



## A direct passive method for measuring water and contaminant fluxes in porous media

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### Abstract

This paper introduces a new direct method for measuring water and contaminant fluxes in porous media. The method uses a passive flux meter (PFM), which is essentially a self-contained permeable unit properly sized to fit tightly in a screened well or boring. The meter is designed to accommodate a mixed medium of hydrophobic and/or hydrophilic permeable sorbents, which retain dissolved organic/inorganic contaminants present in the groundwater flowing passively through the meter. The contaminant mass intercepted and retained on the sorbent is used to quantify cumulative contaminant mass flux. The sorptive matrix is also impregnated with known amounts of one or more water soluble ‘resident tracers’. These tracers are displaced from the sorbent at rates proportional to the groundwater flux; hence, in the current meter design, the resident tracers are used to quantify cumulative groundwater flux. Theory is presented and quantitative tools are developed to interpret the water flux from tracers possessing linear and nonlinear elution profiles. The same theory is extended to derive functional relationships useful for quantifying cumulative contaminant mass flux. To validate theory and demonstrate the passive flux meter, results of multiple box-aquifer

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experiments are presented and discussed. From these experiments, it is seen that accurate water flux measurements are obtained when the tracer used in calculations resides in the meter at levels representing 20 to 70 percent of the initial condition. 2,4-Dimethyl-3-pentanol (DMP) is used as a surrogate groundwater contaminant in the box aquifer experiments. Cumulative DMP fluxes are measured within 5% of known fluxes. The accuracy of these estimates generally increases with the total volume of water intercepted.

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## 1. Introduction

Groundwater hydrologists typically estimate water and contaminant mass flows and fluxes to define boundary conditions and source terms in groundwater models that are then used to predict risk, compliance and contaminant attenuation (Einarson and Mackay, 2001; Schwarz et al., 1998; USEPA, 1998; Feenstra et al., 1996). Accurate estimation of subsurface contaminant mass flows is difficult using ordinary field data; because spatial variations in both concentrations and groundwater flows induce mass flow variations that may range over several orders of magnitude. Notwithstanding this variability, hydrologists typically approximate contaminant mass flows using calculated (i.e., not measured) groundwater fluxes and depth-averaged concentrations gathered from wells; this approach introduces uncertainties into source terms and boundary conditions, which likewise undermine the reliability of model predictions.

Subsurface water and contaminant flow/flux measurements near sources or at control planes can facilitate efforts to predict risk, compliance and contaminant attenuation (USEPA, 1998). Furthermore, timely measurements enhance efforts to control site cleanup and to quantifying achievable endpoints of source zone remediation (Rao et al., 2002; Gallagher et al., 1995). Currently, two methods are used to estimate mass discharge and fluxes from field measurements (Einarson and Mackay, 2001). The first method derives estimates from spatially integrating the product of local flux-averaged contaminant concentration and water flux. Thus,

$$M_Q = \int_{A_s} q_o c_F dA \quad (1)$$

where  $M_Q$  is the contaminant mass discharge (M/T),  $dA$  represents an elemental area ( $L^2$ ),  $A_s$  is the source area or the area of the control plane orthogonal to groundwater flow ( $L^2$ ),  $q_o$  is specific discharge (L/T) and  $c_F$  is the flux-averaged contaminant concentration in the groundwater ( $M/L^3$ ). Point-wise estimates of  $c_F$  are obtained from a sampling transect of single or multilevel monitoring wells. Water fluxes are measured, assumed or calculated at locations of each sampling point. Finally, an integration or spatial averaging of point estimates is performed to quantify contaminant flow over the entire transect. Readers are referred to Borden et al. (1997), King et al. (1999) and Kao and Wang (2001) for additional details and results of field demonstrations.

Research from Holder et al. (1998), Schwarz et al. (1998), Teutsch et al. (2000) and Bockelmann et al. (2001, 2003) describes the development and evaluation of the second approach or the integral groundwater investigation method (IGIM). This technique directly measures  $M_Q$  and it involves one or more wells pumped at constant flow rates to provide partial or complete capture of the dissolved plume. The contaminant concentration histories monitored at the wells are interpreted to estimate contaminant mass flow from a portion of the control plane (vertical cross-section) of the plume. The cross-sectional area of aquifer interrogated,  $A_s$ , is calculated from the well flow rate and the ambient groundwater flux, which may be measured, calculated or assumed. The method provides limited information on the spatial distribution of contaminant fluxes, although mass discharge estimates may reflect less uncertainty because spatial integration/interpolation of point data is not performed.

Contaminant flux values derived from single applications of the above two methods represent short-term evaluations that reflect current conditions and not long-term trends. In the absence of continuous monitoring, it may be sufficient and more cost effective to deploy systems designed to gather cumulative measures of water flow and contaminant mass flow. Cumulative monitoring devices generate flux estimates that reflect long-term transport conditions and therefore incorporate to day-to-day fluctuations in flow and contaminant concentration.

## 2. The passive flux meter

The purpose of this paper is to introduce a new cumulative monitoring technology that provides for simultaneous, direct, in situ, point measurements of time-averaged contaminant mass flux,  $J_c$ , and water flux,  $q_o$  (Hatfield et al., 2002). The contaminant mass flow is then estimated from spatially integrating point measurements of  $J_c$  as indicated in Eq. (2).

$$M_Q = \int_{A_s} J_c dA = \int_{A_s} q_o c_F dA \quad (2)$$

where  $J_c$  denotes the time-averaged mass flux or the mass flow per unit cross section of aquifer ( $M/L^2 T$ ). Here, the contribution of hydrodynamic dispersive flux is ignored.

The new method requires a device, hereafter referred to as a ‘passive flux meter’ (PFM), that is a self-contained permeable unit that is inserted into a well or boring such that it passively intercepts groundwater flow but does not retain it. The interior composition of the meter is a matrix of hydrophobic and hydrophilic permeable sorbents that retain dissolved organic and inorganic contaminants present in the fluid intercepted. The sorbent matrix is also impregnated with known amounts of one or more fluid-soluble ‘resident tracers’. These tracers are leached from the sorbent at rates proportional to the fluid flux.

The PFM is inserted into a well or boring and exposed to groundwater flow for a period ranging from days to months, after which the meter is removed and the sorbent carefully extracted to quantify the mass of all contaminants intercepted and the residual masses of

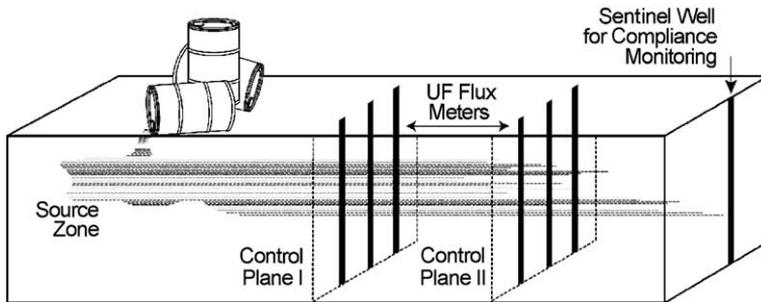


Fig. 1. Deployment of six passive flux meters in six wells distributed over two control planes located downgradient from a contaminant source zone.

all resident tracers. Contaminants mass is used to calculate time-averaged or cumulative contaminant flux, while residual resident tracer mass is used to calculate time-averaged or cumulative groundwater flux.

Fig. 1 illustrates the deployment of six PFMs in six wells distributed over two transects located downgradient from a contaminant source but upgradient from a sentinel well. Depth variations of both water and contaminant fluxes can be measured in an aquifer from a single PFM by vertically segmenting the exposed sorbent packing; thus, at any specific well depth, an extraction from the locally exposed sorbent yields the mass of resident tracer remaining and the mass of contaminant intercepted.

Essentially, the mass flux of any dissolved organic or inorganic contaminant can be measured as long as (1) the PFM sorbent intercepts and retains the contaminant from groundwater flowing through the meter; (2) the contaminant can be extracted from the sorbent or analyzed in the sorbed state for purposes of quantifying the mass captured; and (3) the contaminant does not undergo degradation inside the PFM. Potential contaminants of interest include various organics such as chlorinated solvents, hydrocarbons and pesticides and multiple dissolved inorganics such as nutrients (phosphate and nitrate) and metals.

### 3. Theory (measuring water flux)

Fig. 2 displays a single resident tracer distribution over two circular cross-sections of a PFM configured as a column unit for installation into a well. The initial condition is such that resident tracer is uniformly distributed over the sorptive matrix (Fig. 2a). After installation and following a period of exposure to local groundwater flow, the tracer is displaced from the PFM as depicted in Fig. 2b. The pertinent assumptions supporting this conceptualization are (1) transport is primarily advective; (2) tracer desorption is linear, reversible and instantaneous; and (3) specific discharge within the bounds of the sorbent is uniform, horizontal and in direction parallel to local groundwater flow. Strack and Haitjema (1981) previously demonstrated the uniform flow assumption for a homogeneous permeable element of circular geometry situated in a locally homogeneous aquifer of contrasting permeability.

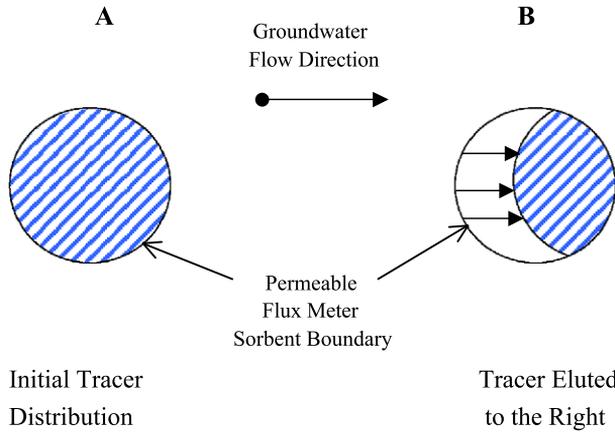


Fig. 2. Conceptual model of resident tracer distribution over two circular cross-sections of a passive flux meter: (a) before meter exposure to groundwater flow and (b) after meter exposure to groundwater flow.

From Fig. 2, it may be surmised that the mass of resident tracer remaining in the PFM is both a function of the initial mass equilibrated with the sorptive matrix and that displaced as a result of groundwater flowing through the matrix; thus,

$$m_R = m_I - m_L \tag{3}$$

where  $m_R$  is the residual resident tracer mass on the sorptive matrix after exposing the meter to a groundwater flow (M),  $m_I$  is the initial mass equilibrated to the sorptive matrix (M) and  $m_L$  is the cumulative mass displaced (M). Because the mass of tracer remaining on the sorbent is inversely proportional to the cumulative groundwater flow intercepted, it may be surmised that cumulative or time-averaged water fluxes can be estimated from measurements of  $m_R$ .

Analytical tools to characterize the relationship between  $m_R$  and groundwater flux can be derived by approximating tracer transport over the PFM cross-section as transport through a bundle of parallel streamtubes. This approach estimates first the mass in each streamtube followed by integration over all streamtubes to obtain the total tracer mass on the sorbent. Important assumptions pertinent to the streamtube approach are discussed in greater detail as the larger PFM model is developed in the following paragraphs.

Fig. 3 presents a simple cross-sectional illustration of a PFM of radius  $r$  with a single highlighted streamtube of length  $2x_D$  (L). The streamtube is located a distance  $y$  from the centroid of the sorptive matrix; this distance is measured parallel to the vertical axis as depicted in Fig. 3. The half-length of the streamtube is obtained from:

$$x_D|_Y = \left( r^2 - y^2 \right)^{1/2} \tag{4}$$

Resident tracer elution from each streamtube is directly proportional to the cumulative specific discharge (the product of the time-averaged specific discharge through the PFM,  $q_D$  and the duration of exposure to the flow field,  $t$ ). More specifically, the dimensionless elution function for a streamtube,  $G(\tau)$ , describes the mass fraction of

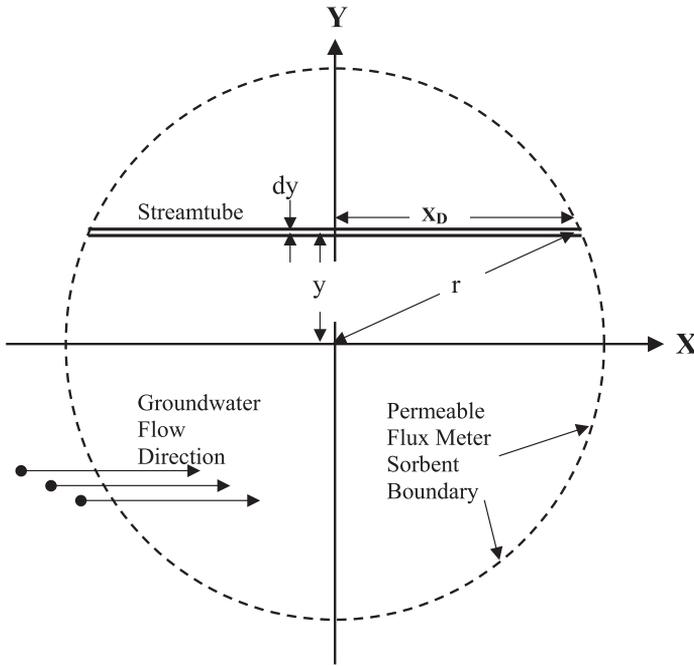


Fig. 3. Simple cross-sectional illustration of a passive flux meter of radius  $r$  with a single highlighted streamtube of length  $2x_D$ .

resident tracer remaining in the streamtube as a function of the cumulative volume of water eluted. The argument  $\tau$  is the elution volume expressed in terms of streamtube pore volumes or:

$$\tau = \frac{q_D t}{2x_D \theta} \tag{5}$$

where  $\theta$  is the dimensionless volumetric water content of the sorptive matrix. Fig. 4 depicts typical elution functions for linear and nonlinear tracer desorption. The parameter  $n$  appearing in the figure represents the Freundlich sorption isotherm exponent (Yaron, 1978; Fetter, 1999). Linear elution functions are generated for  $n \geq 1$ . For both linear and nonlinear elution a consistent initial retardation factor,  $R_d$  can be defined which is equal to the reciprocal slope of  $G(\tau)$  as  $\tau$  approaches zero (see Fig. 4). The pertinent definition is:

$$R_d = \frac{\theta + \rho_b K_P c_o^{n-1}}{\theta} \tag{6}$$

in which  $\rho_b$  is the bulk density of the sorptive matrix ( $M/L^3$ ),  $c_o$  is the initial dissolved aqueous resident tracer concentration in the pore fluid ( $M/L^3$ ) and  $K_P$  is the Freundlich equilibrium partition coefficient or the reversible distribution coefficient for sorbent-aqueous phase partitioning of the resident tracer ( $L^{3n}/M^n$ ). For the both the linear and nonlinear elution functions shown in Fig. 4, the initial retardation factor is the same.

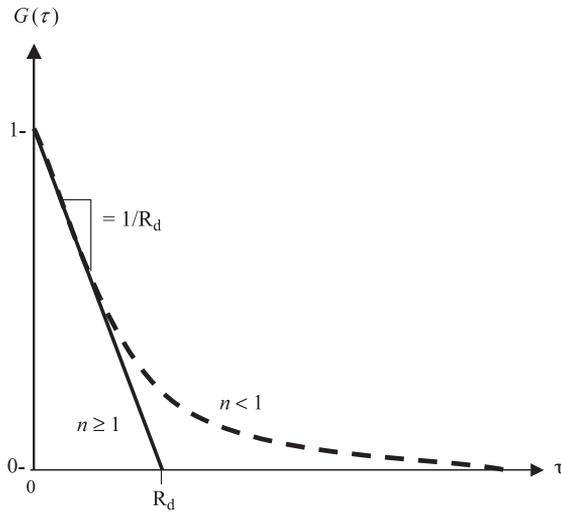


Fig. 4. Typical linear and nonlinear resident tracer elution functions,  $G(\tau)$ , for a streamtube, where  $\tau$  is the aqueous elution volume expressed in terms of streamtube pore volumes.

The product  $G(\tau)$  and streamtube length  $2x_D$  quantify the mass fraction of tracer remaining in a streamtube, while the integration of this product over all streamtubes quantifies the mass fraction of resident tracer remaining in the PFM. This integration is made from the centroid of the sorptive matrix to a radial distance  $r_{\max} \leq r$ . Thus,

$$\Omega_R = \frac{m_R}{m_I} = \frac{2}{\pi r^2 b} \int_0^{r_{\max}} G(\tau)[2x_D] b dy \tag{7}$$

where  $\Omega_R$  represents the mass fraction of initial tracer remaining on the sorptive matrix after exposing the PFM to groundwater flow for period  $t$ ;  $b$  is the thickness of the sorptive matrix or axial length of PFM column (L) and  $dy$  is the elemental width of the streamtube (L). The coefficient 2 appears outside the integral as it reflects the symmetry of integration taken over half the sorptive cross-section from  $y=0$  to the upper limit  $r_{\max}$ . The value of  $r_{\max}$  is usually taken to equal  $r$ , the radius of the PFM when  $G(\tau)$  is a continuous function for all values of  $\tau \geq 0$ . Eq. (7) serves to map residual resident tracer mass  $\Omega_R$  and cumulative specific discharge  $q_D t$  (or  $q_D$ ) irrespective of desorption nonlinearities; it is only critical that  $G(\tau)$  be continuous and known.

Assuming  $G(\tau)$  is linear (i.e., reflects linear elution because  $n \geq 1$  and desorption is instantaneous), an analytical formulation for  $G(\tau)$  and Eq. (7) can be derived even though the elution function is not continuous for all values of  $\tau \geq 0$ . This analytical expression is most convenient as it expresses explicitly time-averaged water flux  $q_D$  (or  $q_D t$ ) in terms of measured residual tracer mass  $m_R$ , parameters of PFM geometry (e.g., circular) and sorptive matrix properties (e.g., tracer partition coefficients). To develop this formulation, the streamtube concept is revisited with consideration given first to defining the initial

tracer mass in the streamtube:

$$dm_I = 2x_D \theta R_d c_o b dy \quad (8)$$

where  $dm_I$  is the initial elemental tracer mass contained in the streamtube (M).

Because  $G(\tau)$  is linear, the mass of tracer displaced from the streamtube is given by the following equation:

$$dm_L = q_D t c_o b dy \quad (9)$$

where  $dm_L$  is the elemental tracer mass displaced (M). From Eq. (1), it is clear that Eqs. (8) and (9) combine to obtain  $dm_R$ , the elemental mass of residual resident tracer in the streamtube (M).

$$dm_R = 2x_D \theta R_d c_o b dy - q_D t c_o b dy \quad (10)$$

Finally, dividing Eq. (8) into Eq. (10) produces the following linear elution function  $G(\tau)$  for a streamtube:

$$G(\tau) = \frac{dm_R}{dm_I} = \begin{cases} 1 - \frac{q_D t}{2x_D \theta R_d} & \text{for } \frac{q_D t}{2x_D \theta R_d} \leq 1 \\ 0 & \text{for } \frac{q_D t}{2x_D \theta R_d} > 1 \end{cases} \quad (11)$$

Because the linear elution function is discontinuous at  $q_D t / (2x_D \theta R_d) = 1$  and is zero for  $q_D t / (2x_D \theta R_d) > 1$ , the upper integration limit  $r_{\max}$  is chosen such that Eq. (11) may be substituted into Eq. (7). The concept of  $r_{\max}$ , as implemented herein, evolves from the realization that resident tracer is completely eluted from streamtubes less-than-or-equal to a length  $\chi$ :

$$\chi = 2X_I \Big|_{r_{\max}} = \frac{q_D t}{\theta R_d} \quad (12)$$

Thus,  $r_{\max}$  in Eq. (12) defines the transverse radial distance from the origin beyond which all resident tracer has been displaced from the cross section of the PFM. Hence,

$$\text{for } y < r_{\max}; \quad dm_R > 0$$

otherwise,

$$\text{for } y \geq r_{\max}; \quad dm_R = 0.$$

Substituting Eq. (12) into Eq. (4) yields the pertinent definition of  $r_{\max}$  for linear elution:

$$r_{\max} = \left( r^2 - \frac{q_D^2 t^2}{4\theta^2 R_d^2} \right)^{1/2} \quad (13)$$

Given relationships  $G(\tau)$  and  $r_{\max}$ , Eqs. (4) (7) (11) (13) may be combined and the resulting expression integrated to yield the following dimensionless equation for the mass fraction of residual tracer on the PFM.

$$\Omega_R = \frac{2}{\pi} \left[ \sin^{-1} \left( \sqrt{1 - \zeta^2} \right) - \zeta \sqrt{1 - \zeta^2} \right] \tag{14}$$

where

$$\Omega_R = \frac{m_R}{\pi r^2 b \theta R_d c_o} \tag{15}$$

and

$$\zeta = \frac{q_D t}{2r\theta R_d} \tag{16}$$

The variable  $\zeta$  represents the dimensionless cumulative pore volume of fluid intercepted by the device over the time period  $t$  divided by the retardation factor  $R_d$ . For the most part, an evaluation of Eq. (14) will show resident tracer being displaced at a rate linearly proportional to  $\zeta$ ; as a result, it is feasible to use in lieu of Eq. (14), Eq. (17) below for values of  $\zeta \leq 0.6$  or  $\Omega_R \geq 0.32$ :

$$\Omega_R = -1.2\zeta + 1.0 \tag{17}$$

Finally, from Eqs. (16) and (17), a convenient formula is produced for estimating the time-averaged specific discharge,  $q_D$  through the PFM.

$$q_D = \frac{1.67(1 - \Omega_R)r\theta R_d}{t} \tag{18}$$

Eqs. (16), (17) and (18) are strictly applicable to tracers producing linear elution functions ( $n \geq 1$ ); however, for resident tracers producing concave elution functions ( $n < 1$ ), the above developments are still useful if the nonlinear elution process can be described through a superposition of  $p$  independent linear elution functions. Under this approach,  $p$  linear elution functions  $G(\tau)_i$  ( $i=1, 2, \dots, p$ ) are superimposed in  $\tau$  to generate an approximate nonlinear elution function  $\hat{G}(\tau)$  comprised of  $p$  piecewise linear segments. Further analysis with  $\hat{G}(\tau)$  produces a new equation for  $\Omega_R$  suitable for both linear and nonlinear tracer elution.

$$\Omega_R = \frac{2}{\pi} \sum_{i=1}^p (\phi_i - \phi_{i+1}) \left[ \sin^{-1} \left( \sqrt{1 - \zeta_i^2} \right) - \zeta_i \sqrt{1 - \zeta_i^2} \right] \tag{19}$$

and

$$\zeta_i = \frac{q_D t}{2r\theta R_{di}} \tag{20}$$

where index  $i$  ( $i=1, 2, \dots, p$ ) identifies each linear segment of the approximate elution function and each elution term of interest; the difference  $(\phi_i - \phi_{i+1})$  quantifies the mass fraction of tracer eluted in accordance to function  $G(\tau)_i$  under retardation factor  $R_{di}$ , for

( $i=1, 2, \dots, p$ ). Eq. (19) is simply a linear combination of terms, where each term possesses the same form as Eq. (14).

The parameters of Eq. (19) can be extracted directly from a plot of  $\hat{G}(\tau)$ , the piecewise linear approximation of the elution function  $G(\tau)$ . In Fig. 5, a hypothetical nonlinear elution curve is illustrated along with an approximate function created with  $p=3$  linear segments. The value of  $R_{di}$  (for  $i=1, 2$  and  $3$ ) is obtained from the terminating abscissa of segment  $i$ , whereas the value of  $\phi_i$  is the intercept of segment  $i$  extended to the vertical axis. Values of  $\phi_1$  and  $\phi_{p+1}$  are always 1 and 0, respectively; consequently, Eq. (19) reduces to the Eq. (14) for  $p=1$ .

For purposes of obtaining convenient estimations of  $q_D$ , applications of Eqs. (17) and (18) can be extended to nonlinear eluting tracers. This is achieved by equating the value of  $R_d$  to the reciprocal slope of  $G(\tau)$  as  $\tau \rightarrow 0$ ; otherwise, the retardation factor appearing in Eqs. (16) and (18) must be redefined as follows:

$$R_d = \frac{1}{\sum_{i=1}^p \frac{\phi_i - \phi_{i+1}}{R_{di}}} \tag{21}$$

In the above discussion, it is assumed here that  $q_D$  can be measured with the PFM, although the ultimate goal is to obtain the time-averaged specific discharge of the local groundwater,  $q_o$  (L/T). Strack and Haitjema (1981) and Klammler et al. (2004) show that  $q_D$  is linearly proportional to  $q_o$ :

$$q_D = \alpha q_o \tag{22}$$

where  $\alpha$  characterizes the convergence or divergence of groundwater flow in the vicinity of the PFM. Fig. 6 illustrates converging groundwater flow on the upgradient side of a meter, parallel streamlines or uniform flow inside the device, and diverging flow as water exits the meter; this depiction is consistent with the hydraulic conductivity of the sorptive matrix,  $k_D$ , being greater than that of the surrounding aquifer,  $k_o$ , and with a PFM installed

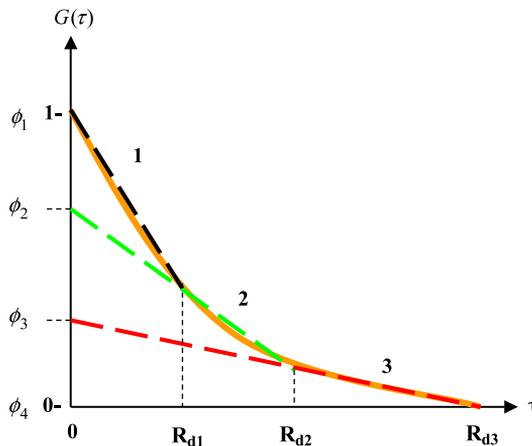


Fig. 5. A hypothetical nonlinear resident tracer elution function,  $G(\tau)$ , for a streamtube and three piece-wise linear segments shown with defining parameters  $\phi_i$  (for  $i=1, \dots, 4$ ) and  $R_{di}$  (for  $i=1, \dots, 3$ ).

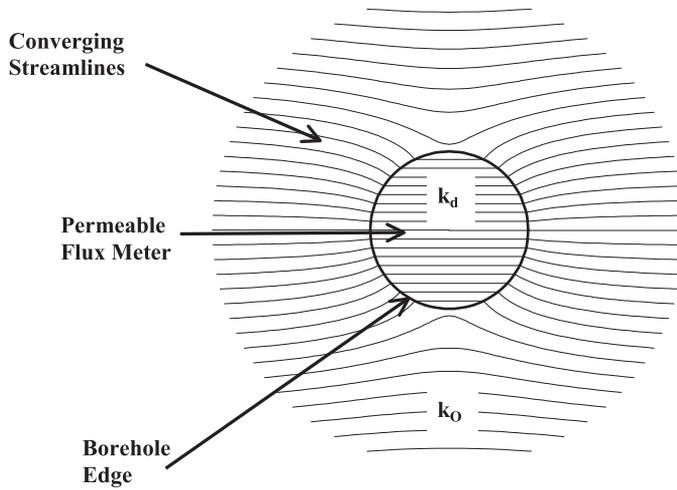


Fig. 6. Groundwater streamlines through a flux meter where the conductivity of the meter  $k_d$  is greater than that of the surrounding aquifer  $k_o$ .

in an open borehole (i.e., in the absence of a well screen). Assuming  $q_D$  is measured with a PFM, the value of  $\alpha$  must be known to assess the ambient groundwater flux or  $q_o$ . For a circular meter installed in an open borehole, [Strack and Haitjema \(1981\)](#) provide the following estimation of  $\alpha$ :

$$\alpha = \left( \frac{2}{1 + \frac{1}{K_D}} \right) \tag{23}$$

where  $K_D = k_D/k_o$ , the dimensionless ratio of  $k_D$ , the uniform hydraulic conductivity of the PFM sorptive matrix (L/T), to  $k_o$ , the uniform local hydraulic conductivity of the surrounding aquifer (L/T). For the problem addressed herein, the following equation derived by [Klammler et al. \(2004\)](#) is required, as it characterizes  $\alpha$  given a PFM installed in a fully screened well without a filter pack.

$$\alpha = \frac{4}{\left(1 + \frac{1}{K_s}\right)\left(1 + \frac{K_s}{K_D}\right) + \left(1 - \frac{1}{K_s}\right)\left(1 - \frac{K_s}{K_D}\right)\left(\frac{1}{R_s}\right)^2} \tag{24}$$

where  $K_s = k_s/k_o$  the dimensionless ratio of  $k_s$ , the well screen hydraulic conductivity (L/T) and  $k_o$ ; and  $R_s = r_o/r$  the dimensionless ratio of  $r_o$ , the outside radius of the well screen (L); and  $r$  the PFM radius (L). The value of  $\alpha$  must be known to assess the ambient groundwater flux or  $q_o$ ; this, in turn, means that prior estimates of hydraulic conductivity parameters  $k_o$ ,  $k_D$  and  $k_s$  are needed. The former two can be measured directly using a permeameter, while  $k_s$  can be estimated indirectly through a borehole dilution test.

When Eqs. (18) and (22) are combined a convenient formulation for direct estimation of groundwater fluxes is obtained.

$$q_o = \frac{1.67(1 - \Omega_R)r\theta R_D}{\alpha t} \quad (25)$$

As expected, Eq. (25) should be limited to applications where the residual tracer mass in the PFM is within the theoretical range of  $0.32 \leq \Omega_R < 1.00$ ; otherwise, Eq. (14) or (19) is used with a measured  $\Omega_R$  and Eq. (22) to yield estimates of  $q_o$ . In the absence of prior estimates of groundwater flow, multiple resident tracers reflecting a broad range of retardation factors can be used to interpret a range of potential groundwater discharges. Taking this approach, one or more tracers are likely to remain in the PFM and within the preferable range of  $\Omega_R$  for the application of Eq. (25).

The above analysis does not explicitly address competitive sorption/desorption, which can occur among multiple tracers co-eluted from a PFM. Competitive tracer interactions are generally embedded in all elution functions. More importantly, these interactions can produce elution profiles that vary with tracer combinations and initial concentrations. Assuming competitive resident tracer sorption/desorption occurs, the above analysis is applicable as long as the elution functions used are generated from co-elution experiments matching PFM conditions. For example, elution profiles are derived from experiments where tracers are eluted as a suite and with initial concentrations matching those used in PFMs.

Finally, sorption nonequilibrium among tracers is not explicitly addressed in the above modeling. However, like competitive tracer sorption/desorption, rate-limited sorption is almost always present to some degree and as such is always embedded in measured elution profiles. Significant nonequilibrium tracer sorption produces an extended elution tail. Conditions giving rise to rate-limited sorption are widely discussed in the literature and are characterized in terms of dimensionless Damkohler numbers (Bahr and Rubin, 1987). Assuming rate-limited sorption exists, the above elution-based analysis is still applicable as long as the elution functions reflect Damkohler numbers comparable with those of PFM applications. Further discussion of sorption nonequilibrium is given later in the paper and in the context of experimental results.

#### 4. Theory (measuring contaminant flux)

The previous sections describe how groundwater fluxes are interpreted from the elution of resident tracers initially equilibrated to a sorptive matrix. In this section, an assumption is made that the same sorptive matrix will retain specific dissolved contaminants in the groundwater intercepted by the PFM. The retained contaminant mass is then used to calculate the local cumulative advective mass flux or the flux-average contaminant concentration over sampling duration,  $t$ .

Fig. 7 provides a cross-sectional illustration of how the contaminant would be retained on the sorbent of a PFM. The illustrated crescent of sorbed contaminant has an area defined by the product  $\pi r^2 A_{RC}$ . The dimensionless term  $A_{RC}$  quantifies the fraction

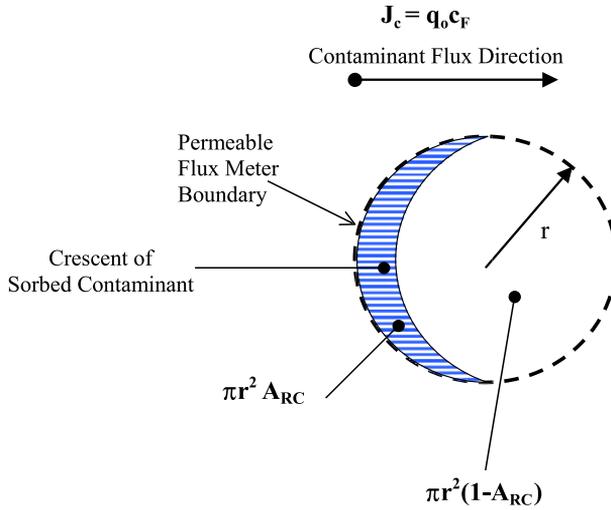


Fig. 7. Conceptual model of how contaminant would be retained on the sorbent of a passive flux meter.

of sorptive matrix containing contaminant and is calculated from the following relationship:

$$A_{RC} = (1 - \Omega_{RC}) \tag{26}$$

in which  $\Omega_{RC}$  is the relative mass of a hypothetical resident tracer retained after exposure period  $t$ , where this tracer has a retardation factor equal to that of the contaminant  $R_{DC}$ .  $\Omega_{RC}$  is calculated using  $R_{DC}$  in the appropriate Eq. (14), (18), or (19) and  $q_D$  as determined from resident tracers.

The PFM is used to measure cumulative advective contaminant mass flux from a finite sampling duration. The operable definition of advective contaminant flux is:

$$J_c = q_o c_F \tag{27}$$

where  $J_c$  is the time-averaged advective contaminant mass flux ( $M/L^2 T$ ) and  $c_F$  is the flux averaged concentration of contaminant in the groundwater ( $M/L^3$ ). The measured flux is valid over the transverse (vertical and horizontal) dimensions of porous medium contributing flow to the device.

Assuming the contaminant mass retained by the PFM,  $m_c$ , is confined to a bulk volume of sorbent equaling  $\pi r^2 A_{RC} b$ , the flux-average concentration of contaminant in the groundwater intercepted is:

$$c_F = \frac{m_c}{\pi r^2 b A_{RC} \theta R_{DC}} \tag{28}$$

Thus, combining Eqs. (22), (27) and (28) yields the following relationship for the time-averaged advective contaminant mass flux:

$$J_c = \frac{q_D m_c}{\alpha \pi r^2 b A_{RC} \theta R_{DC}} \tag{29}$$

where  $m_c$  is the mass of contaminant sorbed (M),  $b$  is the length of sorptive matrix sampled or the vertical thickness of aquifer interval interrogated (L) and  $R_{DC}$  as indicated previously is the retardation factor of contaminant for the sorbent. If it can be assumed that  $R_{DC}$  is sufficiently large and that the hypothetical value of  $\Omega_{RC}$  permits the application of Eq. (18), then it may be assumed that  $0 < A_{RC} \leq 0.68$  and that Eqs. (18) (27) (29) may be combined to yield the following reduced equation for estimating time-averaged contaminant flux.

$$J_c = \frac{1.67m_c}{\alpha\pi rbt} \quad (30)$$

Nonequilibrium contaminant sorption is not explicitly addressed in the above analysis nor is the occurrence of competitive sorption between contaminants and resident tracers. Competitive and rate-limited sorption undermine the efficiency of contaminant interception and retention on PFM sorbents. Hence, when either is significant, PFM measurements can underestimate true contaminant fluxes. Nonequilibrium contaminant sorption is most likely to occur when high groundwater velocities and/or small PFM diameters produce small Damkohler numbers (Bahr and Rubin, 1987).

## 5. Experimental design

Laboratory box aquifer experiments were conducted to evaluate the PFM. Experiments involved placement of meters in a box aquifer such that measurements of cumulative water and contaminant fluxes could be made. Granular activated carbon (Fisher Scientific, 6–12 mesh) was the sorbent used in the meters. The carbon had a mean grain size of 2 mm and a hydraulic conductivity of 0.59 cm/s. The packed carbon porosity and dry bulk density were respectively 0.62 and 0.552 g/cm<sup>3</sup>. Ethanol, methanol, isopropyl alcohol and *n*-hexanol served as resident tracers pre-equilibrated on the activated carbon. A branched alcohol, 2,4-dimethyl-3-pentanol (DMP), functioned as a surrogate aquifer contaminant.

A stainless steel container (Cole-Parmer, 27×20×18 cm deep) was used to create the box aquifer. A 16-cm section of well screen (5.24 cm I.D. and 5.87 cm O.D.) was positioned upright and in the center of box. The box was packed with sand (under standing water) to a height of 13.1 cm and then overlaid with 2–3 cm of saturated bentonite. The sand was commercial grade medium grain size having a hydraulic conductivity of 0.01 cm/s.

The two ends of the container were used for flow injection and extraction and were packed with coarse gravel (8 mm mean grain diameter). This was done to provide a constant head across the width of the box and a uniform gradient across the length of the box. The phreatic surface was set to a height of 13.1 cm and the applied flow rate ranged from 0.78 to 4.7 ml/min giving a Darcy flux from 0.20 to 1.19 cm/h. The total depth of water in the well,  $l_w$ , was maintained at 12.6 cm, and it extended 0.5 cm from bottom of the box to an elevation of 13.1 cm. Within the water saturated interval the slotted screen length,  $l_s$ , equaled 12.1 cm.

PFMs were pre-equilibrated, wet, activated carbon packed into crinoline socks. Pre-equilibration constituted 24 h of gently mixing 320 g of dry activated carbon in a 2-l aqueous solution containing 1.18 g ethanol, 1.19 g methanol, 2.36 g isopropyl alcohol and

2.44 g *n*-hexanol. The cotton crinoline socks were 16 cm long and 5.24 cm in diameter and were pre-washed in water. Each sock was packed to contain approximately 150 g of activated carbon (dry mass); this produced a PFM with a length that typically ranged from 13.3 to 13.5 cm. During the construction of each PFM, the activated carbon was sampled to establish initial concentrations of the sorbed resident tracers. These concentrations were used in subsequent calculations to ascertain  $\Omega_R$ , the relative mass of each tracer remaining in the PFM following a period of exposure to flow in the box aquifer.

Preceding each box experiment, DMP influent/effluent concentrations were measured to verify that initial contaminant conditions were quasi-steady-state. Among the several experiments conducted, influent DMP concentrations ranged from 72.0 to 83.0 mg/l and produced quasi-steady-state box aquifer effluent concentrations ranging from 72.0 to 77.5 mg/l. During each experiment, a meter was inserted into the well screen and influent/effluent concentrations of DMP were monitored. Because the PFM was designed to intercept and retain DMP, box-aquifer effluent concentrations inevitably decreased to new quasi-steady-state levels, which again among the several experiments ranged from 44.0 to 49.5 mg/l. After a desired period of exposure, the meter was pulled and the carbon sampled for subsequent resident tracer and contaminant analyses. Between experiments, constant flow through the box aquifer was maintained to re-establish DMP effluent concentrations representing quasi-steady-state initial conditions.

Sampling of the PFM involved extracting the activated carbon with isobutyl alcohol. From the extract all resident tracers and DMP were analyzed using a Perkin-Elmer gas chromatograph (GC) equipped with automated liquid injection and a flame ionization detector (FID). *n*-Hexanol has an aqueous/activated-carbon retardation factor in excess of 8000; thus, it functionally behaves as a non-desorbing resident tracer as compared to methanol, isopropyl alcohol and ethanol. *n*-Hexanol was used as an internal standard whereby changes in  $\Omega_R$  for methanol, isopropyl alcohol and ethanol were assessed from measured changes in tracer mass ratios with respect to *n*-hexanol. Measured values of  $\Omega_R$  were used in Eqs. (19) and (25) to determine local water fluxes  $q_o$  and compared to known experimental water fluxes. Mass measurements of DMP intercepted and retained on activated carbon,  $m_c$ , were used in Eq. (30) to obtain measured cumulative contaminant fluxes, these were subsequently compared to experimental fluxes imposed on the system.

In support of the box aquifer experiments, ancillary experiments were conducted to ascertain the resident tracer elution functions  $G(\tau)$  and to quantify the well screen permeability. Resident tracer elution functions were derived from a column elution experiment. Glass columns 5 cm long and 2.4 cm inside diameter were packed with 11.8 g (expressed as dry weight) of activated carbon that had been pre-equilibrated as described above with ethanol, methanol, isopropyl alcohol and *n*-hexanol. The column was then eluted with water at a flow rate of 0.5 (ml/min). Frequent volumetric measurements were taken to develop plots of cumulative elution volume versus time. Whenever the eluent volume was measured, a sample was collected analyzed to assess transient changes in dissolved concentrations of resident tracers and DMP. The dissolved constituent concentrations were determined by direct injection of the eluent sample on a Perkin-Elmer GC with FID.

To estimate the well screen hydraulic conductivity, it was necessary to conduct a borehole dilution test (Drost et al., 1968) in the box aquifer well where flow was known;

however, this approach should not be construed as a method for determining screen permeabilities in the field. The test required a few drops of concentrated NaCl solution and use of an electrical conductivity meter (Orion Model 115Aplus). Initially, the ambient electrical conductivity of water in the box aquifer,  $c_{sb}$  ( $\mu\text{S}$ ), was measured in the well with steady-state flows through the box aquifer. Next, a few drops of saturated NaCl solution were added to the volume of water in the well followed by subsequent measurements of electrical conductivity,  $c_s$  ( $\mu\text{S}$ ), taken at recorded time intervals. During this experiment, complete mixing of the well water was maintained. The resulting conductivity data were normalized to the initial electrical conductivity condition, using the following transform:

$$S^* = \frac{c_s - c_{sb}}{c_{so} - c_{sb}} \quad (31)$$

where  $S^*$  was dimensionless conductivity and  $c_{so}$  was the initial electrical conductivity of water in the well immediately after the addition of a few drops of concentrated NaCl ( $\mu\text{S}$ ). The transformed data were used to generate a plot of the natural log  $S^*$  versus time. The slope of this plot,  $s_c$ , was used to quantify the convergence of flow through the well screen,  $\alpha_w$ , and ultimately the hydraulic conductivity of the screen,  $k_s$ , from equations developed by Ogilvi (1958).

## 6. Results

The column elution experiment generated resident tracer concentrations as a function of  $\tau$ , the cumulative column pore volumes of eluted water. Integrating this data defined the relationship between  $\tau$  and  $dm_L(\tau)$ , the displaced tracer mass. The initial mass of tracer on the activated carbon  $dm_I$  was equated to the total mass displaced from the column; this was equivalent to assuming reversible sorption. For ethanol and methanol, the eluted tracer mass respectively equated to 98% and 92% of the tracer initially equilibrated to the carbon packed in the columns. For isopropanol, 31% more tracer was eluted than initially determined on the column.

Using  $dm_L(\tau)$  and  $dm_I$  data for ethanol, methanol and isopropanol, elution functions were developed for each tracer. This was accomplished using Eqs. (8) and (10) to quantify the mass fraction of residual tracer in the column at each sampling event and then plotting results against cumulative column pore volumes of eluted water. Plotted in Fig. 8 were the resultant nonlinear ethanol elution function  $G(\tau)$  (in circles) and the three piece-wise linear segments used to approximate the profile. The chosen number of segments was arbitrary; however, the number, slope and extent defined approximately the same area under the experimental profile. Two and three linear segments, respectively, were used to approximate the elution functions of isopropanol and methanol. The experimental profiles for these tracers were similar to ethanol (not shown).

Table 1 lists for ethanol, methanol and isopropanol values for  $R_{d1}$ ,  $R_{d2}$  and  $R_{d3}$  and associated sorbed phase mass fractions  $[(\phi_i - \phi_{i+1})$  for  $(i=1, 2, 3)]$ . Values for these parameters are extracted from the type of plot illustrated for ethanol in Fig. 8. From Table 1, it is seen that the ethanol elution curve  $G(\tau)$  is approximated using retardation factors

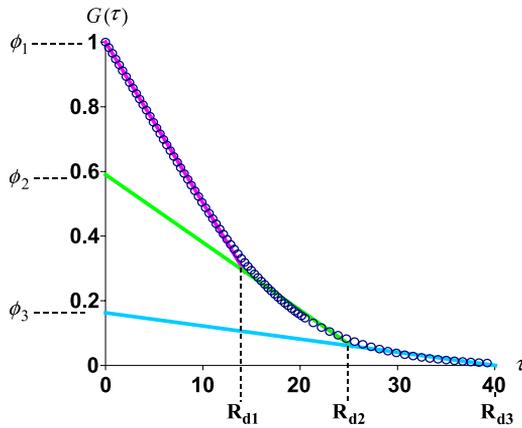


Fig. 8. The actual nonlinear ethanol resident tracer elution function,  $G(\tau)$ , from a column experiment (open circles) and three piece-wise linear segments shown with defining parameters  $\phi_i$  (for  $i=1, \dots, 4$ ) and  $R_{di}$  (for  $i=1, \dots, 3$ ).

14.3, 25.3 and 40.0 in the three linear functions that, respectively, describe the elution of 41%, 43% and 16% of the initial ethanol mass equilibrated on the activated carbon.

The well screen hydraulic conductivity was estimated from data derived from a borehole dilution test performed in the box aquifer. The conductivity estimate was subsequently used to calculate  $\alpha$ , the flow convergence to the flux device. Results generated from the borehole dilution test were illustrated in Fig. 9. The slope of the line  $s_c=0.0048 \text{ min}^{-1}$  was substituted into the following equation to calculate  $\alpha_w$  or the ratio of specific discharge in the well,  $q_w$ , to the box aquifer specific discharge,  $q_o$ .

$$\alpha_w = \frac{q_w}{q_o} = \frac{s_c(\pi l_w r^2 - \nabla_p)}{2r l_w q_o} \tag{32}$$

where  $\nabla_p$  represented the volume of the electrical conductivity probe ( $L^3$ ). Eq. (32) was derived from Drost et al. (1968). During the experiment, the imposed flow was  $0.011 \text{ cm/}$

Table 1  
Parameters derived from resident tracer elution profiles

Parameter	Resident tracer		
	Ethanol	Methanol	Isopropyl alcohol
$\phi_1$	1.00	1.00	1.00
$\phi_2$	0.59	0.59	0.19
$\phi_3$	0.16	0.12	0.00
$\phi_4$	0.00	0.00	–
$\phi_1 - \phi_2$	0.41	0.41	0.81
$\phi_2 - \phi_3$	0.43	0.47	0.19
$\phi_3 - \phi_4$	0.16	0.12	–
$R_{d1}$	14.3	2.8	111.0
$R_{d2}$	25.3	4.8	148.0
$R_{d3}$	40.0	9.9	–
$R_d$ (Eq. (21))	20.1	3.9	117.0

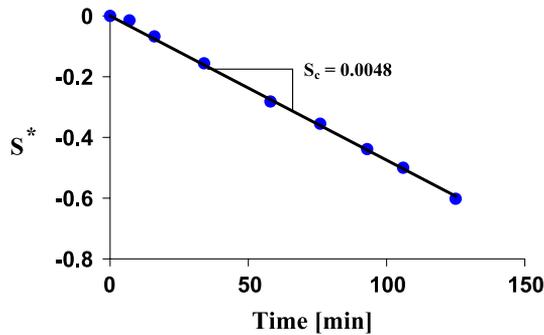


Fig. 9. Dimensionless electrical conductivity of water in the box aquifer well versus time during a borehole dilution test.

min. Parameters  $r$  and  $l_w$  were, respectively, 2.62 and 12.6 cm. The displacement volume of the conductivity probe,  $\forall_p$ , measured 41 cm<sup>3</sup>. Using the aforementioned parameter values in Eq. (32) yielded a value of 1.55 for  $\alpha_w$ .

From  $\alpha_w$ , a well screen hydraulic conductivity  $k_s$  of 0.0027 cm/s was calculated using Eq. (33), which was derived from Ogilvi (1958) and Drost et al. (1968).

$$k_s = \frac{k_o \alpha_w (R_s^2 - 1)}{R_s^2 (4 - \alpha_w) - \alpha_w} \tag{33}$$

For this calculation, the assumed aquifer hydraulic conductivity  $k_o$  was 0.01 cm/s, while 1.12 and 1.55 were the respective dimensionless values of  $R_s$  and  $\alpha_w$ .

With the well screen hydraulic conductivity known, a direct determination was made of  $\alpha$ . Using Eq. (24), a value of 1.53 was calculated for the flow convergence parameter. This value of  $\alpha$  essentially predicted that resident tracers would be displaced and that contaminant mass would be intercepted at rates consistent with contaminant fluxes and specific discharges that were 53% greater inside the PFM than in the surrounding porous media.

Tracer results from multiple PFM experiments are shown in Fig. 10. The plot illustrates the mass fraction of residual tracer measured in each PFM versus  $\xi$ . Eqs. (17) and (19) are also plotted for comparison, although values from Eq. (19) reflect parameter values for ethanol alone (see Table 1). An evaluation of Eq. (19) using parameter values for isopropanol is not necessary, because cumulative fluxes are sufficiently small that calculated  $\xi$ 's are less than 0.15 and therefore within the applicable range of Eq. (17).

For the most part, resident tracers are displaced at rates linearly related to the cumulative volume of water intercepted. Fig. 10 illustrates the claim that Eq. (17) can be used for all tracers and in lieu of Eq. (19) whenever the relative mass retained is within the range of  $0.32 \leq \Omega_R \leq 1.00$ . However, as demonstrated for the ethanol tracer, Eq. (19) describes the relationship between residual tracer mass and cumulative groundwater flux when measured groundwater flows result in  $\xi$  values greater than 0.56 or reduce resident tracer masses to relative values less than 0.32.

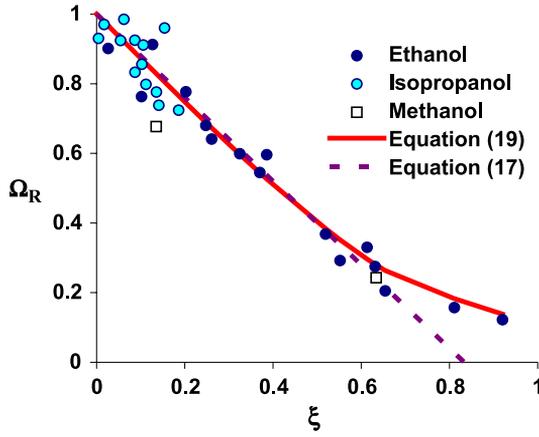


Fig. 10. Mass fraction of residual tracer,  $\Omega_R$ , measured and simulated in each passive flux meter versus the dimensionless pore volumes of water intercepted,  $\xi$ .

Fig. 11 provides a comparison of true versus measured cumulative water flux based on the ethanol tracer. The average water flux prediction error is on the order of 4% with 97% of the variability characterized by the Eq. (19). Of the three mobile resident tracers, ethanol produces the most accurate estimate of cumulative water flux.

To evaluate nature of the water flux measurement uncertainty derived from the current meter design, a first-order error analysis was performed. To conduct the analysis two critical assumptions were made. First, it was assumed that the absolute relative error in predicted cumulative water flux was proportional to the absolute relative error in the estimated residual mass fraction of resident tracer, hence from Eq. (18):

$$\delta_{qt} = \frac{\Delta q_{ot}}{q_{ot}} \propto \frac{\Delta \Omega_R}{(1 - \Omega_R)} \tag{34}$$

where  $\delta_{qt}$  was the absolute relative error in estimated cumulative aquifer specific discharge and  $\Delta q_{ot}$  and  $\Delta \Omega_R$  were the respective absolute errors in estimated cumulative specific

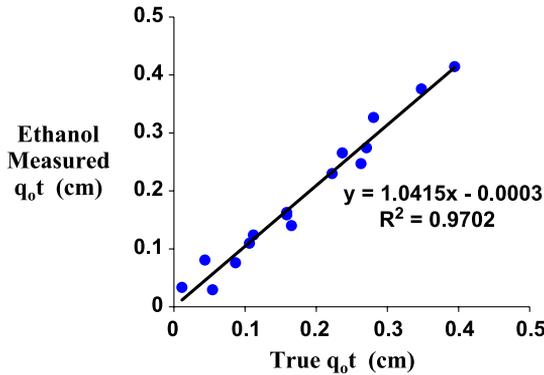


Fig. 11. Measured cumulative water fluxes using the ethanol resident tracer versus true fluxes.

discharge and residual tracer mass fraction. Further, it was assumed that that the magnitude of  $\Delta\Omega_R$  was inversely proportional to  $\Omega_R$ ; thus,

$$\Delta\Omega_R \propto \frac{K}{\Omega_R} \tag{35}$$

in which  $K$  was a constant of proportionality. Predicated on this second assumption, flux estimation errors would increase as residual tracer mass approached zero (an analytical consideration). By combining Eqs. (34) and (35), the following error relationship was formed:

$$\delta_{qt} \propto \frac{K}{\Omega_R(1 - \Omega_R)} \tag{36}$$

Eq. (36) suggests that two conditions give rise to large errors in flux prediction. The first is, when the cumulative water flux,  $q_{ot}$  is small such that minimal amounts of tracer are displaced. Under this condition, the relative flux error  $\delta_{qt} \rightarrow \infty$  as  $\Omega_R \rightarrow 1$ ; hence, small analytical errors produce small cumulative flux errors  $\Delta q_{ot}$ , which are large compared to  $q_{ot}$ . The second condition likely to induce significant flux errors emerges when  $q_{ot}$  is large and almost all of the tracer mass has been eluted; as a result,  $\delta_{qt} \rightarrow \infty$  as  $\Omega_R \rightarrow 0$ . Both conditions can exist simultaneously with a suite of tracers because  $\Omega_R$  depends on the tracer (the value of  $R_d$ ) and on the cumulative discharge intercepted the meter,  $q_{Dt}$ .

Fig. 12 depicts Eq. (36) with a plot of flux prediction errors versus measured  $\Omega_R$  for each tracer. An arbitrary value of 0.0125 is assumed for the constant  $K$  and only to demonstrate that Eq. (36) defines a 5% absolute flux error as  $\Omega_R \rightarrow 0.5$ . The experimental data depicted in Fig. 12 appear to support the general form of Eq. (36), and it appears that the best flux estimates are obtained from any given tracer after sufficient flows have leached 30–80% of the mass ( $0.2 < \Omega_R < 0.7$ ). This finding suggests that the optimum range for the application of Eqs. (17) (18) (25) is not the previously defined theoretical range, but for  $\Omega_R$  values within the range of 0.32–0.70.

Calculations of DMP fluxes were made assuming  $m_t$ , the total contaminant mass extracted from a carbon sample, reflected the mass intercepted by advection  $m_c$ . In reality  $m_t = m_c + m_o$ , where  $m_o$  represents the contaminant mass acquired during PFM installation.

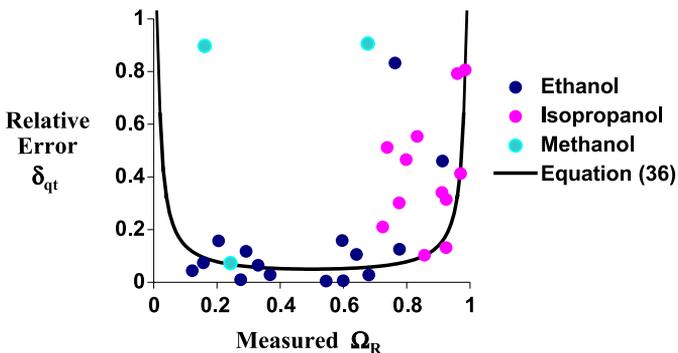


Fig. 12. Absolute water flux prediction errors versus the relative mass of resident tracer remaining in the meter with Eq. (36).

For the experiments conducted, PFMs were inserted into wells with the sorbent void volume partially unsaturated; as a result,  $m_o$  was acquire during installation as groundwater and dissolved DMP flowed into the meter to saturate these voids.

Fig. 13 was created to compare measured and true cumulative DMP fluxes. Fewer points were shown compared to previous figures (see Figs. 11 and 12) because fewer experiments were conducted where DMP was monitored. Eq. (30) was used to calculate contaminant fluxes assuming  $m_o$  could be ignored such that  $m_t = m_c$ . Furthermore, Eq. (30) was used in lieu of Eq. (29) because previous sorption experiments had indicated for DMP an  $R_{DC}$  on activated carbon greater than a 1000 (data not shown). In general, a high correlation was obtained between measured and true cumulative contaminant fluxes. Measured fluxes averaged 5% lower than true values and measurement accuracy did not demonstrate a dependence on the duration of meter exposure to the flow field.

To evaluate the significance of ignoring  $m_o$ , consideration must be given to volume of water intercepted by the meter under natural gradient conditions versus the volume taken up during meter installation. For example, if the cumulative volume of water intercepted is small, such that  $\xi$  is on the order of  $1/R_{DC}$ , then equating  $m_c$  and  $m_t$  can lead to erroneous flux estimates because much of sorbed contaminant reflects  $m_o$  and not  $m_c$ . In general, with an increase in the volume of water intercepted,  $m_c$  will increase and flux estimation errors will decrease to a value proportional to  $m_c$  and the analytical limitations of the methods used for contaminant extraction/analysis. These observations are summarized in the following contaminant flux error Eq. (37).

$$\delta_{J_t} = \frac{\Delta J_c t}{J_c t} = \frac{\Delta m_t}{m_t - m_o} = \frac{\Delta(m_c + m_o)}{m_c} = \frac{\Delta(2q_o t r b c_F + \pi r^2 b \theta c_F)}{2q_o t r b c_F} \tag{37}$$

where  $\delta_{J_t}$  is the absolute relative error in estimated cumulative contaminant flux,  $\Delta J_t t$  is the absolute error in the cumulative contaminant flux (M) and  $\Delta m_t$  is the absolute error in the total contaminant mass extracted from a carbon sample (M). Eq. (37) states that large relative errors in measured contaminant fluxes can be expected when small volumes of water are intercepted under low flow conditions or from brief sampling periods resulting in an  $m_t \rightarrow m_o$ ; however, from long-term monitoring giving rise to values of  $m_t \gg m_o$ , it can be

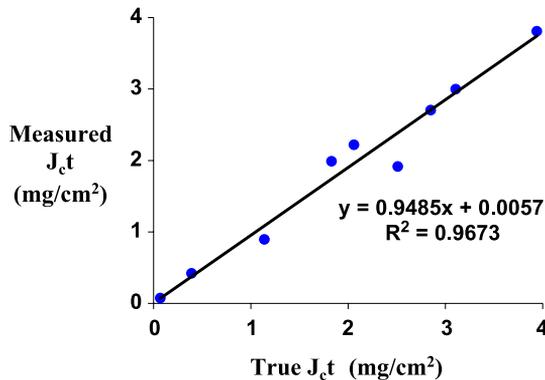


Fig. 13. Measured cumulative DMP fluxes versus true fluxes.

seen that  $\delta_{Jt} \rightarrow \Delta m_c / m_c$ . This later finding assumes the application of Eq. (30) and all appurtenant restrictions coupled to that equation.

The accuracy of measured water and contaminant fluxes depend on the exactness of the flow convergence parameter  $\alpha$ . Normally, the value of  $\alpha$  is not known in advance because the local aquifer permeability is not known. Klammler et al. (2004) suggests a PFM design whereby the value of  $\alpha$  is forced to assume a constant and predictable value; the design requires that sorbent and well screen possess hydraulic conductivities at least an order of magnitude greater than the hydraulic conductivity of the aquifer. In lieu of this approach, a short-term field test can be performed involving a sequence of two water flux measurements. The test requires two meters designed with significantly different sorbent hydraulic conductivities. Assuming the groundwater regime is steady between measurements and that the effective well screen hydraulic conductivity is known, this approach will yield the local hydraulic conductivity of the surrounding aquifer, the value of  $\alpha$  and the water flux.

To validate the value of  $\alpha$  used in the box aquifer experiments, two methods were applied to obtain independent confirmation. The first method calculated an apparent flow convergence,  $\alpha_e$ , using quasi-steady-state box-aquifer effluent concentrations of DMP and the following mass balance equation:

$$\alpha_e = \frac{(c_{\text{eff}|o} - c_{\text{eff}|f})A_{\text{box}}}{2c_{\text{eff}|o}l_s r} \quad (38)$$

where  $c_{\text{eff}|o}$  was the steady-state DMP effluent concentration before the PFM was installed ( $\text{M/L}^3$ ),  $c_{\text{eff}|f}$  was the steady-state DMP effluent concentration established after meter installation ( $\text{M/L}^3$ ) and  $A_{\text{box}}$  was the cross-sectional area of flow through the box aquifer,  $257 \text{ cm}^2$ . The average value of  $\alpha_e$  determined from this analysis was 1.52.

Under steady transport conditions, with no additional internal contaminant losses, and prior to PFM installation, effluent DMP concentrations equal the applied influent concentrations. Thus, a similar calculation can be made using a slightly different mass balance.

$$\alpha_e = \frac{(c_{\text{inf}|o} - c_{\text{eff}|f})A_{\text{box}}}{2c_{\text{inf}|o}l_s r} \quad (39)$$

in which  $c_{\text{inf}|o}$  is the influent concentration of DMP. Using this approach and monitored influent concentrations, the calculated apparent flow convergence was 1.54. Both independent estimates of  $\alpha_e$  bracket the applied  $\alpha$  value of 1.53.

The second approach taken to confirm the value of  $\alpha$  relied on resident tracer data and Eq. (25). The approach used residual ethanol data alone and values of  $\Omega_R$  within the optimum limits identified from the above error analysis of water flux measurements ( $0.32 < \Omega_R < 0.7$ ). This analysis produced an average value of  $\alpha$  equaled to 1.52, which again corroborated the original flow convergence obtained independently through Eq. (22).

PFMs deliver at best point measurements of cumulative or time-integrated contaminant mass flux and water flux. When installed along a transect perpendicular

to the mean flow direction multiple PFMs are used to estimate the integral discharge of water and contaminant mass. The magnitude and uncertainty in these contaminant discharge estimates can be used to forecast the likelihood of violating pollutant concentration limits at a down gradient sentinel well. Furthermore, differences in measured contaminant mass flows between transects can be used to estimate natural attenuation (USEPA, 1998).

The accuracy of PFM measurements can vary with the magnitude of groundwater flow and the occurrence of transient changes in groundwater flow direction. The theory assumes a purely horizontal and unidirectional flow field across a PFM. In reality, vertical flow exists and when a PFM is emplaced over a long period of time, seasonal changes in groundwater level and flow direction induce resident tracer elution in multiple directions. Any transient change in the direction of groundwater flow tends to undermine the validity of PFM measurements; therefore, directional variations in flow need to be considered when interpreting field results.

PFM theory assumes advective flux dominates diffusive flux and that the latter can be ignored. If the magnitude groundwater flow through a PFM is sufficiently low, diffusive transport may invalidate flux measurements. Peclet numbers are typically evaluated to determine if advective flux dominates (Thibodeaux, 1996).

$$P_e = \frac{qD\ell}{\theta^{7/3}D} \quad (40)$$

where  $P_e$  is the dimensionless Peclet number,  $D$  is the aqueous phase diffusion coefficient for a resident tracer ( $L^2/T$ ) and  $\ell$  is a characteristic length. For a PFM cross-section comprised of multiple parallel streamtubes,  $\ell$  is equated to the area-weighted average streamtube length over a PFM cross-section; thus,  $\ell=1.7r$ . PFM Peclet numbers in the box aquifer experiments range from 43 to 415 and hence indicate advective dominated transport.

Valid field measurements of both water and contaminant flux require that a minimum ambient groundwater flux exist to ensure advective dominated flows inside the PFM. For example, a minimum groundwater specific discharge of  $\sim 0.7$  cm/day is needed to maintain an order of magnitude relative difference between advective and diffusive transport processes (i.e.,  $P_e=10$ ); this assumes values of  $r=2.54$  cm,  $\theta=0.62$ ,  $\alpha=1.0$  and  $D=1.0$  cm<sup>2</sup>/d (Heyse et al., 2002).

Obtaining valid PFM measurements in rapid groundwater flows can also be problematic because of nonequilibrium sorption. Both tracer elution and contaminant retention are less efficient under conditions of rate-limited sorption. Dimensionless Damkohler numbers are typically used to characterize conditions giving rise to nonequilibrium sorption in transport systems (Bahr and Rubin, 1987).

$$\omega = \frac{kR_d(1 - \beta_T)\ell}{q_D} \quad (41)$$

where  $\omega$  is the dimensionless Damkohler number,  $k$  is the tracer or contaminant desorption rate coefficient ( $1/T$ ),  $\ell$  equals  $1.7r$  for a PFM or the length of the column used to generate a tracer elution profile and  $\beta_T$  is the fraction of sorption sites where equilibrium sorption is assumed.

Damkohler numbers were estimated for all three resident tracers used in the column elution experiment and for the PFMs used in box aquifer experiments. For these, Damkohler numbers values of  $k$  were calculated as described by Brusseau and Rao (1989) and  $\beta_r$  was equated to a typical value of 0.5 (Heyse et al., 2002). Calculated PFM Damkohler numbers ranged from 10 to 77 (methanol), from 18 to 106 (ethanol) and from 16 to 97 (IPA), while 2, 3 and 4 were the respective column Damkohler numbers obtained for methanol, IPA and ethanol.

Nonequilibrium sorption produces extended tails in tracer elution functions not unlike nonlinear sorption ( $n < 1$ ) except that the degree of tailing is now dependent on the fluid hydraulic residence time. The magnitudes of the Damkohler numbers calculated above indicate rate-limited sorption may exist with all three tracers (Bahr and Rubin, 1987). To evaluate this potential problem, model simulated tracer elution functions were generated under conditions of equilibrium and nonequilibrium sorption. The elution functions were found to be essentially identical with minor differences evolving after 70 to 80 percent of the tracer mass was eluted (curves not shown). This finding would indicate the above equilibrium-based analysis should remain applicable under nonequilibrium conditions, as long as flux calculations were based on values of  $\Omega_R > 0.3$ .

When rate-limited sorption is a concern, the effects on PFM measurements can be evaluated qualitatively by normalizing PFM Damkohler numbers to those of the column experiments used to generate tracer elution profiles. Created is a parameter,  $\lambda$ , representing a ratio of hydraulic residence times between the PFM and the reference elution column.

$$\lambda = \frac{1.7Rq_{\text{col}}}{q_D L_{\text{col}}} \quad (42)$$

where  $q_{\text{col}}$  is the specific discharge in the elution column (L/T) and  $L_{\text{col}}$  is the length of the elution column (L). Note that the value of  $\lambda$  does not depend on the tracer. A value of  $\lambda = 1$  indicates the PFM application and the column experiment exhibit the same degree of sorption nonequilibrium.

For  $\lambda > 1$  transport conditions inside the PFM are closer to equilibrium; thus, on the basis of cumulative flow intercepted, the meter is more efficient at eluting tracers than the elution column. Under this scenario, a PFM tends to overestimate water flux, but according to Eq. (30) continues to provide valid measures of contaminant flux.

For  $\lambda < 1$ , transport conditions inside the column are closer to equilibrium than those extant in a particular PFM application. In this situation, a PFM is less efficient at eluting tracers or intercepting contaminants; consequently, both water and contaminant fluxes are underestimated.

Assuming rate-limited sorption is occurring, the above elution-based analysis is applicable as long as elution functions reflect Damkohler numbers comparable to those of PFM applications; otherwise, to obtain valid measures of contaminant flux, the following condition must exist:  $\lambda \geq 1$ . In the box aquifer experiments values of  $\lambda$  range from 5 to 29.

## 7. Summary

A PFM is a new device for obtaining point measurements of cumulative water and contaminant fluxes. The device is essentially a self-contained permeable unit properly sized to fit tightly in a screened well or boring. The meter is designed to accommodate a mixed medium of hydrophobic and/or hydrophilic permeable sorbents, which retain dissolved organic/inorganic contaminants present in the groundwater flowing passively through the meter. The sorptive matrix is also impregnated with known amounts of one or more water-soluble resident tracers. These tracers are displaced from the sorbent at rates proportional to the groundwater flux.

Resident tracers were used in the current system design to quantify cumulative groundwater flux, while the contaminant mass intercepted and retained on the sorbent was used to quantify cumulative contaminant mass flux. Theory was presented and quantitative tools were developed to interpret the water flux from tracers possessing linear and nonlinear elution profiles. The same theory was extended to derive functional relationships useful for quantifying cumulative contaminant mass flux.

To validate the theory and demonstrate the PFM, multiple box-aquifer experiments were performed. Here, it was seen that accurate water flux measurements were obtained when the tracer used in calculations, resided in the meter at levels representing 20–70% of the initial condition. Exposure periods leaching more or less tracer from the meter produced larger measurement errors. The same experiments also showed the tracer ethanol generated the most accurate measurements of water flux with average relative errors of 4 percent.

DMP functioned as a surrogate groundwater contaminant in the box aquifer experiments. The cumulative contaminant flux measurements obtained were within 5% of known fluxes. The accuracy of these estimates generally increased with the total volume of water intercepted; although, because Eq. (30) was used, care was taken not to exhaust more than 67% of meter capacity to retain contaminant.

The PFM approach possesses several advantages. For example, the method provides for simultaneous evaluation of both water and contaminant fluxes under natural gradient conditions and vertical variations in horizontal fluxes can be monitored. All flux measurements are cumulative; and as a result, become increasingly less sensitive to daily fluctuations in groundwater flow or contaminant concentrations as the sampling period increases. Prior knowledge of the ambient groundwater discharge rate is not critical because multiple resident tracers are used to estimate flux. Furthermore, a meter can be designed to operate over a wide range of aquifer conductivities and yield a relatively constant  $\alpha$  ( $\alpha \approx 2$ ) (Klammler et al., 2004); hence, PFM application does not require precise prior knowledge about local aquifer hydraulic conductivities.

Use of PFMs in the field poses several challenges. First of all, multiple wells and PFMs are needed to estimate total contaminant discharge at a control plane. The resultant discharge estimate is sure to contain uncertainties, as it is generated from spatially integrating point measures of flux. Second, competitive sorption or rate-limited sorption may undermine the ability of the PFM to capture and retain target contaminants. If either are not considered in the interpretation of results, calculations

may not reflect true contaminant fluxes. Finally, long-term flux monitoring may be problematic, because natural changes in flow direction can invalidate flux measurements.

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