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Passive Flux Meter Measurement of Water and Nutrient Flux in Saturated Porous Media: Bench-Scale Laboratory Tests

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The passive nutrient flux meter (PNFM) is introduced for simultaneous measurement of both water and nutrient flux through saturated porous media. The PNFM comprises a porous sorbent pre-equilibrated with a suite of alcohol tracers, which have different partitioning coefficients. Water flux was estimated based on the loss of loaded resident tracers during deployment, while nutrient flux was quantified based on the nutrient solute mass captured on the sorbent. An anionic resin, Lewatit 6328 A, was used as a permeable sorbent and phosphate (PO_4^{3-}) was the nutrient studied. The phosphate sorption capacity of the resin was measured in batch equilibration tests as 56 mg PO_4^{3-} g^{-1}, which was determined to be adequate capacity to retain PO_4^{3-} loads intercepted over typical PNFM deployment periods in most natural systems. The PNFM design was validated with bench-scale laboratory tests for a range of 9.8 to 28.3 cm d^{-1} Darcy velocities and 6 to 43 h deployment durations. Nutrient and water fluxes measured by the PNFM averaged within 6 and 12% of the applied values, respectively, indicating that the PNFM shows promise as a tool for simultaneous measurement of water and nutrient fluxes.

Input of excess nutrients into confined water bodies leads to long-term environmental problems including eutrophication (Correll, 1998; Daniel et al., 1998; Pieterse et al., 2005). Nonpoint-source pollution, especially from agricultural activities, has been identified as a major source of excess nutrients in surface waters (Reddy et al., 1999; Harter et al., 2002). Nutrients released from agricultural activities are then transported to hydrologically linked groundwater. The polluted groundwater can subsequently discharge to surface waters, accelerating the deterioration in water quality of streams, lakes, and reservoirs (Parry, 1998; Nolan and Stoner, 2000; Harter et al., 2002). To effectively control excess nutrients, a better understanding of nutrient transport pathways and associated mass fluxes is essential.

Current methods for measuring nutrient flux in groundwater monitoring wells typically involve sampling by manual or automatic samplers at selected time intervals (USEPA, 1996). This method provides the depth-averaged concentration at specific sampling times. Multilevel samplers (Einarson and Cherry, 2002) can be an alternative method to measure the nutrient concentration with depth. These methods, however, are laborious and costly when attempting to characterize a large area. Since subsurface water is typically hydrologically linked to surface water, nutrient concentration in groundwater can vary greatly with time (Reddy et al., 1999). Long-term sampling is, therefore, required to obtain a representative mass flux in aquifers discharging to surface water.

A new device has recently been developed for in situ measurement of both water and solute mass fluxes in groundwater (Hatfield et al., 2002a, 2002b). Its usefulness and effectiveness have been evaluated in the laboratory for hydrophobic organic contaminants (Hatfield et al., 2004) and arsenic (Clark et al., 2005), and in field tests for organic contaminants (Annable et al., 2005; Basu et al., 2006). Here, we present the first application of the passive nutrient flux meter (PNFM) for measuring nutrient and water fluxes. The objective of this study was to select an appropriate sorbent and tracer suite to evaluate the PNFM as a method for measuring both nutrient (e.g., phosphate) and water fluxes through laboratory tests. This included development of

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Abbreviations: PNFM, passive nutrient flux meter; PV, pore volume.

methods to characterize system parameters related to flux measurement involving sorption/desorption of phosphate, elution rates of resident alcohol tracers from the adsorbent, and degree of flow distortion. In laboratory experiments the PNFM was evaluated by comparing measured and applied water and nutrient fluxes in a laboratory sand tank.

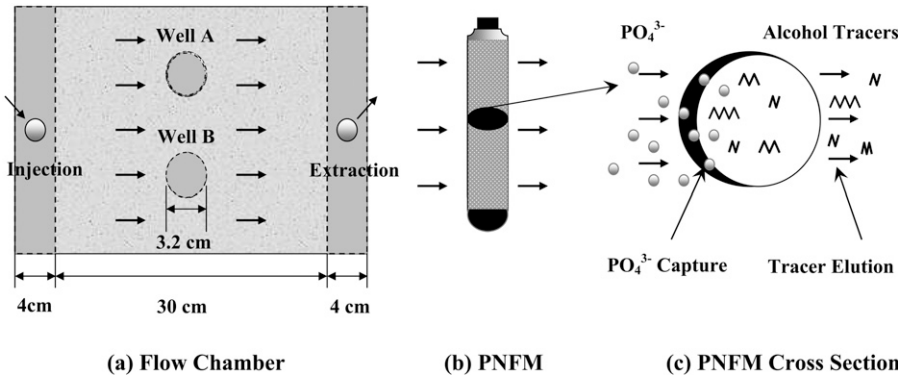

Fig. 1. Schematic diagram for bench-scale flow chamber (plan view) to evaluate performance of the passive nutrient flux meter (PNFM) (shown vertically in center) including tracer elution and PO_4^{3-} accumulation in the PNFM (horizontal section shown). Note that tracers are represented as straight-chain molecules with varying lengths; PO_4^{3-} is represented with spheres.

Materials and Methods

Description of Passive Flux Meter

The passive flux meter (Hatfield et al., 2002a, 2004; Annable et al., 2005) is a new device that simultaneously measures time-averaged solute mass flux, J_N, and water flux, q, with depth in a flow field in a porous medium. The interior composition of the PNFM consists of a permeable sorbent that can intercept and retain nutrients (or contaminants) from up-gradient groundwater flow. An appropriate sorbent (e.g., activated carbon, activated alumina, anionic/cationic resin, etc.) can be selected according to the target solute (Hatfield et al., 2004; Annable et al., 2005; Clark et al., 2005). The sorbent is pre-loaded with known amounts of water-soluble tracers. When the PNFM is exposed to groundwater flow, the resident tracers are desorbed and eluted from the sorbent matrix at rates proportional to groundwater flow through the PNFM. Since the magnitude of groundwater flow is unknown in the actual application, multiple resident tracers, which have different elution rates, are used. The degree of tracer elution is related to the retardation factor, which can be measured by laboratory column elution or batch sorption/desorption tests (Hatfield et al., 2004). After sufficient exposure to groundwater flow, the PNFM is removed from the well and the sorbent is extracted to quantify the nutrients (or contaminants) intercepted and resident tracers remaining. The extracted nutrients and residual tracer mass are used to estimate time-averaged nutrient and water flux, respectively.

Figure 1 depicts how resident tracers are gradually removed from the sorbent with elapsed time, while intercepted solutes are accumulated. Assuming reversible, linear, instantaneous partitioning of the resident tracer between water and sorbent, and uniform and parallel stream lines within the PNFM, the time-averaged specific discharge, q, through the PNFM is calculated as follows (Hatfield et al., 2004):

$$q = \frac{2r\theta R_d \xi}{t} \quad [1]$$

where r (m) is the radius of the PNFM cylinder, θ is the water content in the PNFM ($m^3\,m^{-3}$), R_d is the retardation of the resident tracer on the sorbent, and t (s) is the sampling duration. Here, ξ is the dimensionless cumulative volume of water intercepted by the PNFM at a specified well depth and it is obtained iteratively using the following relation (Hatfield et al., 2004):

$$\xi = \left\{1 - \left[\sin\left(\frac{\pi M_R}{2} + \xi\sqrt{1-\xi^2}\right)\right]^2\right\}^{\frac{1}{2}} \quad [2]$$

where M_R is the relative mass of tracer remaining in the flux meter sorbent. A simplified equation based on Eq. [1] and [2] can be used for the time-averaged specific discharge, q ($m\,s^{-1}$) through the PNFM (Hatfield et al., 2004):

$$q = \frac{1.67r\theta(1-M_R)R_d}{t} \quad [3]$$

While Eq. [3] is applicable to tracers following linear elution functions, Hatfield et al. (2004) provided an extension for non-linear elution behavior using a piecewise linear approximation. Incorporating the piecewise retardation factor, R_{di}, enables R_d to be redefined as follows (Hatfield et al., 2004):

$$R_d = \frac{1}{\sum_{i=1}^{p} \frac{\varphi_i - \varphi_{i+1}}{R_{di}}} \quad [4]$$

where i (i = 1, 2,…, p) identifies each linear segment of the approximate elution function, φ is the intercept of segment i extended to the y axis, and R_{di} is obtained from the terminating abscissa of segment i.

The PNFM sorbent intercepts and retains the solute of interest and this accumulated mass is used to calculate the time-averaged solute flux over the sampling period. Assuming linear and instantaneous partitioning of the nutrient between water and the sorbent, and that all nutrient mass entering the PNFM is retained, the time-averaged advective nutrient mass flux can be calculated by the following relationship (Hatfield et al., 2004):

$$J_N = \frac{qM_N}{\alpha\pi r^2 L(1-M_{RN})\theta R_{dN}} \quad [5]$$

where M_N (Kg) is the mass of nutrient sorbed, L (m) is the length of the sorptive matrix or the vertical thickness of

Table 1. Distribution coefficients (K_d) and retardation factor (R_d) values measured from batch and column tests. [2,4-dimethyl-3-pentanol (2,4-DMP); 2-ethyl-1-hexanol (2E1H)]

Parameter	2,4-DMP	1-hexanol	1-heptanol	2-octanol	2E1H	1-octanol
Tracer concentration (mg L^{-1})	350	350	150	100	100	60
From batch isotherm test						
Distribution coefficients, K_d (L g^{-1})	0.0084	0.0098	0.0339	0.0504	0.0638	0.1169
Retardation factors, R_d	14.1	16.2	53.7	79.4	100.2	182.8
From column elution test						
Distribution coefficients, K_d (L g^{-1})	0.0115	0.0113	0.0440	0.0572	0.0765	0.1209
Retardation factors, R_d	18.9	18.6	69.4	90	120	189

aquifer interval interrogated, α is a factor that characterizes the convergence or divergence of flow around the PNFM, R_{dN} is the retardation of nutrient on the sorbent, and M_{RN} is the relative mass of a hypothetical resident tracer retained after time period t where that tracer has the same retardation as R_{dN} (calculated using Eq. [1] and [2]). If it is assumed that R_{dN} is sufficiently large and all nutrient mass is retained on the PNFM sorbent, Eq. [5] can be reduced to the following form for estimating time-averaged nutrient flux (Hatfield et al., 2004):

$$J_N = \frac{M_N}{2\alpha r L t} \quad [6]$$

When the Darcy flux in the aquifer is estimated using the PNFM, flow distortion at the well must be considered. Assuming a uniform flow field and a locally homogeneous aquifer, the difference in hydraulic conductivity between the flux meter and ambient aquifer produces convergence or divergence of groundwater flow. For an open bore hole with a well screen and no filter pack, the following convergence (or divergence) factor α can be derived (Klammler et al., 2006):

$$\alpha = \frac{4}{\left(1+\frac{1}{K_S}\right)\cdot\left(1+\frac{K_S}{K_D}\right)+\left(1-\frac{1}{K_S}\right)\cdot\left(1-\frac{K_S}{K_D}\right)\cdot\left(\frac{1}{R_S}\right)^2} \quad [7]$$

where K_S is the dimensionless ratio of the hydraulic conductivities of the well screen, k_S (m s^{-1}), and the aquifer, k_0 (m s^{-1}); K_D is the dimensionless ratio of the PNFM hydraulic conductivity, k_D (m s^{-1}), and k_0; and finally R_S is the dimensionless ratio of the radii of the PNFM, r (m), and the outside of the well screen, r_0 (m). The value of α depends on local aquifer hydraulic conductivities and varies from 0 to 2 (Klammler et al., 2006). For $\alpha > 1$, flow converges as pore water velocity inside the PNFM is greater than the local velocity in the aquifer, whereas flow diverges for $\alpha < 1$.

Sorbent Material

An anion exchange resin, Lewatit S 6328 A (Sybron Chemicals Inc. Birmingham, NJ), was selected as a sorbent for nutrient flux measurement through a preliminary screening test with several anion exchange resins. This material is a strongly basic, macroporous-type resin and its matrix consists of a cross-linked polymer made of styrene and divinylbenzene with a relatively uniform charge distribution of ion-active sites throughout the structure. The macroporous structure facilitates rapid adsorption and desorption of inorganic and organic substances.

Adsorption Isotherm and Recovery of Phosphate

Batch adsorption isotherms were developed for PO_4^{3-} by adding 0.1 to 3.5 g of Lewatit resin to 40 mL of varying concentration of phosphate (KH_2PO_4, Fisher Scientific, Pittsburgh, PA) solution. The equilibrium concentrations, C_{eq}, of phosphate as PO_4^{3-} ranged from 0.1 to 19.5 mg L^{-1}. These mixtures were rotated for 24 h and then filtered through 0.45-μm glass filters. The filtered solution was analyzed for PO_4^{3-} colorimetrically (Method 8190, acid persulfate digestion method; Hach Company, Loveland, CO). Sorbed phosphate was recovered from the drained resin using 30 mL of 2 *M* KCl (Fisher Sci.), rotated for 24 h, and analyzed using the same method above.

Adsorption Isotherm and Recovery of Resident Tracers

Batch adsorption isotherm experiments were conducted to measure distribution coefficients between resident tracers and Lewatit resin. Tracers used in this study were 1-hexanol (Fisher, 98%), 2,4-dimethyl-3-pentanol (2,4-DMP) (Acros, 99+%), 1-heptanol (Fisher, 99%), 2-octanol (Fisher, 99%), 2-ethyl-1-hexanol (2E1H) (Fisher, 99%), and 1-octanol (Fisher, 99%). The tracer solution was prepared in a 1-L volumetric flask and transferred in 30-mL aliquots to 40-mL vials with Teflon-lined screw caps. The aqueous concentration of tracers used is provided in Table 1. Varying amounts of resin (0.2 to 13 g) were then added to the vials with the tracer solution. The vials were rotated for 24 h and allowed to settle before analysis. The equilibrated aqueous samples were analyzed for the alcohol tracers using a gas chromatograph with a flame ionization detector (GC/FID, Autosystem XL; PerkinElmer, Wellesley, MA).

Tracers were recovered from decanted sorbent using isopropyl alcohol (IPA). Approximately 5 g of the wet Lewatit resin was transferred into 40-mL vials filled with 30 mL of IPA. The vials were rotated for 24 h to extract the tracers from the resin and allowed to settle. The extracted samples were analyzed for the alcohol tracers using GC/FID.

Column Tests for Tracer Elution and Phosphate Uptake

Several laboratory column experiments were conducted to evaluate the relationship between water flow and elution of resident tracers, and phosphate uptake on the resin in a continuous flow system. A small glass column (2.5 cm i.d. and 5 cm long, Kontes Co. Vineland, NJ) was wet-packed with Lewatit resin that had been pre-equilibrated with a suite of alcohol tracers (see Table 1) for 24 h. Equilibrated aqueous solution was used for wet-packing to prevent loss of preloaded tracers from the resin. The packed column was flushed with phosphate solutions of 0.7 and 20 mg L^{-1} as PO_4^{3-} at steady water flow 0.5 mL min^{-1} for several days. Effluent

samples were analyzed for eluted alcohol tracers using a GC in-line sampling method (Jawitz et al., 2002). The experimental data were used to characterize tracer elution behavior. For assessing phosphate uptake, dynamic column elution tests were conducted under two different mass-loading conditions: 0.9 mg L^{-1} PO_4^{3-} concentration for 300 pore volumes (PV) and 20 mg L^{-1} for 140 PV of water flushing. During both elution tests, PO_4^{3-} breakthrough (at 0.09 mg L^{-1} detection limit) was never observed in the effluent, confirming that phosphate breakthrough did not occur. After each elution test, the adsorbent in the column was divided into three sections (front 0–1.7 cm, middle 1.7–3.4 cm, and end 3.4–5.0 cm from the column injection port). The separated adsorbent was extracted for PO_4^{3-} accumulated in each section by the extraction method and analyzed colorimetrically as described above.

Experimental Design for Passive Nutrient Flux Measurement

Bench-scale aquifer model experiments (Fig. 1) were conducted to evaluate application of the PNFM. A rectangular stainless steel box (38 by 30.7 cm and 12 cm deep) was used to contain the model aquifer. Two cylindrical PVC well screens (NSF-dwv, 16 cm long, 3.2 cm i.d., and 4.2 cm o.d.) were placed upright at the center of the chamber as shown in Fig. 1. The box was wet-packed with commercial grade sand (medium size, Quickrete Company Inc., Atlanta, GA) that was pre-washed several times with the injection-phosphate solution. The particle size distribution of sand used for box packing was measured using sieve analysis: 1.4 to 0.6 mm (diameter), 8.8% (weight); 0.6 to 0.425 mm, 12%; 0.425 to 0.25 mm, 52.8%; 0.25 to 0.18 mm, 20%; 0.18 to 0.075 mm, 6.4%. The sand was packed with a bulk density of 1.64 g cm^{-3}. The water table was set to a height of 10 cm. The injection and extraction ends of the flow chamber were packed with glass marbles (1.5 cm mean diameter) to facilitate uniform flow through the model. An aluminum mesh was used to separate the marbles from the sand. A 10-L aspirator bottle (Kimax Co. Vineland, NJ) was used as a water reservoir to maintain a constant head at the inlet during flow experiments.

Flushing experiments were conducted with an injection solution of 4.8 mg L^{-1} phosphate (as PO_4^{3-}). Preceding each flux test, the flow chamber was flushed with sufficient injection phosphate solution until it reached a quasi-steady-state condition. That is, flux experiments were initiated once the phosphate concentration in the effluent was approximately equal to the influent concentration.

The PNFMs were constructed using sewn fabric socks (10 cm long and 3.2 cm i.d) filled with Lewatit resin. Before packing, the resin was pre-equilibrated with an aqueous solution of alcohol tracers. The tracer pre-loaded resin was prepared by adding 500 mL of the Lewatit resin to a 1.5-L aqueous solution of alcohol tracers and was rotated for 24 h (Table 1). The PNFM assembly and installation entailed the following steps: First, a porous fabric sock was placed in a solid PVC packing pipe (about 10 cm long) of the same inside diameter as the well screen. The prepared resin was poured into the sock using a funnel. Pre-equilibrated tracer solution was then poured through the sock to saturate the resin within the sock and packing pipe. Mechanical vibration was applied to compact the resin, and then the added solution was drained from the packing pipe. Approximately 80 mL of resin were used for each flux meter. During packing, a resin subsample (approximate 5 g of wet resin) was collected to measure the initial concentration of resident tracers. These initial values were used to calculate the fraction of tracer removed by groundwater flow from the PNFM samples. Finally, the packing tube containing the PNFM was placed on top of the screen well and the PNFM was slowly extruded from the packing tube into the flux measurement well. Following deployment durations of 6 to 45 h, the PNFMs were retrieved from the wells and divided into two sections. These sections were homogenized and two resin samples were collected from each. The extraction and analysis of alcohol tracers and captured phosphate from the resin samples were performed using the procedures described above. Experiments were conducted under various applied flow rates and flushing volumes to assess the accuracy of flux estimation by the PNFM.

Results and Discussion

Parameter Determination for Flux Measurement

Nutrient and water flux measurements are based on the mass of nutrient intercepted and the mass of pre-loaded resident tracers eluted by water flow. Therefore, the sorbent used in the PNFM should have an appropriate affinity for both inorganic nutrient (i.e., PO_4^{3-}) and organic resident alcohol tracers. Preliminary batch tests for selecting an appropriate sorbent were conducted with several anionic exchange resins (Amberlite IRA 400 [Alfa Aesar, Ward Hill, MA], Lewatit S 6328A, Dowex marathon 11 [Sigma-Aldrich, Saint Louis, MO], and SBG1P [ResinTech, Cherry Hill, NJ]). All of the resins tested showed strong PO_4^{3-}sorptive ability, but Lewatit resin was the only sorbent that also showed an appropriate affinity for organic alcohol tracers. Based on this preliminary result, Lewatit resin was selected in this study. To assess the performance of Lewatit as a PNFM sorbent, a series of batch and column tests were conducted. The following paragraphs discuss the adsorbent characteristics associated with the flux measurement including sorption capacity, extraction efficiency, and tracer retardation. Finally, the resin hydraulic characteristics are discussed, including hydraulic conductivity and flow convergence or divergence.

First, adsorption capacity and recovery efficiency of the Lewatit resin for phosphate (as PO_4^{3-}) were evaluated. Adsorbed PO_4^{3-} mass is shown as a function of the equilibrium aqueous PO_4^{3-} concentration in Fig. 2. The data were fit with a Freundlich isotherm model (Fetter, 1999):

$$C_s = K_f C_e^{\frac{1}{n}} \qquad [8]$$

where c_s (mg g^{-1}) is the equilibrium value of PO_4^{3-} mass adsorbed per unit mass of the Lewatit resin, C_e (mg L^{-1}) is the equilibrium PO_4^{3-} concentration in the aqueous phase, and K_f and n are the empirical constants where n >1. The Freundlich isotherm model fit the measured values well with K_f = 6.67 and n = 1.41, and a coefficient of determination R^2 > 0.98. The observed sorption capacity of Lewatit resin for PO_4^{3-} (21.7 mg g^{-1} at 5.3 mg L^{-1} C_{eq}) was much higher than other resins used in preliminary tests (5.3 mg g^{-1} at 5.7 mg L^{-1} C_{eq}

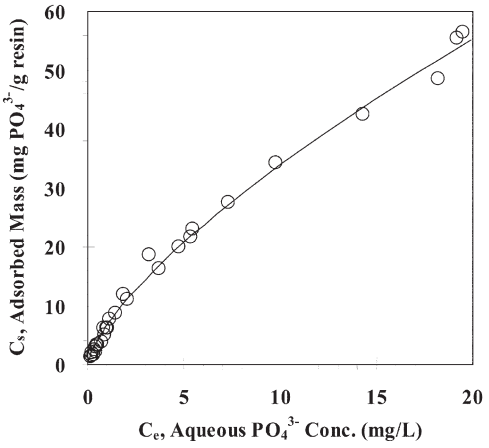

Fig. 2. Adsorption isotherm of PO_4^{3-} on Lewatit S 6328A resin with a Freundlich model fit.

for Amberlite IRA 400, 5.6 mg g^{-1} at 4.1 mg L^{-1} C_{eq} for Dowex marathon 11, and 0.28 mg g^{-1} at 5.7 mg L^{-1} C_{eq} for SBG1P).

Since PO_4^{3-} flux measurement using the PNFM is based on the cumulative PO_4^{3-} mass retained on the sorbent over the test period, solute loss due to early breakthrough can lead to errors in PO_4^{3-} flux estimation. The PO_4^{3-} breakthrough loss through the PNFM was assessed by dynamic column elution tests conducted at steady water flow. After each test, the adsorbent in the column was extracted to investigate the PO_4^{3-} mass distribution along the column length. The detailed results are shown in Table 2. The results show that more than 98% of PO_4^{3-} mass was retained in the first section (0–1.7 cm: 4.1 mg g^{-1} and 0.37 mg g^{-1} for the high and low concentration tests, respectively) of the column and less than 2% of the PO_4^{3-} mass was found in the middle and end sections. Assuming that the typical diameter of the PNFM inserted into a well screen ranges from approximately 2.5 to 5 cm, these results imply that PO_4^{3-} breakthrough loss is likely to be insignificant for deployment durations equivalent to hundreds of flushed pore volumes. Considering that typical PO_4^{3-} concentrations in groundwater are typically lower than used in these tests, the observed sorption capacity of Lewatit resin is sufficient to retain the PO_4^{3-} intercepted over a typical PNFM deployment period.

Table 2. Results and parameter values of column elution tests for assessing PO_4^{3-} breakthrough loss.

Parameter†		Distance‡	Mass out	Mass recovery
		cm	mg	%
Column 1	Front	1.7	2.6	97.1
	Middle	3.4	0.02	0.7
	End	5	0.01	0.5
	Total	5	2.7	98.3
Column 2	Front	1.7	27.8	100.1
	Middle	3.4	0.13	0.5
	End	5	0.05	0.1
	Total	5	28.0	100.7

† Flow rate was 0.5 mL min^{-1} for both tests (Pore water velocity was 15 cm/h); total flushing volume was 300 and 140 pore volumes for Column 1 and 2, respectively; input PO_4^{3-} concentration was 0.92 and 20 mg L^{-1} for Column 1 and 2, respectively; total mass injected was 2.71 and 27.8 mg as PO_4^{3-} for Column 1 and 2, respectively.

‡ Distance from column injection port.

Batch tests conducted to determine the extraction efficiency of PO_4^{3-} from the Lewatit resin resulted in an observed recovery efficiency of 94% ± 2.6 (n = 7, with R^2 > 0.99). Based on this high recovery percentage, it was concluded that 2 M KCl is an effective extractant for removing PO_4^{3-} from the anionic resin. Also, note that the measured recovery value was used to correct calculated nutrient mass fluxes.

Retardation of resident alcohol tracers was determined by column elution tests and the R_d values were compared with those estimated from batch sorption tests (Table 1). The retardation of each tracer is a measure of its affinity for the resin used in the PNFM. For example, 1-hexanol, which is a less hydrophobic tracer, was eluted earlier than 1-octanol, which is more hydrophobic (Fig. 3A). The tracer concentration eluted from the column was monitored throughout the test period and integrated, and the mass of tracer remaining in the column was determined by difference from the initial mass. The piecewise linear approximation approach of Hatfield et al. (2004) is illustrated in Fig. 3B for 1-hexanol with four segments. Retardation factors were determined for each tracer based on this technique using Eq. [4] (Table 1).

Retardation factors for tracers on Lewatit were also estimated from the batch adsorption isotherms. The batch isotherm experiments were conducted with varying amounts of Lewatit resin and concentrations of tracers (Table 1). The mass of tracers adsorbed onto the resin was determined using the equilibrium aqueous concentration of tracers. The

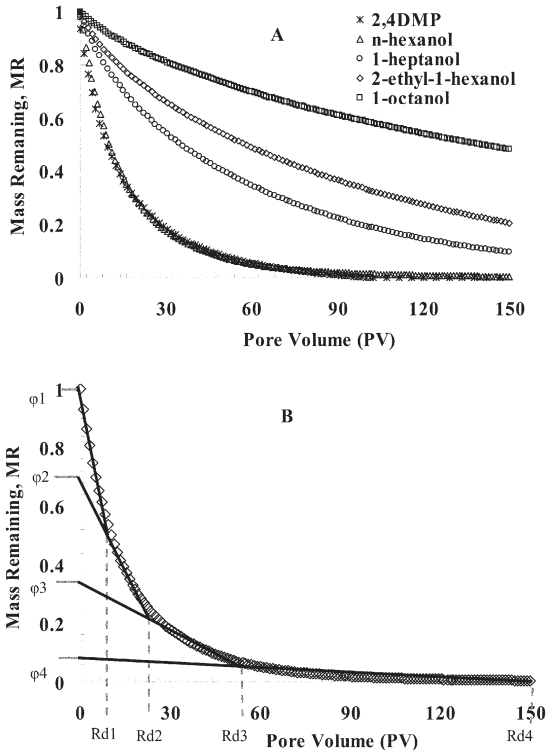

Fig. 3. (A) Resident alcohol tracer elution curves along with cumulative water pore volume and (B) an example plot for retardation factor determination using four piece-wise linear segments from the nonlinear 1-hexanol elution curve. 2,4-dimethyl-3-pentanol (2,4-DMP); 2-ethyl-1-hexanol (2E1H).

distribution coefficients, K_d (L g^{-1}), obtained from the batch and column tests are compared in Table 1. Retardation factors were calculated as follows (Freeze and Cherry, 1979):

$$R_d = 1 + \frac{\rho_b K_d}{\theta} \quad [9]$$

where ρ_b (g cm^{-3}) is the bulk density of resin. These parameters were measured for the Lewatit resin and found to be ϕ = 0.405 and ρ_b = 0.63 g cm^{-3}. The resulting R_d values from the batch test are shown along with the values obtained from the column elution tests in Table 1. The R_d values from both methods agreed reasonably well, with 15% higher values, on average, for the column-based values estimated from piecewise linear approximation. Since the column-based values better reflect conditions in the PNFM, these were used to estimate water fluxes from the PNFM in the bench-scale aquifer model tests discussed below.

Tracer retardation factors obtained from the column elution tests were plotted as a function of tracer aqueous solubility (Fig. 4). The results indicate that retardation factors and aqueous solubility of tracers follow a log-linear relationship:

$$\ln R_d = 11.18 - 0.941 \ln S_W \quad [10]$$

where S_W (mg L^{-1}) denotes the tracer aqueous solubility. Equation [10] provides a useful tool for selection of a resident tracer suite for use in PNFMs constructed with Lewatit resin.

Finally, a hydraulic correction factor, α, associated with flow convergence was calculated using Eq. [7] (Klammler et al., 2006). Flow convergence to the flux device is caused by the difference in hydraulic conductivities between the flux meter sorbent, the surrounding porous media, and the well screen. Hydraulic conductivities were measured using the falling head method (Freeze and Cherry, 1979) to be k_D = 212 m d^{-1} for the Lewatit resin and k_0 = 8.64 m d^{-1} for the sand packed in the aquifer model. The k_S value for the PVC well screen was 2.3 m d^{-1} based on Hatfield et al. (2004), and the dimensionless ratio of the PNFM radius and the outside radius of the well screen, R_S, was 1.12. Thus, for the PNFM system used in this study, α = 1.50.

Evaluation of Passive Nutrient Flux Meter

A series of bench-scale aquifer model studies were conducted to evaluate the PNFM for measuring simultaneous time-averaged water and nutrient fluxes in porous media. Flux measurement was performed with PNFMs deployed in two screened wells during each test. After deployment, each PNFM was segmented into two samples and the data from the resulting four samples were averaged and compared with the applied water and solute fluxes.

Nutrient flux experiments were conducted with steady-state water flow rates of 2 to 6 mL min^{-1}, producing Darcy fluxes between 0.4 and 1.2 cm h^{-1}. Time-averaged cumulative water fluxes were measured with PNFMs using six resident alcohol tracers (Table 1) having different retardation values, such that after a given deployment duration each tracer exhibited a different mass remaining (M_R). Results of only two tracers (1-hexanol and 2,4-DMP) showed appropriate M_R values (M_R between 0.5 and 0.7 for best

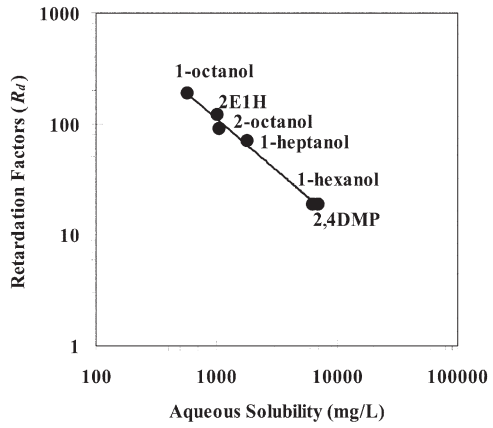

Fig. 4. Log-log relationship between retardation factor (R_d) and aqueous solubility for resident alcohol tracers. 2,4-dimethyl-3-pentanol (2,4-DMP).

results) for the deployment durations used here (Hatfield et al., 2004). The Darcy fluxes, q (cm h^{-1}), measured using 1-hexanol and 2,4-DMP, were plotted with respect to the applied Darcy flux values in Fig. 5. The average Darcy fluxes measured by the PNFM were within 13% for 1-hexanol and 11% for 2,4-DMP of the applied values. The two measurements that represented the poorest estimate of the applied Darcy flux were calculated using M_R < 0.4. If these values are excluded, the estimated fluxes averaged 94 and 96% of the applied values for 1-hexanol and 2,4-DMP, respectively. The deviation of the two data points is likely due to the tracer nonlinear elution characteristics. The elution for each tracer followed a linear function until about 50% mass removal below which nonlinearity was observed (Fig. 3A). The two data points were determined using M_R values of 0.37 and 0.25, which is in the nonlinear elution region. The M_R values for 1-heptanol (0.85–0.95), 2-octanol (0.94–1.0), and 2-ethyl-1-hexanol (0.95–1.0) (not shown) were all larger than 0.85 and the flux estimates using these values were more variable. Thus, it is suggested that Darcy flux estimation using the PNFM (with Lewatit resin used as the sorbent) is best applied in the range 0.4 < M_R < 0.85.

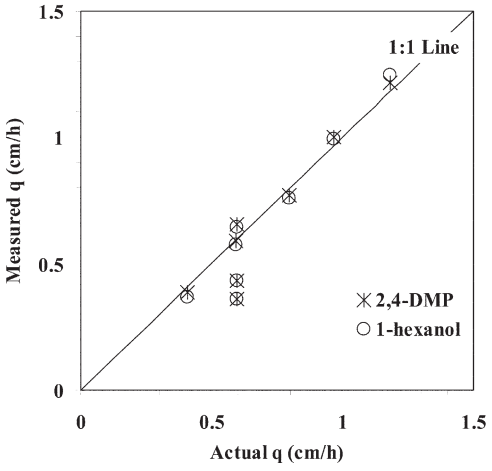

Fig. 5. Comparison between Darcy flux, q, estimated from the passive nutrient flux meter (PNFM) using the 1-hexanol and 2,4-dimethyl-3-pentanol (2,4-DMP) tracers and the actual applied values.

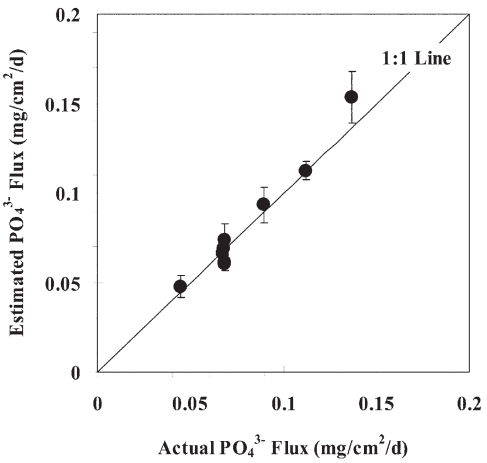

Fig. 6. Comparison between passive nutrient flux meter (PNFM)-estimated and applied PO_4^{3-} fluxes. Mean estimated values are shown with standard deviation (n = 4).

The nutrient flux estimation was based on the assumption that all the PO_4^{3-} mass passing through the PNFM was intercepted and retained. Under steady water flow, the PO_4^{3-} concentration was maintained at about 4.8 mg L^{-1} over the entire PNFM test period. The stabilized PO_4^{3-} concentration in both wells before installing PNFM ranged from 4.6 to 4.8 mg L^{-1}, which with variable Darcy fluxes produced applied PO_4^{3-} fluxes of 0.04 to 0.14 mg cm^{-2} d^{-1}. These PNFM-measured PO_4^{3-} flux values compared well with the applied values, with a range of 0.05 to 0.15 mg cm^{-2} d^{-1} (Fig. 6). The estimated average PO_4^{3-} mass fluxes were within 6% of the applied mass fluxes. As observed in Fig. 5 and 6, the magnitude of the applied flow velocity used in this study did not limit the effectiveness of the PNFM for estimation of water or nutrient flux.

Conclusions

The PNFM was evaluated in the laboratory for measuring both water and nutrient fluxes in porous media. An anion exchange resin, Lewatit 6328 A, was selected as a sorbent with adequate phosphate retention and the capability of sorbing long-chain alcohols for resident tracers. A suite of tracers was selected that provided a range of partitioning characteristics and retardation factors suitable over a typical range of groundwater velocities. The selected alcohols included between six and nine carbon atoms with R_d values between 14 and 180.

The PNFM was tested in a laboratory aquifer model using standard PVC well screens. The PNFMs were deployed for 6 to 45 h. The recovered resin was extracted for PO_4^{3-} and tracers to quantify nutrient flux and groundwater flow. The measured average Darcy flux values were within about 12% of applied values when between 40 and 85% of the original tracer mass remained following deployment. The measured average PO_4^{3-} fluxes were within 6% of the applied mass fluxes.

Overall, the PNFM was capable of quantifying water and nutrient flux in the range of fluxes applied in the laboratory studies. Further testing is needed at lower Darcy velocities, as expected at sites with low hydraulic conductivity or hydraulic gradients, to evaluate the influence of diffusive transport during the extended deployment time required to remove tracer mass and accumulate nutrients. Field trials are needed to assess PNFM performance in the presence of additional complexities associated with field conditions including degradation of tracers and/or sorbed nutrients, and aquifer heterogeneities.

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