APPENDIX A

1) Details on the sorbents and tracers used for the HPFMs

1.1. Sorbent for alcohol tracers

Silver impregnated activated carbon (AC) served as sorbent for the resident alcohol tracers. The AC used for the HPFM in this study was provided by the University of Florida, Gainesville.. The AC had a bulk density of 550 g L^{-1}, a grain size ranging from 0.42 to 1.68 mm and a hydraulic conductivity k = 300 m d^{-1}. Further, physical and chemical characterization of the AC as well as absorbing and elution behavior of alcohol tracers on the AC have been established by Hatfield et al. (2004) and Annable et al. (2005).

1.2. Alcohol tracers

Multiple resident tracers with a wide range of tracer elution rates were employed, because the magnitude of water flow through the flux meter is unknown prior to the field applications (Hatfield et al. 2004, Cho et al. 2007). The retardation factor of a substance R_d is a measure for the rate of elution of the substance from a particular carrier. Alcohols offer a wide range of retardation factors and can easily be mixed and sorbed to the AC (Hatfield et al., 2004; Cho et al., 2007). By choosing the same manufacturer for the AC and the same alcohol mixture as used in the above mentioned studies, we could rely on physical and chemical characterizations and calculated R_d for alcohol partitioning behavior which have been established by Hatfield et al. (2004), Annable et al. (2005) and Cho et al. (2007) (**table A1**).

Table A1. Resident tracers per liter of aqueous solution and their partitioning characteristics. Retardation factors (R_d) for the specific set of tracers and AC used in this study had previously been determined by Cho et al. (2007)

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

For 10 HPFMs an alcohol tracer mixture 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).

1.3. Preparation of AC

In order to prepare the resident alcohol tracers on the AC, the AC was soaked in an aqueous solution containing the resident alcohol tracers. A standard ratio of 13 mL tracer mixture was added to 1 L of 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 h to homogenize the AC tracer mixture. After mixing, the supernatant water was discarded and the AC tracer mixture was stored in a sealed container and refrigerated, preventing the evaporation of the alcohol tracers

1.4. Absorber for nutrients

Purolite® A500 MB Plus is a macroporous anion exchanger on the basis of polyvinylbenzyl-trimethylammonium with a typical granular size of 0.88 mm diameter, an average density of 685 g L^{-1} and an effective porosity of 63 %. The theoretical absorbing capacity is indicated in the product sheet as 1.15 eq L^{-1} (molar weight equivalences per liter of resin), corresponding to 71.3 g NO_3^--N L^{-1}.

Realistic absorbing capacities and nutrient background on the sorbents under field conditions in an HPFM application have been evaluated by Kunz et al. (2017).

1.5. Extracting nutrient from the resin

Concentration and fluxes in this publication for NO_3 refer to mg NO_3^--N L^{-1}. For extraction, 30 mL of 2M KCl was added to 5 g of resin and rotated for 24 hours. The solution was then analyzed on a Segmented Flow Analyser Photometer (DR 5000, Hach Lange): NO_3 at 540nm (precision of 0.042 mg L^{-1}), SRP at 880nm (precision 0.003 mg L^{-1}).

2) Equations for calculating horizontal Darcy velocities q_x and nutrient flux J_N through the HPFM

2.1. Water flux q_x

The AC samples were shipped to the University of Florida for analysis. In the laboratory, the mass of the previously applied mixture of alcohol tracers in standard AC samples and the tracer mass remaining in the final AC samples were extracted with iso-butyl alcohol (IBA). About 10 g of AC samples were transferred 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 with a GC-FID (Perkin Elmer Autosystem) (Cho et al.,2007).

The relationship between time averaged specific horizontal discharge q_x (m s^{-1}) through the device and tracer elution is given by equation (1) (Hatfield et al., 2004)

$$q_x = \frac{1.67\, r\theta\, (1-M_R)\, R_d}{t} \quad \text{(A1)}$$

where r (m) is the radius of the HPFM, θ is the volumetric water content in the HPFM ($m^3\ m^{-3}$), M_R (-) is the relative mass of tracer remaining in the HPFM sorbent, t (s) is the sampling duration and R_d (-) is the retardation factor of the resident tracer on the sorbent.

2.2. Nutrient flux J_N

NO_3^- and PO_4^- were extracted and analyzed in the laboratory at UFZ in Magdeburg, Germany, similarly to the analysis of background concentrations on the resin: subsamples of 5g resin were treated with 30 mL of 2 M KCl each and rotated for 24h for extraction. The solution was then analyzed as described above.

The time-averaged advective horizontal nutrient flux J_N (mg $m^2\ d^{-1}$) can be calculated using the following relationship (Hatfield et al., 2004):

$$J_N = \frac{q_x M_N}{2\alpha r L t} \quad \text{(A2)}$$

where M_N (kg) is the mass of nutrient adsorbed, L (m) is the length of the vertical thickness of the segment and α (-) is a factor ranging from 0 to 2 that characterizes the convergence ($\alpha > 1$) or divergence ($\alpha < 1$) of flow around the HPFM. If, like in the case presented here, the hydraulic conductivity of the HPFM sorbent (resin or AC) is much higher than that of the surrounding medium and the HPFM is in direct contact with the sediments (i.e. in absence of an impermeable outer casing or well wall), α can be estimated after Strack and Haitjema (1981)

$$\alpha = \left(\frac{2}{1+\frac{1}{K_o}}\right) \quad \text{(A3)}$$

where $K_D = k_D\, k_0^{-1}$ is the dimensionless ratio of the uniform hydraulic conductivity of the HPFM sorptive matrix k_D ($L\, T^{-1}$) to the uniform local hydraulic conductivity of the surrounding sediment k_0 ($L\, T^{-1}$). For more details on the correction factor α and applications where a solid casing is required or the permeability of the surrounding sediments is higher than of the device see Klammler et al. (2004) and Hatfield et al. (2004).

3) Deployment and retrieval procedure and preparation of samples for analysis

3.1. Deployment and retrieval

HPFM were built, stored dry 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. In the field, prior to installation, 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 diameter of the steel tube for installation tightly fitted with the rubber washers at the top and bottom end of the HPFM, so that vertical water flow through tube and HPFM during installation was inhibited. 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 7 days of exposure, the HPFMs were 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 HPFM were transported to the laboratory.

3.2. Preparation of samples

In the laboratory, the retrieved HPFM were instantly (after maximal 12 hours) sampled for analysis. Therefor one segment after the other was cut open and the sorbent was segment-wise recovered, homogenized and a subsample transferred to 40 mL glass vials. The subsamples from resin segments were then analyzed for nutrient content, the subsamples from AC segments were analyzed for the remaining alcohol tracers as described in point 2.

4) Differences between HPFM types A) and B)

A) Pairs of resin only and AC only HPFMs

4 HPFMs were constructed with 2 containing 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

The HPFMs L5, L6, L7 and L8 consisted of 7 segments each starting and ending with an AC segment and segments altering between resin and AC (also see **figure 2**). 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.