for SRP. To investigate whether the AC could be cleaned by washing, we repeatedly treated AC samples with distilled water or KCl as depicted in the extraction description above. Nutrients did not leach ~~of~~ under water treatment and neither did KCl treatment satisfactorily reduce extractable background concentration on the AC. After the third washing of AC with KCl, ~~still~~ 0.02 mg PO_4^--P and 0.04 mg NO_3^--N could be extracted per g AC. Further, it is unclear to which degree replacing absorbed nutrients by KCl would alter the alcohol tracer retardation and extraction on the AC. For those reasons ~~it was~~ decided to keep the nutrient absorbing resin separated from the AC. As AC did not release background nutrients water flowing through AC and afterwards resin layers ~~was~~ not considered problematic.

2.4. Field testing of hyporheic passive flux meters (HPFMs)

2.4.1. Study site

A 30 m long stretch of the Holtemme River, a 3rd order stream in the Bode catchment, TERENO Harz/Central German Lowland Observatory, served as study site (51°56'30.1"N, 11°09'31.8"E) (**figure 3**). The testing reach is located in the lowest part of the river, where the water chemistry is highly impacted by urban effluent and agriculture (Kamjunke et al., 2013). Long stretches have been subjected to changes in the natural river morphology by canalization (Sachsen-Anhalt Landesbetrieb für Hochwasserschutz und Wasserwirtschaft, 2009).
The sediment at the selected site ~~is~~ mainly sand~~y with~~ gravel and stones ~~mixing in~~. Clay lenses are present in the deeper sediments below 35 cm.
Mean discharge is 1.35 $m^3 s^{-1}$ with highest peaks around 5-6 $m^3 s^{-1}$. Discharge is continuously recorded by the local authorities at the gauge Mahndorf, 15 km upstream of the testing site. In the course of the year, NO_3^--N concentrations in the lower Holtemme vary between 2 and 8 mg NO_3^- -N L^{-1}(LHW, 2015/2016).

2.4.2. HPFM testing

The equipment was installed for a period of 7 days from 4th to 11th June 2015 as illustrated in **figure 2**.
Based on the laboratory results for the nutrient backgrounds, two approaches for constructing and deploying HPFMs were ~~field~~ tested.

A) Resin only and AC only HPFMs

4 HPFMs were constructed of which 2 contained only resin (R1 and R2) and the other two contained only AC (AC3 and AC4). The HPFMs were then installed in pairs: AC only and resin only next to each other with a separation distance of 30 cm. Those 4 HPFMs were sectioned in 5 horizontal flow segments, each with a vertical length of 10 cm.
For the calculation of the nutrient flux through each segment of R1 and R2, we used the corresponding water flux through the respective segment of AC3 and AC4.

B) Alternating segments of AC and resin HPFMs

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HPFMs L5 and L6 consisted of 7 segments starting and ending with an AC segment and interjacent segments altering between resin and AC (also see **figure 1**). Each segment had a length of 7 cm.

For the calculation of the nutrient flux through the resin segments we used the interpolated water flow measured in the two adjacent AC segments.

A control HPFM equal to the HPFMs with alternating segments was stored and transported together with the other HPFMs. After deploying the control HPFM, it was immediately retrieved, transported back to the laboratory and stored until it was sampled and analyzed along with the other HPFMs.

2.4.3. Additional measurements

Vertical Darcy velocity (q_y)

The vertical Darcy velocity (q_y) (m d^{-1}) in the streambed was calculated using temperature profiles measured between January 2015 and October 2015. According to Schmidt et al. (2014) vertical flow velocities can be computed from the temporal shift of the daily temperature signal in the subsurface water relative to the surface water. A multi-level temperature sensor (Umwelt und Ingenieurtechnik GmbH, Dresden, Germany) was installed at the test site in January 2015. Temperature was recorded at the surface-subsurface interface and at depths of 0.10, 0.125, 0.15, 0.2, 0.3 and 0.5 m in the sediment at a 10 min interval (accuracy of 0.07 °C over a range from 5 to 45 °C, and a resolution of 0.04 °C)

Oxygen profiles

Two oxygen loggers (miniDO$_2$T, Precision measurement engineering Inc.) were installed in the river bed at depths of 25 and 45 cm below surface-subsurface boundary. Installation was carried out 4 weeks prior to the experiments, allowing enough time for re-equilibration of the surrounding media. The measurement time step was 5 min.

Multi-level samplers (MLS)

Multi-level samplers as described by (Saenger and Zanke (2009)) are devices for the manual extraction of hyporheic pore water from several distinct depths. The two samplers A and C used in these experiments were manufactured by the institutional workshop of the UFZ. They consisted of an outer stainless steel tube with a length of 50 cm and a diameter of 5 cm. Ceramic filters were inserted in this outer steel mantle marking the extraction depths at 5, 15, 25 and 45 cm. The inner sides of the filters were attached to steel pipes that ran to the top of the sampler so that Teflon tubes could be attached. A protective hood was threaded on the upper end of the sampler to preclude particles and sediment entrance. Pore-water was manually extracted by connecting syringes to the open end of the Teflon tubes and slowly sucking up water.

A sample volume of about 10 mL was filtered in the field and placed in glass vials for transport to the laboratory. Analysis for NO_3^- , SRP, sulphate (SO_4^{2-}) and Boron (B) were conducted in the analytical department of the UFZ. Analytical procedure for NO_3^- and SRP was according to the description above.

SO_4^{2-} and B were used as natural tracers for groundwater and surface water respectively. SO_4^{2-} was analyzed on an ion chromatograph (ICS 3000, ThermoFisher, former DIONEX), B was analyzed on an inductively coupled plasma mass spectrometer (ICP-MS 7500c, Agilent)

Manual pore-water samples were taken twice during the installation period of the HPFM: on the 4th and 11th of June 2015, both times between 1 pm and 4 pm local time.

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Due to conflicting findings in the pore water samples taken on June 4th and 11th 2015, the sampling was repeated on the 8th of October. In October, each device was sampled twice, the first time in the early morning before sun rise and again in the early afternoon (around 2 pm).

Surface water chemistry was monitored with two sets of sensors: upstream and downstream of the reach. For this we installed automated UV absorption sensors for NO_3^- (ProPS WW, TriOS) on the beginning of the testing reach and 1.5 km downstream for the duration of the experiments. The pathway-length of the optical sensor was 10 mm, measuring at wavelengths 190-360 nm with a precision of 0.03mg NO_3^--N L^{-1} and an accuracy of ± 2 %. The measurement time step was set to 15 min.

Both UV sensors were supplemented with a multi-parameter probe YSI 6600 V2/4 (YSI Environmental, Yellow Springs, Ohio) recording the following parameters: pH (precision 0.01 units, accuracy ± 0.2 units), specific conductivity (precision 0.001mS cm^{-1}, accuracy ± 0.5 %), dissolved oxygen (precision 0.01 mg L^{-1}, accuracy ± 1%), temperature (precision 0.01 °C, accuracy ±0.15 °C), turbidity (precision 0.1 NTU, accuracy ± 2 %) and chlorophyll-a (precision 0.1 µg L^{-1}, linearity: $R^2>0.9999$ relative to dilution of Rhodamin WT solution of 0 to 400 µg L^{-1}).

2.4.4. Nitrate transport and denitrification

Flux and denitrification activity for the specific conditions at the study site during the HPFM testing phase were calculated using the morphological and hydrological parameters summarized in **table 2.**

The proportion of water infiltrating the hyporheic zone was then calculated as the ratio $\frac{Q_{HZ}}{Q_{SW}}$~~. W~~here Q_{HZ} ($m^3 s^{-1}$) is the product of the average horizontal Darcy velocity q_x ($m\ s^{-1}$) measured in the HPFM and the cross sectional area of the upper 50 cm of the hyporheic zone A_{HZ} (m^2).

The NO_3^- removal activity of the hyporheic zone (%) was calculated from the difference in surface water concentration $C_{NO3\text{-}SW}$ and the average concentration observed in the HPFM ($C_{NO3\text{-}HZ}$).

3. Results

3.1. Laboratory experiments

3.1.1. Loading capacity

Break-through in the sorbent column experiments occurred after 300 pore volumes (PVs) or 21 days at selected drainage for both NO_3^- and SRP. The minimal absorbing capacity as calculated from parameters indicated in the product sheets of Purolite® A500 MB Plus was 265 PVs, equaling 19 days in the described set up.

In the biofouling experiment, the NO_3^- concentration in the draining water gradually decreased again after beak-through. SRP in the draining water was completely depleted 6 h after the break-through. We attributed the decrease of nutrients in the draining solution after breakthrough to biotic consumption of SRP (limiting nutrient) and NO^{3-} .

Under the laser scanning microscope growth of biofilm could be observed on all of the examined Purolite® beads.

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3.2. Field testing

Deployment required approximately 15 min per HPFM and could be conducted by two persons. The water depth during the installation was 40 to 100 cm, depending on the specific location in the stream. The results from the control HPFM proved that tracer loss or nutrient accumulation during transport, deployment and retrieval was negligible.

The average horizontal water flow q_x and nutrient flux measured in the HPFM during the 7 day field testing are illustrated in **figure 3**. All flux meter except ~~5L~~ showed declining concentrations and q_x with depth. Average horizontal q_x was 76 cm d^{-1}, ranging from 115 cm d^{-1} in the shallowest layer of ~~5L~~ to 20 cm d^{-1} in the deepest layer of AC4)

With an average water flux of $Q_{HZ} = 2.65\ e^{-5}\ m^3\ s^{-1}$ through the assessed upper 50 cm of the hyporheic zone and across the 6 m width of the stream, 0.008 % of water transported in the river entered the hyporheic zone (**table 3**). While the average surface water concentration was 2.86 mg NO_3^- -N L^{-1}, the average concentration in the subsurface measured with the HPFMs was only 1.39 mg NO_3^--N L^{-1}. Accordingly, 52 % of the infiltrating NO_3^- was removed in the hyporheic zone. For SRP the average surface water concentration from 4th to 11th June 2015 was 0.165 mg PO_4^-P L^{-1}, the average concentration in the hyporheic zone was 0.11 mg PO_4^--P L^{-1}.

Temperature profile

Vertical water flow q_y in the stream bed was predominantly downward from January to October 2015. It was continuously downward during the HPFM testing phase, ranging from 40 to 55 cm d^{-1}. The relation between q_y and q_x ($\tan\alpha = \frac{q_y}{q_x}$) results in an approximate angle of hyporheic flow of 32° downwards, assuming that q_x is directed downstream.

Oxygen profiles

We observed strong diel variations in oxygen concentration in the hyporheic zone. During several nights oxygen was nearly depleted (**figure 4**).The minima and maxima oxygen concentration in the subsurface occurred contemporarily with the respective extremes in the surface water.

Multi-level samplers

The results from the manual pore-water sampling conducted in June 2015 are illustrated in **figure 5.** In order to facilitate direct comparison, nutrient fluxes as measured in the HPFM were converted to flux average concentrations using the measured q_x.

In general, nutrient concentrations in the manually sampled pore-water were higher than the average concentration derived from the HPFM. The expected increase of SRP and decrease of NO_3^- and water flow with depths was observed in the HPFM, whereas pore water extracted with the MLS showed no change over depth for neither of the two substances.

Observations during installation and retrieval of the HPFM suggest that HPFM L6 and R4 hit a clay lens in the lowest segments (deeper that 35 cm in the subsurface).

On both sampling dates (04.06. and 11.06.2015) neither SO_4^{2-} nor B showed a vertical gradient in concentrations in the pore water samples. SO_4^{2-} concentrations of 170 mg L^{-1} on the 4th June and 190 mg L^{-1} on the 11th June were in the same range than surface water concentrations. Likewise were B concentrations with 50 to 60µg L^{-1} in consistence with the concentrations in the surface water. Conclusively, manually sampled hyporheic zone water was originating exclusively from the surface water.

The repeated manual pore-water sampling in October (**figure 6**) showed clear differences in SRP and NO_3^- concentration between early morning and afternoon.

NO_3^- concentrations in the subsurface were in general higher in the early morning hours than in the afternoon. SRP shows the opposite trend: higher concentrations in the early morning.

Surface water NO_3^- concentrations on the sampling day were 2.5 mg NO_3^--N L^{-1} in the morning and 2.7 mg NO_3^--N L^{-1} in the afternoon. SRP concentrations were consistently 0.15 mg L^{-1}.

4. Discussion

The application of the HPFM proved as an innovative tool for the quantitative in situ measurement of NO_3^- and SRP fluxes through the hyporheic zone. Earlier applications of passive flux meter (SBPFM) in river bed studies (Layton, 2015) exclusively assessed vertical flow, so that this is the first study which used HPFM for the quantification of horizontal nutrient transport in the hyporheic zone. (Layton, 2015)In the current work adaptations were developed, tested and improved. Those include the choice of an appropriate resin, assessment of biofilm growth on the instruments and a practice that avoids contamination of the absorber with sorbent inherited nutrients. While both of the latter mentioned practices examined in this study delivered reliable results, each inherits designated characteristics being more or less beneficial for different specifications. .

1) Deploying two HPFMs of which one is used to assess the water flux and the second to capture nutrients. This approach is preferable if a high resolution depth profile is needed (a heterogeneous flux distribution in the vertical direction). Since this approach assumes that local horizontal heterogeneity is negligible in the range of 20-30 cm, we recommend this type for the use in uniform systems such as channelized river reaches.
2) Alternating nutrient absorbing and water flux measuring segments is a good choice if local lateral flux heterogeneity is expected to be high and/or if the vertical profile is moderately heterogeneous.

Further improvements of the HPFM for nutrient studies in the subsurface of rivers could be achieved by identifying a nutrient free carrier for the tracers. First, because this would allow measuring nutrient and water flux at the same location within the device and thereby increase spatial resolution. Second because in a mixed texture of nutrient absorber and tracer carrier the antibacterial nature of the activated carbon would suppress biofouling on the absorbent. Here we showed that substantial biofilm growth occurred on the resin in the laboratory as well as under field conditions. Even though the observations on the column experiments suggest that biofilm growth on the resin porous media did not affect its loading capacity, it is unclear, to what extent the biofilm bound nutrients can be captured by the implemented extraction procedure. As a result, it is not possible to completely exclude that biofouling might lead to underestimation of actual nutrient flux through the HPFMs.

In addition to instrumental adaptations we presented an installation practice, which allows for smooth deployment with minimal disturbance of the system. Unlike typical well screen deployments where PFMs (Verreydt et al., 2013;Annable et al., 2005) or SBPFM (Layton, 2015) have been inserted into a screened plastic or steel casing, our technique enabled the direct contact of the HPFMs with the surrounding river sediments. Compared to other intrusive measurements of hyporheic flow, the disturbance created by a HPFM is low, because the measuring time is long relative to the duration of the installation. By removing the solid casing, we further improved the integration of the instrument in the natural system and avoid the generation of artificial flow paths along the walls of the device. For very coarse sediments, a protection of the HPFM with a screened plastic or steel casing might still be preferential. A mayor gain of the HPFM method is highlighted by the findings of the 7 day long field testing: Concurrent manual sampling of pore-water from MLSs showed diurnal variations of SRP and NO_3^- in the subsurface of the testing reach. Whereas, as in the first MLS assessment in June 2015 only a single time specific snap shot sampling was conducted, the results may not realistically represent the overall conditions at the target site. Diurnal cycles in benthic metabolism cause temporal variations in various water quality parameters, including many nutrients. As the majority of sampling is commonly conducted during daylight hours, night time conditions are underrepresented in studies relying on single manual sampling events. Th~~at~~ flux average concentrations can ~~derivate~~ by more than 50 % from estimates based on single event sampling was illustrated by comparison between our manual samples and the average pore-water concentrations calculated from the HPFM data.

We consider that a combination of pore water samples for diurnal dynamics and long term recording of nutrient transport through the hyporheic zone via HPFM is a valuable approach that can be efficiently used to characterize and quantify nutrient dynamics in a sediment system. Presumably, for our field test, the lower NO_3^- concentrations in the subsurface in the early morning hours compared to afternoon samples detected in the MLS samples in October can be attributed to a dominance of night time denitrification. DO exhibited strong diurnal cycles with anoxic periods occurring in the subsurface during night times periods. This temporal pattern, owing to microbial consumption of O_2 in the sediment, is commonly found in nutrient rich streams (Nimick et al., 2011;Harrison et al., 2005) and identified as triggering factor for night time denitrification in the hyporheic zone (O'Connor and Hondzo, 2008;Laursen and Seitzinger, 2004;Christensen et al., 1990). Presumably, the redox conditions in the subsurface also regulated the mobilization/demobilization of phosphate (Smith et al., 2011). Reducing conditions during night periods enhanced the mobilization of PO_4^-. During day elevated O_2 and NO_3^- concentrations suppressed the reduction of Fe^{3+} (Miao et al., 2006), PO_4^- was therefore demobilized and SRP was decreasing (Gabriel et al., 2006). Accordingly, SRP concentration in hyporheic pore water samples was higher in the early morning than in the afternoon. Concurrent measurements of pore water oxygen concentrations as presented in this study are therefore essential to interpret nutrient dynamics. To our knowledge there is a lack of studies which examine the diurnal pattern of nutrients in the hyporheic zone and no studies which actually measured them.

Like solute concentrations and water flow patterns, the vertical extension of the hyporheic zone varies in time and space and between different rivers and reaches. Our set up assessed exclusively the upper 50cm of the hyporheic zone. We found that this entire area (and potentially deeper) of the subsurface contained active sites for denitrification. While some studies have found that denitrification is limited to the upper few cm of the hyporheic zone close to the sediment-water interface (Hill et al., 1998;Harvey et al., 2013), our results are in accordance to findings by Zarnetske et al. (2011b) and Kessler et al. (2012) who also report extended active hyporheic zones. As vertical water movement was constantly downward and the lowest concentrations of NO_3^- were observed in the deepest segments of the HPFMs, the hyporheic zone at this study site likely extends deeper than the 50 cm evaluated. The length of an HPFM can easily be increased, depending on the individual site conditions.

The hyporheic removal potential of more than 50 % of infiltrating NO_3^- and 30 % of SRP is clearly an indication of an active hyporheus. Evaluation of the effect of hyporheic denitrification activity on overall nitrate removal in the stream or the normalization of hyporheic uptake to a benthic area requires the length of the hyporheic flow path, which can be derived from the residence time of water and solutes in the hyporheic zone τ_{HZ} and the Darcy velocity q_x. Assuming a downward flow direction, τ_{HZ} could be inferred from the vertical Darcy velocity q_y as assessed from the temperature profiling and the hyporheic zone depths of 50 cm. Thereafter, τ_{HZ} conceptually corresponds to the time the water travels through the hyporheic zone before exiting to groundwater and s_{HZ} to the horizontal vector of the flow paths. The denitrification rate $U_{NO3\text{-}HZ}$ (mg NO_3^--N m^{-2} d^{-1}) is then the difference between the theoretically transported NO_3^- mass $M_{NO3\text{-}HZ\ theor}$, which is the product of Q_{HZ} and $C_{NO3\text{-}SW}$ and the measured mass flux $M_{NO3\text{-}HZ\ real}$. During the testing phase $U_{NO3\text{-}HZ}$ was calculated as 693 mg NO_3^--N m^{-2} d^{-1}. The same procedure yields a removal rate for SRP of $U_{PO4\text{-}HZ}$ = 24 mg PO_4^--P m^{-2} d^{-1}.

5. Conclusion and Outlook

The role of the hyporheic zone as a hot spot for instream nutrient cycling is indisputable (Mulholland et al., 1997;Fellows et al., 2001;Fischer et al., 2005;Rode et al., 2015). The loss of this essential function may be crucial under anthropogenic forcing, such as morphological alteration (Borchardt and Pusch, 2009), eutrophication (Ingendahl et al., 2009)and sediment loading (Hartwig and Borchardt, 2015). In all these cases, mass transfer to the hyporheic zone may be the rate limiting step for nutrient removal (Basu et al., 2011).

Despite decades of research on hyporheic nutrient cycling, robust quantitative data on horizontal nutrient fluxes through the hyporheic zone are limited, which is mainly due to methodological constraints in measuring nutrient concentrations and water flux in the subsurface of streams (O'Connor et al., 2010;Boano et al., 2014;Gonzalez-Pinzon et al., 2015).

Passive flux meters have the potential to fill the gap in measured quantitative nutrient fluxes to the reactive sites in the sediments of rivers. Up to date, this is virtually the only method which can simultaneously capture nutrient and water flux through hyporheic zone within the same device and at the same spatial location. The successful field testing of several devices proved their applicability for quantifying NO_3^- and PO_4^- flux to reactive sites in the hyporheic zone. Hyporheic flux rates of nutrients and denitrification rates measured in an agricultural 3rd order stream were generally in agreement with contemporary alternative measurements and rates reported in literature.

Our results clearly highlight the advantages of HPFM compared to commonly used methods, first of all their capability to integrate longer time spans.

Quantifying nutrient flux to the potentially reactive sites in the hyporheic zone is an essential step to further improve our process based knowledge on hyporheic nutrient cycling. In the future, long-term measurements of nutrient fluxes as obtained from HPFM can feed into and advance the transport part of nutrient cycling models.

We anticipate further improvement and increased use of hyporheic zone passive flux meter approaches in order to advance conceptual models of nutrient cycling in the hyporheic zone. We demonstrated modifications which extended PFM application from groundwater to hyporheic zones. Taking a similar approach, passive flux meters may be adapted for the use in other environments: e. g. lakes, estuaries, etc. While we focused on nutrients, PFMs may also be used for a wide range of other substances like contaminants or trace elements. Their deployment should be considered whenever

- flux instead of concentration is needed
- the focus is on general transport characteristics of a stream rather than short term dynamics,
- the use of sensors is impractical because sensors for the target solute are not available, or the hyporheic environment is not accessible with electronical sensors.

Being labor efficient and attractive with respect to relatively low costs, numerous HPFM can be efficiently used to cover larger areas and assess the degree of local heterogeneity. Further, neither sensitive technology, maintenance, nor power supply are needed which can be extremely advantageous for the use in remote areas or study sites without power infrastructure.

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Figures and tables

Table 1. Resident Tracers and Partitioning Characteristics

Resident tracers	Aqueous concentration (g L^{-1})	Rd
methanol	1.2	4.9
ethanol	1.2	20
Isopropyl alcohol (IPA)	2.3	109
tert-butyl alcohol (TBA)	2.3	309
2,4-dimethyl-3-pentanol (DMP)	1.2	>1000

Table 2. Selected morphological and hydrological parameters of the testing site. All parameters are averages for the duration of the testing phase from 04.06.2015-11.06.2015

	~~Surface water~~	unit	
cross sectional area	A_{SW}	m^2	3.41
depth (mean)	h	m	0.565
width (mean)	w	m	6.03
mean velocity	v	$m\ s^{-1}$	0.097
discharge	Q_{SW}	$m^3\ s^{-1}$	0.32
NO_3^--N	$C_{NO3\ SW}$	$mg\ m^{-3}$	2863
NO_3^--N mass flux	$M_{NO3\ SW}$	$mg\ s^{-1}$	896
PO_4^--P	$C_{PO4\ SW}$	$mg\ m^{-3}$	165
PO_4^--P mass flux	$M_{PO4\ SW}$	$mg\ s^{-1}$	51
	Hyporheic zone upper 50cm		
depth of HZ assessed with HPFM	h_{HZ}	m	0.5
cross sectional area of HZ	A_{HZ}	m^2	3.02

Table 3. Summarized parameters of NO_3^- transport and removal through the upper 50 cm of the hyporheic zone at the test site. Values are averages for the testing phase from 04.06.-11.06.2015.

parameter	token	unit	
water flow through HZ	Q_{HZ}	$L\ s^{-1}$	0.0265
% of river water entering HZ	% water HZ	%	0.008
Horizontal Darcy velocity	q_x	$cm\ d^{-1}$	76
average NO_3^- concentration in the HZ	$C_{NO3\ HZ}$	$mg\ m^{-3}$	1389
% NO_3^- entering the HZ which is denitrified	% denitri in HZ	%	52
potential NO_3^- load entering HZ	$M_{HZ\ theory}$	$mg\ s^{-1}$	0.08
NO_3^- load measured in HZ	$M_{HZ\ measured}$	$mg\ s^{-1}$	0.037

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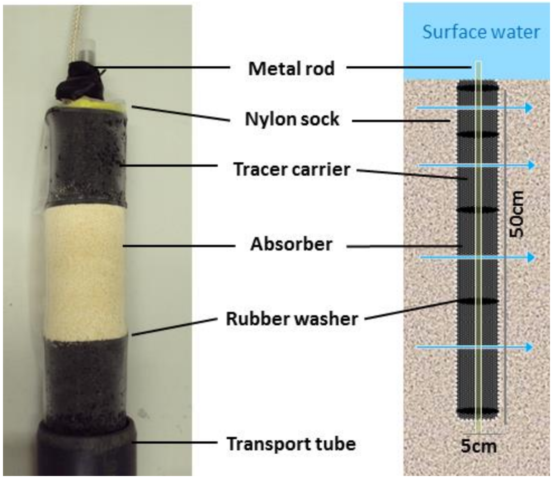

Figure 1. Photograph of an HPFM before deployment (left) and schematic profile of a deployed HPFM (right)

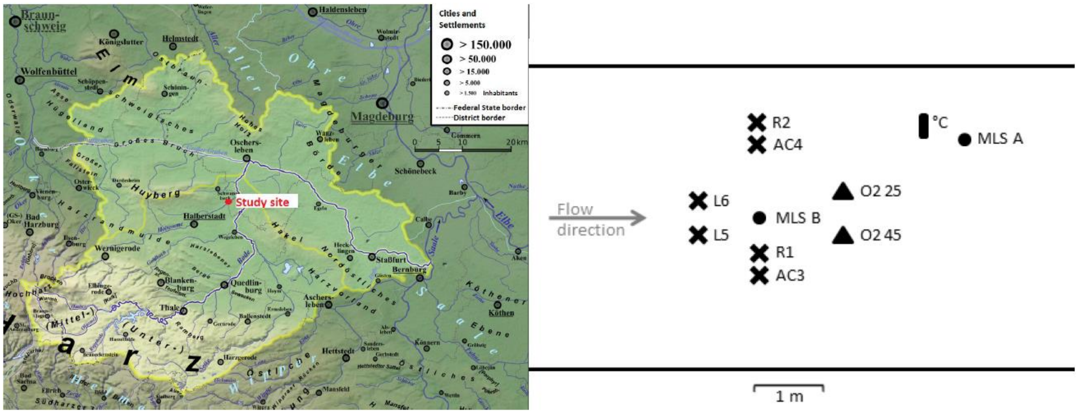

Figure 2. Map of Bode catchment, the study site is marked in red (left) and overview of instrumental setup at the Holtemme for the testing phase in June 2015 (right).

R1, R2 resin only HPFMs; AC3, AC4 activated carbon only HPFMs; L5,L6 alternating layered HPFMs; MLSA, MLSB Multi-level sampler; O2 25, O2 45 subsurface oxygen logger; °C vertical temperature profile

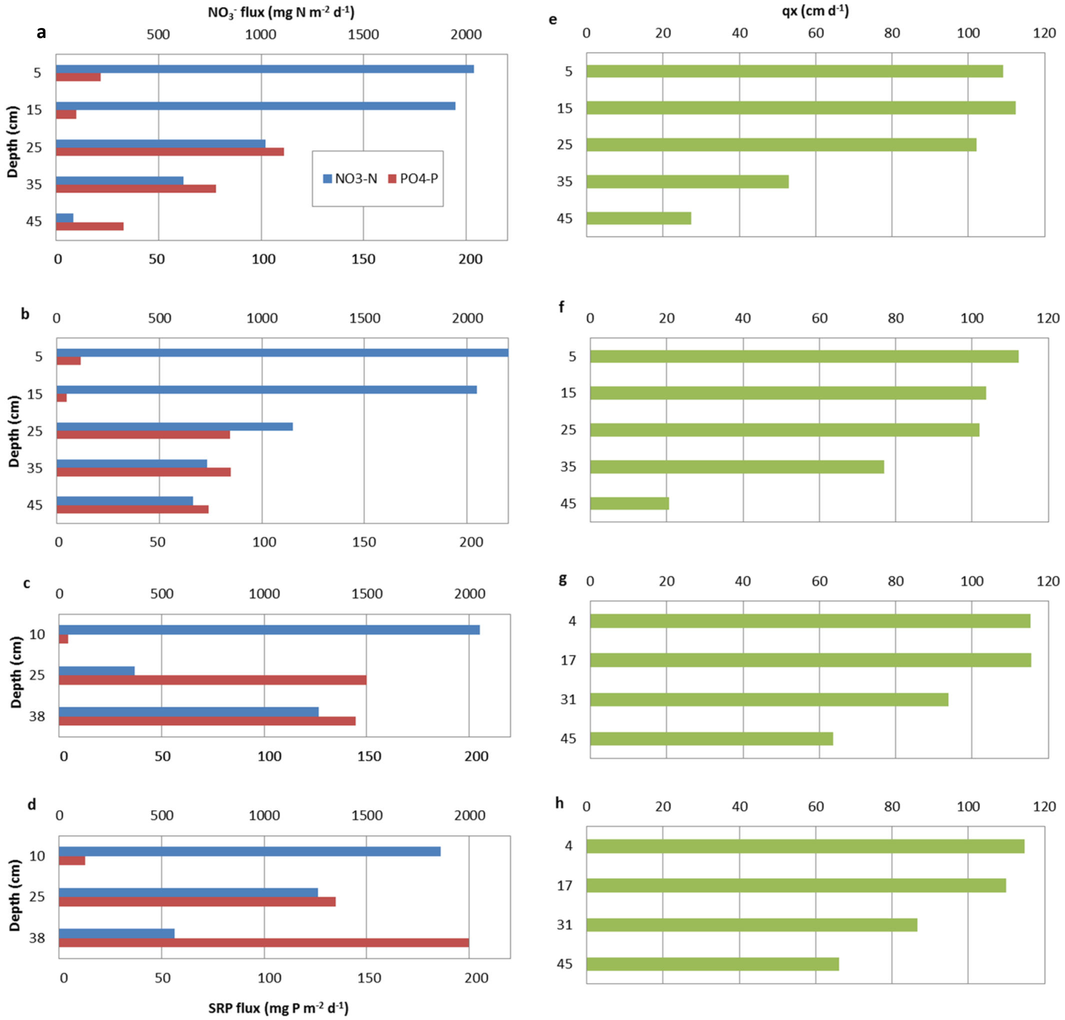

Figure 3. Time integrative measurements for the 04.-11.06.2015. Left side: Horizontal NO_3^--N and SRP-P flux in mg m^{-2} d^{-1} through the resin HPFMs R1 (a), R2 (b) and the layered HPFMs L5 (c) and L6 (d). Right side: corresponding Darcy velocities q_x in cm d^{-1} through the activated carbon HPFMs AC3 (e) and AC4 (f) and the layered HPFMs 5L (g) and 6L (h)

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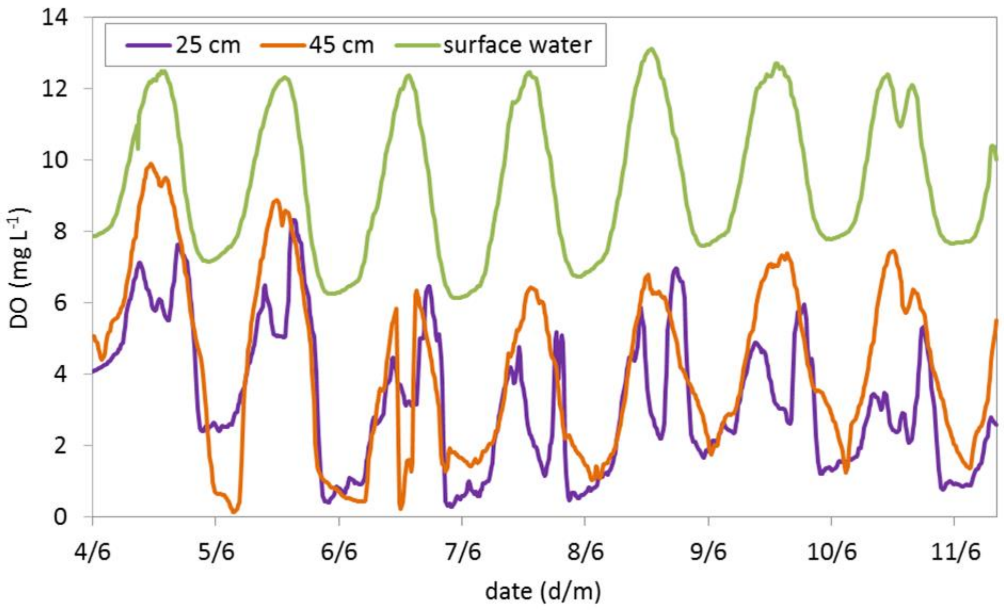

Figure 4. Time series of dissolved oxygen concentrations in the surface water (green) and the subsurface water (depth 25 cm, purple and depth 45 cm orange) at the study site from 04.-11.06.2015

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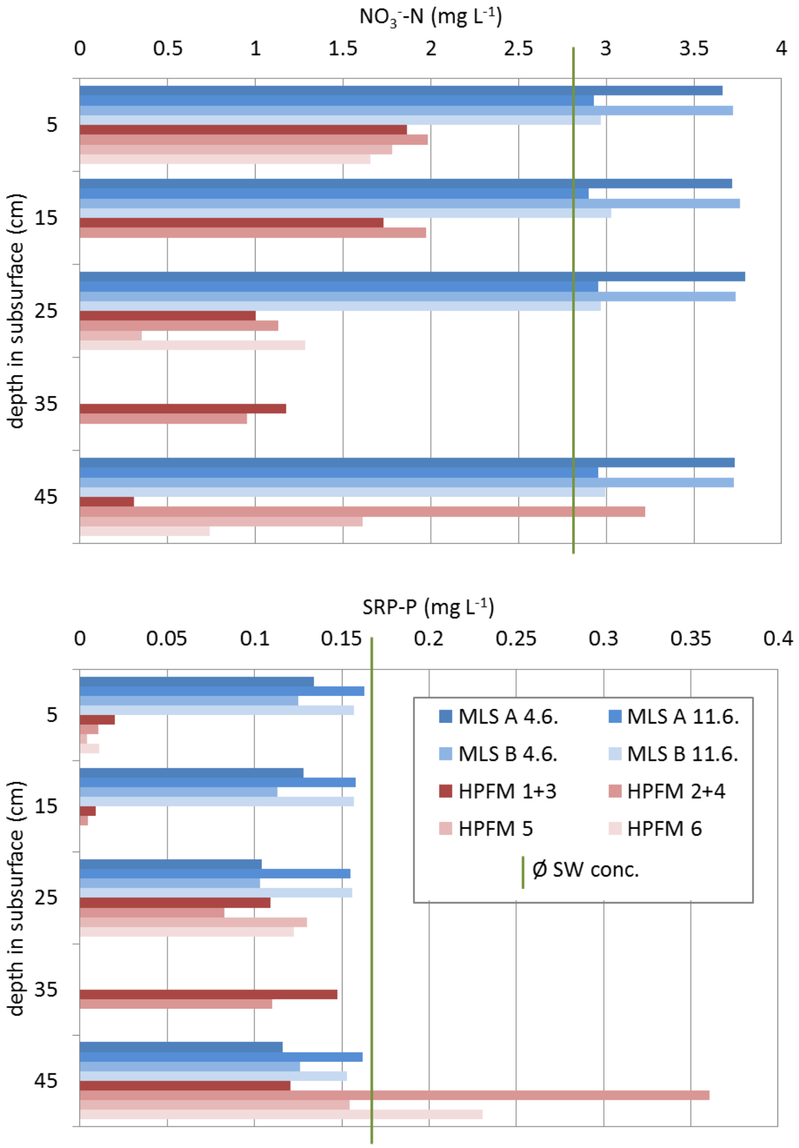

Figure 5. Comparison between manually sampled pore water from MLS (red) and HPFM (blue) for NO$_3^-$-N (top) and SRP-P (bottom). Each MLS was sampled on the 04. and 11.06.2015. Average surface water concentration during the deployment time is marked in green.

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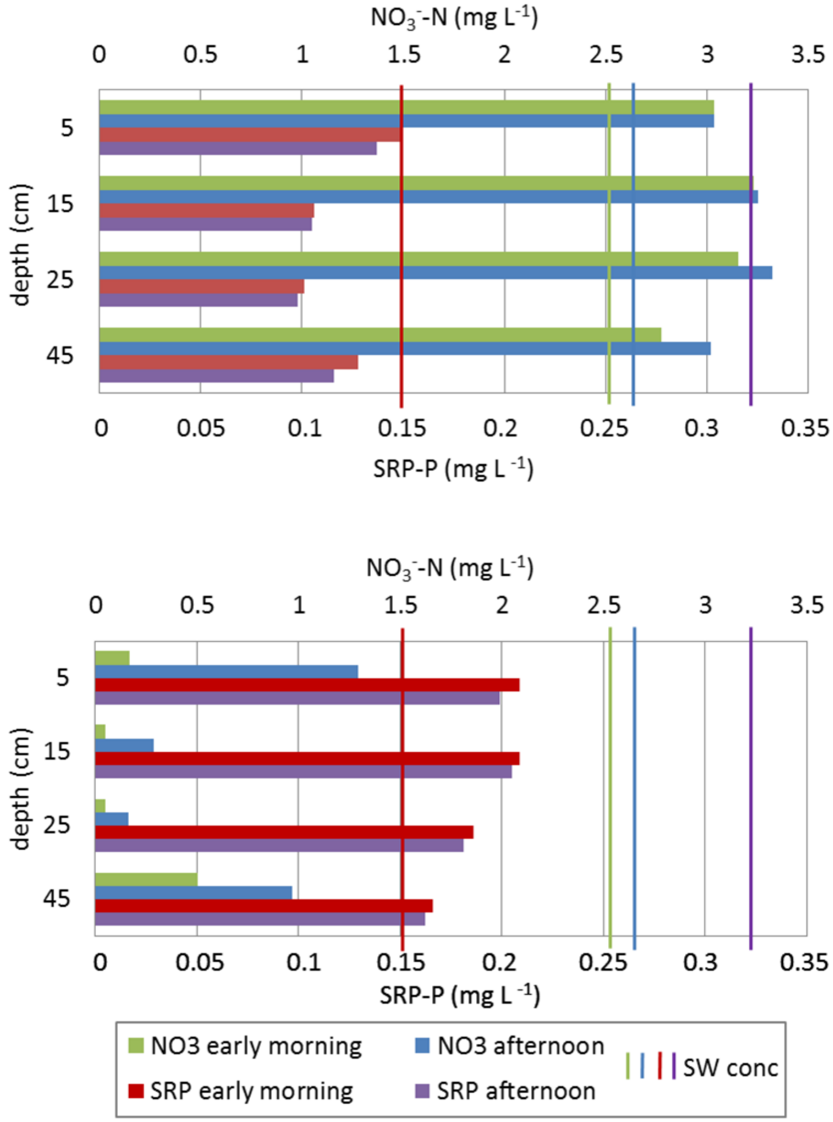

Figure 6. Concentrations of NO_3^--N and SRP in time differentiating manually taken pore-water samples from MLS A (bottom) and MLS B (top) on 8th October 2015. Corresponding surface water concentrations are marked as vertical lines.

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