

# Field-Scale Evaluation of the Passive Flux Meter for Simultaneous Measurement of Groundwater and Contaminant Fluxes

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A new method, passive flux meter (PFM), has been developed and field-tested for simultaneously measuring contaminant and groundwater fluxes in the saturated zone at hazardous waste sites. The PFM approach uses a sorptive permeable medium placed in either a borehole or monitoring well to intercept contaminated groundwater and release "resident" tracers. The sorbent pack is placed in a groundwater flow field for a specified exposure time and then recovered for extraction and analysis. By quantifying the mass fraction of resident tracers lost and the mass of contaminant sorbed, groundwater and contaminant fluxes are calculated. Here, we assessed the performance of PFMs at the Canadian Forces Base Borden field site in Ontario, Canada. Two field tests were conducted under imposed groundwater flow fields: (1) radial flow to a well and (2) linear flow in a test channel confined by sheet pile walls on three sides. Both tests demonstrate that the local fluxes measured by PFM and averaged over the screen interval were within 15% of imposed groundwater flow and within 30% of measured contaminant mass flux. Patterns in depth variations in groundwater and contaminant fluxes, determined by the PFM approach, allow for site characterization at a higher spatial resolution. These results support the PFM method as a potential innovative alternative for measuring groundwater and contaminant fluxes in screened wells.

## Introduction

The need to quantify contaminant mass flux in groundwater has recently increased as implementation of remedial activities accelerates (1). Flux measurements have many applications in contaminant hydrogeology. In situ measurements of contaminant flux generate critical data needed to

optimize the design and assess performance of proposed contaminant source and groundwater remedial systems (2). These fluxes, when integrated over a source area, produce estimates of the contaminant source strength, that is, the total mass discharge rate (M/T) to groundwater and surface water. Such information is useful for model inputs and for management of contaminated sites. Furthermore, contaminant fluxes measured at locations down-gradient of source zones permit verification of remediation technology performance, assessment of natural attenuation rates, and evaluation of environmental risks. Current methods available for measuring mass flux include multilevel sampler (MLS) transects (3, 4) and integral pump tests (5, 6).

A new field method has been developed for direct in situ measurement of both cumulative water and contaminant fluxes in groundwater (7–9). This method has been evaluated in the laboratory (9) and was recently proposed for vertical flow in the vadose zone (10). We present here the results of the first field tests of the new method conducted at the Canadian Forces Base Borden site in Ontario, Canada. Two primary tests were conducted. The first involved radial flow to a well surrounded by eight boreholes used for flux measurements. The second test involved linear groundwater flow through a subsurface channel created by sheet pile walls on three sides; fluxes were measured in two sets of three boreholes placed across this channel, while multilevel samplers were placed up-gradient of the boreholes for local-scale (point) mass flux comparison. In both tests, the magnitude of the groundwater and contaminant fluxes measured by the new approach was evaluated by comparing with extraction well and MLS-based fluxes under forced-gradient (pumping) conditions.

**Description of the Passive Flux Meter Approach.** The new method (7–9) involves a device, hereafter referred to as a passive flux meter or PFM, a self-contained permeable unit that is inserted into a well or boring so that it allows groundwater flow through the device. The interior composition of the PFM is a matrix of a permeable sorbent that retains dissolved contaminants present in the groundwater intercepted by the unit. The PFM can be used for a broad range of contaminants (hydrophobic organic compounds, organic or inorganic ions, etc.) by selecting appropriate sorbent matrices. The sorbent matrix is preloaded with specified amounts of one or more resident tracers that have a known range of affinity for the sorbent (as characterized by the sorption coefficient,  $K_d$ , values). These tracers are displaced from the sorbent at rates proportional to groundwater flux and the tracer retardation on the sorbent. Tracer retardation,  $R_d$ , is a function of  $K_d$  and the sorbent bulk density and moisture content and can be measured in the laboratory (9, 11).

After a specified period of exposure to groundwater flow, the PFM is removed from the well or boring. The sorbent is then carefully extracted to quantify the mass of all contaminants intercepted by the PFM and the residual masses of all resident tracers. The contaminant masses are used to calculate time-averaged contaminant fluxes, while residual resident tracer masses are used to calculate cumulative groundwater flux. Depth variations of both water and contaminant mass fluxes can be measured in an aquifer from a single PFM by vertically segmenting the exposed sorbent packing and analyzing for resident tracers and contaminants. 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. These data are

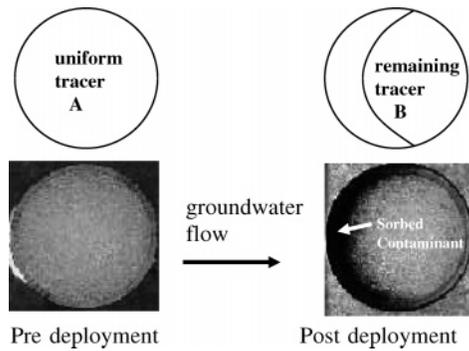
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**FIGURE 1. Tracer loss and mass loading across the passive flux meter. Dark area in postdeployment photo represents sorbed contaminant (water-soluble dye). A, Predeployment; B, postdeployment.**

used to estimate local cumulative water and contaminant fluxes.

As groundwater flows through the PFM, the resident tracers are desorbed from the sorbent and displaced out of the device. Figure 1 displays two cross-sections of a PFM configured as circular column (i.e., installed in a monitoring well); cross section A reveals a resident tracer uniformly distributed over the cross section before any fluid has passed through the PFM, while cross section B reflects the subsequent spatial distribution of tracer after exposure to a fluid flow field. Here, the tracer has been displaced to the right in a manner consistent with the assumption that fluid streamlines are parallel within the circular domain of the PFM.

The assumption of parallel streamlines within the PFM is consistent with Strack and Haitjema (12) for a homogeneous permeable element of circular geometry situated in a locally homogeneous aquifer of contrasting permeability. The permeability contrast between the PFM and the aquifer can produce aquifer flows that converge or diverge near the meter; however, the specific discharge within the circular bounds of the meter remains spatially uniform. Strack and Haitjema (12) presented the following relationship between the specific discharge in the PFM,  $q$ , and the undisturbed aquifer flow,  $q_0$ :

$$\frac{q}{q_0} = \frac{2k}{k + k_0} \quad (1)$$

where  $k$  and  $k_0$  are the respective permeabilities of the PFM and the aquifer.

The mass of resident tracer remaining within section B of Figure 1 can be used to estimate the cumulative fluid volume intercepted by the meter. If reversible, linear, instantaneous resident tracer partitioning between the sorbent and water is assumed, the dimensionless cumulative volume of water,  $\xi$ , intercepted by the PFM at a specified well depth is obtained iteratively by use of (9)

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

where  $M_R$  is the relative mass of tracer remaining in the PFM sorbent at the particular well depth. The specific discharge through the PFM,  $q$ , can then be calculated from

$$q = \frac{2r\theta R_d \xi}{t} \quad (3)$$

where  $r$  is the radius of the PFM cylinder,  $\theta$  is the water content in the PFM,  $R_d$  is the retardation of the resident tracer

on the sorbent, and  $t$  is the sampling duration. The actual specific discharge of the aquifer,  $q_0$ , is then found from  $q$  and eq 1.

A simplified form of eqs 2 and 3 can be used for  $M_R$  values greater than 0.3. In this case

$$q = [1.67r\theta R_d(1 - M_R)]/t \quad (4)$$

Because in most field applications the magnitude of flow is unknown, multiple resident tracers should be used to represent a broad range of tracer retardation factors. Likewise, multiple tracers provide for PFMs designed for both long and short exposure periods.

The contaminant mass retained on the sorbing porous matrix can be used to estimate solute flux intercepted by the meter. The measured flux is valid over the dimensions of porous medium contributing flow into the PFM. For example, a meter designed to sample the entire vertical depth of an aquifer could be used to characterize horizontal groundwater and contaminant fluxes averaged over the vertical extent of an aquifer. If reversible, linear, and instantaneous contaminant partitioning between the sorbent and water is assumed, the contaminant mass flux ( $J_c$ ) can be determined (9):

$$J_c = \frac{qM_c}{\pi r^2 L(1 - M_{RC})\theta R_{dc}} \quad (5)$$

where  $M_c$  is the mass of contaminant sorbed,  $L$  is the length of the sorbent matrix or the vertical thickness of aquifer interval sampled,  $R_{dc}$  is the retardation of contaminant on the sorbent, and  $M_{RC}$  is the relative mass of a resident tracer retained after time period  $t$  where that tracer has the same retardation as  $R_{dc}$ .

For high values of  $R_{dc}$ , or alternatively, short exposure periods, the contaminant flux can be calculated:

$$J_c = \frac{M_c}{2\alpha r L t} \quad (6)$$

where  $\alpha$  is the convergence or divergence of flow around the PFM. Equation 6 assumes all contaminant mass entering the well is retained by the PFM sorbent.

#### Field Evaluation of the Passive Flux Meter Approach.

The PFM was field-tested at the CFB Borden (Borden) site in Ontario, Canada. The hydrogeology of the site consists of a shallow surficial glacial outwash consisting of relatively homogeneous sand with a mean hydraulic conductivity of 5 m/day. This is underlain by a clay aquitard at a depth ranging from 1.3 to 2.5 m (13, 14). The water table depth ranges from 0.2 to 1.5 m below ground surface. The surficial aquifer has a natural gradient of about 0.001 and discharges to a small stream.

The PFM was tested at two locations. The first location was in a chlorinated solvent plume approximately 4 m up-gradient of a stream discharge boundary. This location was selected because the surficial aquifer thickness was approximately 1.2 m and the depth to groundwater was about 0.3 m. Additionally, the induced pumping had a minimal impact on the plume study being conducted. The plume was the result of a research study in which 50 L of a three-component dense nonaqueous phase liquid (DNAPL) was released into the aquifer (13). The DNAPL release point was approximately 80 m up-gradient of the PFM testing site, and the controlled release occurred 3 years prior to this study. The DNAPL was composed of equimolar fractions of chloromethane (CM), trichloroethylene (TCE), and perchloroethylene (PCE). Testing of the PFM focused on PCE and TCE because the CM pulse had predominantly transported beyond the study location. The site was instrumented for this study with a single pumping well surrounded by eight

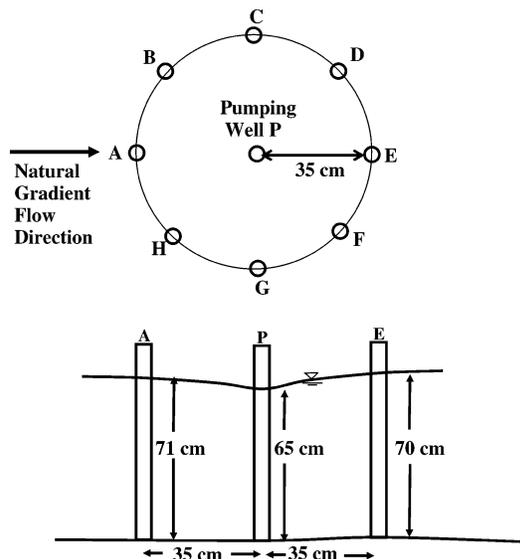


FIGURE 2. Pumping test well configuration.

wells used for PFM installation (Figure 2). The wells were fully screened 3.2 cm PVC (1.25 in. with 0.01 in. slots). The central well was pumped at a steady flow rate of about 255 mL/min, and samples were collected for TCE and PCE concentration measurements. The mass discharge from the pumping well was compared to estimates based on integrating the PFM values across the cylinder represented by the eight PFM wells.

The second location for PFM testing was in a controlled subsurface flow channel (14, 15). The channel was 30 m long and 2 m wide, constructed from sealable Waterloo sheet pile driven into the aquitard at a depth of approximately 2.2 m. The channel was closed on one end and opened on the other to allow groundwater to enter. At the closed end, a single, fully screened 5.1 cm (2 in.) well was pumped to produce steady groundwater flow through the channel. Previous experiments conducted in the channel investigated degradation of methyl *tert*-butyl ether (MTBE) (15). Following these experiments, a MTBE plume remained in the channel. This system provided an opportunity to test the PFM.

Steady flow was established in the channel by pumping at approximately 203 mL/min from the extraction well. Groundwater and contaminant fluxes were assessed by use of two rows of three wells, each oriented in transects

perpendicular to the flow in the channel (Figure 3). The wells installed for this study were constructed from 5.1 cm PVC screen (2 in. with 0.01 in. slot) with the front row of wells having no sand pack and the back row installed with a uniform sand pack with a mean grain diameter of 2.0 mm. Multilevel samplers (MLSs) were installed a distance of 1 m up-gradient of the wells with 15 sampling depths spaced at 20 cm intervals. Groundwater flux estimated from the PFMs was compared to the extraction well flow and MTBE flux at the two well transects was compared to flux based on the multilevel samplers.

**Passive Flux Meter Installation, Retrieval, and Sampling.**

The PFMs were deployed in both 3.2 and 5.1 cm PVC well screens. The construction and retrieval procedure for the different well diameters was approximately the same. The PFMs were constructed from an open mesh cotton fabric (Crinolyn) that was sewn to a 3.2 and 5.1 cm diameter sock, closed at the bottom end. The sock was attached to a threaded rod (US 8-32 thread or 1/4 in. coarse thread) between two rubber washers tightened with two steel washers and nuts. The threaded rod extended up through the center of the sock and was used to slide (pull down from the bottom of the sock) the PFM into the well (Figure 4).

Prior to packing, silver-impregnated granular activated carbon (GAC) was prepared by equilibration with an aqueous solution of resident alcohol tracers. The GAC was used as received (989 12 × 30: Barnebey Sutcliffe Corp., Columbus, OH). This aqueous solution was combined with dry GAC at a volume-to-mass ratio of 2:1 (e.g., 1.5 L to 0.75 kg), and rotated in 2-L jars for a period of 12 h. The tracer-loaded GAC was then decanted and sealed for shipment to the site.

On site, the socks were packed with the GAC. The socks were placed in a PVC pipe nearly matching the inside diameter of the well screens. The socks were packed by transferring a measured volume of activated carbon to a funnel entering the top of the sock. The pipe and sock were vibrated to facilitate packing. After each lift, a rubber washer (Neoprene) was inserted onto the threaded rod and pushed down to the packing depth with a 3/4-in. PVC pipe to compact the material in place. The rubber washers had a hole the diameter of the threaded rod and an outer diameter matching the well screen (e.g., 5.1 cm diameter with 0.64 cm hole). These washers were intended to minimize vertical flow of groundwater within the PFM and were used to delineate vertical sampling intervals.

During the packing process, a field sample of GAC was collected to measure the initial concentration of tracers

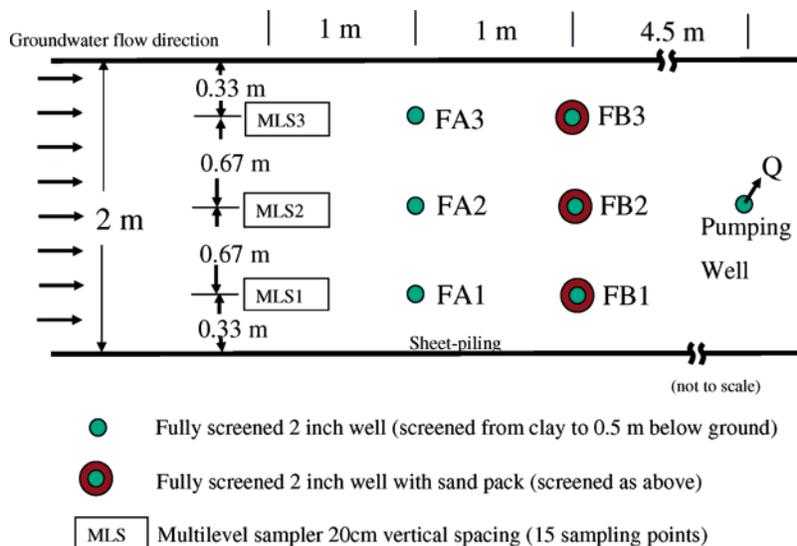


FIGURE 3. Channel test well configuration.

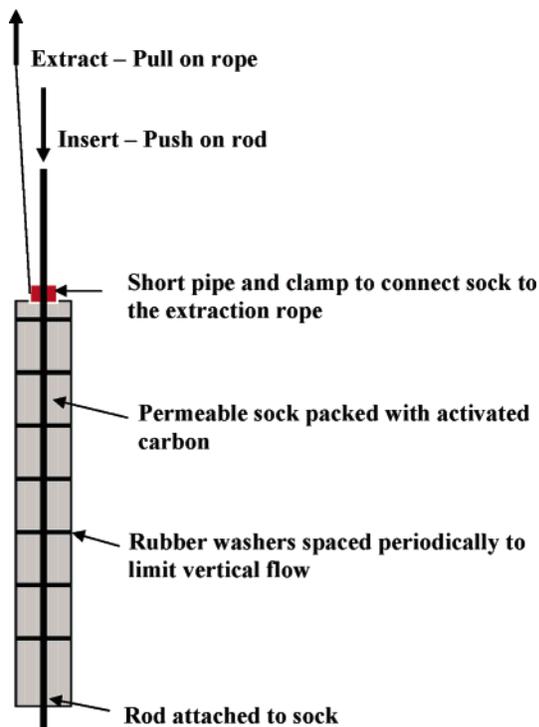


FIGURE 4. Passive flux meter installation method.

present. After all lifts were packed, the top of the sock was attached to a short section of 1.9 cm PVC pipe with a worm-drive clamp. A rope was attached for retrieval of the PFM by pulling the sock out of the well (Figure 4). The completed PFM was then inserted into the well by placing the packing pipe directly over the top of the well and pushing the PFM in place by use of the threaded rod. Additional threaded rods were attached as needed to position the PFM in the desired screen interval.

After a specified period of exposure, the PFM was retrieved from the well directly into a pipe to minimize volatile losses of tracers during sampling. The bottom end of the PFM was then pulled from the pipe and the section of sock was cut for sampling. The entire section of the GAC was transferred to a bowl and mixed vigorously for a few seconds to homogenize. A subsample (approximately 10 g) was transferred to preweighed vials containing 20 mL of isobutyl alcohol (IBA, 2-methyl-1-propanol). The interval length was then recorded and sampling continued. The samples were shipped on ice to the University of Florida for analysis.

In the laboratory, the initial and final GAC samples were analyzed for tracer and contaminant concentrations by a two-step liquid extraction process. The GAC samples in IBA were slowly rotated for 24 h and subsamples were collected for alcohol tracer analysis. The IBA liquid was then decanted and a 7/25 (vol/vol) mixture of hexane and acetone was introduced to extract contaminants (i.e., TCE, PCE, and MTBE). These samples were again rotated and subsampled. Fluid volumes for all extractions were recorded for later concentration calculations. All samples were analyzed on a Perkin-Elmer Autosystems GC with FID and high-performance liquid chromatography (HPLC) with a reverse-phase column (C-18, Supelco).

**Tracer Elution Column Tests and Batch Extraction Efficiency.** To evaluate the relationship between water flow through GAC and the loss of tracers, column studies were conducted. GAC was preequilibrated with tracers by the same method as for the field studies. The GAC was packed into a glass column (Kontes 2.5 cm by 5 cm) and flushed with deionized water to elute the tracers. Effluent samples were

analyzed, with alcohol concentration quantified by use of GC FID inline sampling (16). The effluent breakthrough curves were integrated to quantify the mass removal as a function of the pore volumes of water applied.

The extraction efficiency of the two-step solvent extraction method was evaluated by use of spiked GAC samples. A known mass of contaminant was added to vials containing GAC and water. These samples were rotated for 24 h and extracted by the method outlined above for the field samples. The extracts, IBA and hexane/acetone, were then analyzed for PCE and TCE concentrations. The known liquid volumes for each extraction were used to calculate the extraction efficiency of the process. A range of tracer and contaminant concentrations was used to assess the extraction efficiency over the range of concentrations observed for the field samples.

**Laboratory Testing for Flow Convergence or Divergence around Wells.** When groundwater flows through a well, the flow lines tend to be distorted by the hydraulic conductivity contrast between the well and the surrounding aquifer (12). To determine the convergence for the wells, a calculation was made based on measured (or estimated) values for hydraulic conductivity of the aquifer, PFM, and well screen. Values for hydraulic conductivity were measured in the lab by falling head methods (18). Measuring the hydraulic conductivity of the well screen in the presence of the aquifer material was conducted by packing Borden sand, contained within a mesh tube, around a well screen and measuring the combined properties under a constant head difference (additional details are provided in the Supporting Information). The measured hydraulic conductivity of the Borden sand was then used to determine the effective screen hydraulic conductivity. When these values were known, convergence could be calculated (19, 20):

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

where  $K_D = k_D/k_0$ , the dimensionless ratio of  $k_D$ , the uniform hydraulic conductivity of the PFM sorptive matrix [L/T], to  $k_0$ , the uniform local hydraulic conductivity of the surrounding aquifer [L/T];  $K_S = k_S/k_0$ , the dimensionless ratio of  $k_S$ , the well screen hydraulic conductivity [L/T], to  $k_0$ ; and  $R_S = r_0/r$ , the dimensionless ratio of  $r$ , the PFM radius [L], to  $r_0$ , the outside radius of the well screen [L].

## Results and Discussion

The results of the two field tests conducted to evaluate the PFMs are discussed in the following three sections. Parameters used in PFM calculations, including tracer retardation, contaminant extraction efficiency, and borehole flow convergence/divergence, are discussed first, while the pumping well test and the subsurface flow channel test are covered in the two subsequent sections.

**Determination of Flux Meter Characteristics.** To assess the performance of the PFMs in the field experiments, three critical characteristics of the system were required. The first was the relationship between water flow through the activated carbon and the loss of tracers. The second was the degree of flow convergence (or divergence) experienced locally around the well with a PFM in place. The third was the contaminant extraction effectiveness from activated carbon by a two-step liquid–solid extraction method.

The rate at which each tracer was eluted from the activated carbon was determined on a small laboratory column packed with the tracer-equilibrated activated carbon used in the field tests. Tracer concentrations in column effluent were monitored, and from this information, the mass of tracer

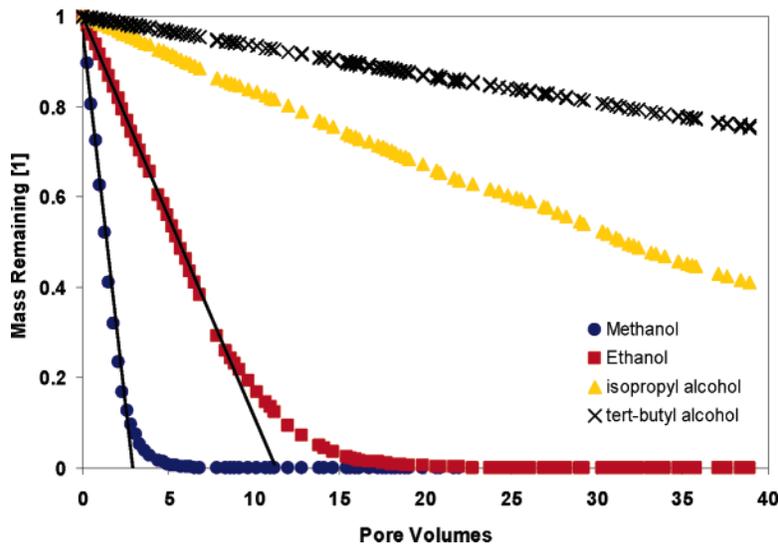


FIGURE 5. Alcohol tracer elution curves for activated carbon.

TABLE 1. Resident Tracers and Partitioning Characteristics

resident tracers	aqueous concn (mg/L)	$R_d$
methanol	1200	4.9
ethanol	1200	20
isopropyl alcohol (IPA)	2300	109
tert-butyl alcohol (TBA)	2300	309
2,4-dimethyl-3-pentanol (DMP)	1200	> 1000

remaining in the column was plotted as a function of pore volumes applied (Figure 5). The relationship between tracer mass loss and the cumulative water flow is linear until about 70% of the tracer mass was removed from the column ( $M_R = 0.3$ ). After this, the relationship is nonlinear with asymptotic mass removal at low  $M_R$ . This suggests that a linear model for mass removal could be applied (up to about 70% mass removal). The use of a calculated retardation coefficient  $R_d$  was applied here where the  $R_d$  was determined from the straight-line portion of the tracer elution data (Figure 5, Table 1). In calculating the reported  $R_d$  values, a water content,  $\theta$ , of 0.55 was applied on the basis of gravimetric analyses of the activated carbon. Note that the water content value used is not a factor in estimating water flow from the PFM since the combined term  $\theta R_d$  is used for calculations (eq 3). The  $R_d$  values reported above were used to estimate Darcy fluxes based on the PFMs deployed in the field selecting tracers with  $M_R > 0.3$ . A system of linear segments can be used for conditions where  $M_R$  is less than 0.3; however, that was not employed for the field data presented here.

The degree of convergence/divergence of flow around a well screen, with a PFM in place,  $\alpha$ , can be calculated from eq 7 with appropriate estimates of the media hydraulic properties. Based on falling head tests for the Borden sand,  $k_O = 17 \pm 2$  m/day, the  $k_D$  for the activated carbon was  $330 \pm 30$  m/day, and  $k_S$  for the PVC well screen was  $2.9 \pm 0.5$  m/day measured in the presence of the Borden sand (note errors reported throughout this paper are propagation of 1 standard deviation of measurement error). For the radius of the well of 1.6 cm, the convergence for the system  $\alpha = 0.97 \pm 0.15$  is used for the later calculations presented. The 2-in. wells used in the flow channel have  $\alpha = 0.83 \pm 0.12$  for no sand pack as a result of a measured  $k_S$  for the 2-in. PVC well screen of  $2.0 \pm 0.2$  m/day. The well with the gravel pack is more difficult to assess. We assume here that the Borden sand was fine enough to fill the pore space of the gravel pack and produce an effective hydraulic conductivity for the gravel pack of 6 m/day and a  $k_S$  for the PVC well screen with the

sand pack and Borden sand was 3.4 m/day, producing  $\alpha = 1.05 \pm 0.18$  with the sand pack.

The third parameter needed to quantify contaminant mass flux is the extraction effectiveness of the laboratory analytical method used. For the experiments conducted here, a two-step liquid extraction process was used. The effectiveness of this method was assessed by conducting laboratory batch extraction tests. The extraction effectiveness for each constituent was used to calculate mass flux of contaminants for the field sites samples. On the basis of the concentrations of PCE measured, extraction effectiveness was  $48\% \pm 2.5\%$ , and for TCE,  $95\% \pm 2.7\%$ . The extraction effectiveness for MTBE and the alcohol tracers was  $100\% \pm 3\%$ . A set of extraction experiments were conducted that included sample mixing as conducted in the field. The test indicated an extraction efficiency for PCE of 50%, suggesting that volatile losses were not significant during mixing.

**Pumping Well Flux Assessment.** The central well was pumped at an average rate of  $255 \pm 20$  mL/min for a period of 48 h. During that time, water samples were collected at approximately 6-h intervals. These were analyzed for PCE and TCE where the mean concentrations were  $6.3 \pm 0.2$  and  $7.2 \pm 0.2$  mg/L, respectively. The measured flow rates during the test and the PCE concentration data can be combined to provide a mass discharge at the well during the pump test. The average mass discharge was  $96 \pm 7.9$  mg/h for PCE and  $110 \pm 9.1$  mg/h for TCE. The water flow and total mass discharge of PCE measured at the extraction well were compared to water and mass discharge estimates based on the eight PFMs installed around the well. The 80-cm-long PFMs installed in each of the eight wells surrounding the pumping well were deployed for a period of about 48 h. After extraction from the wells, the PFMs were segmented into 20-cm-long intervals for analysis. The mass of tracer and contaminant were used to estimate local Darcy fluxes [L/T] and local mass fluxes [ $M L^{-2} T^{-1}$ ]. Local values of velocity and PCE flux have been contoured on a flat surface in Figure 6. This surface represents a cylinder with a radius of 35 cm that has been split at the location of well A (approximately up-gradient) and rolled to a flat plane. The velocity data and local flux values indicate that the highest velocity zones were near the water table and the lowest were near the clay confining unit. The highest local PCE flux values were near the water table and in general correlate with the highest Darcy flux. The spatial distribution of mass and Darcy fluxes can be useful in efforts to improve mass recovery through pumping strategies and addition of new capture wells at sites.

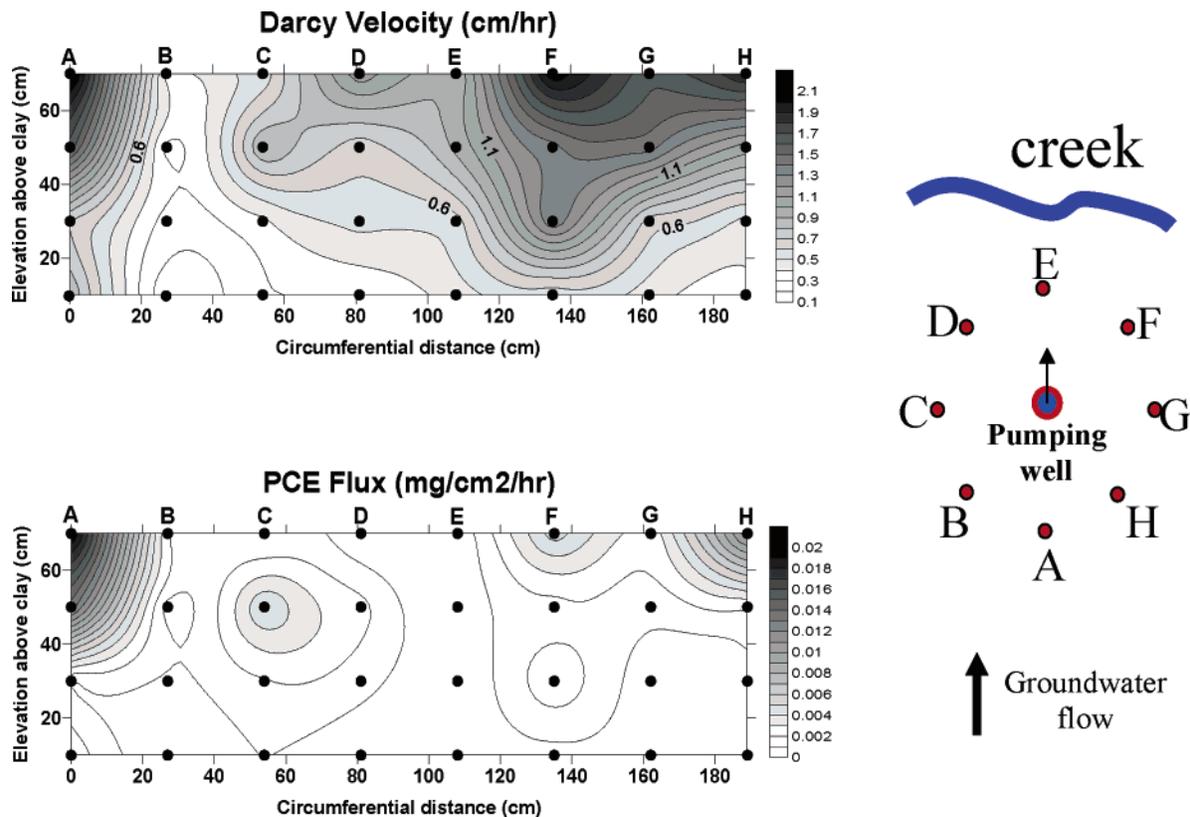


FIGURE 6. Flux meter based values for Darcy flux (a, upper panel) and PCE mass flux (b, lower panel) on the pumping well flux well cylinder (wells A–H in Figure 2).

Often inefficient systems extract large volumes of water in order to remove small quantities of the remaining contaminant present in the aquifer.

To compare both the water flow and contaminant mass discharge at the extraction well with the local Darcy and mass flux measured at the PFM wells, the spatial data must be integrated to produce a total water flow and contaminant mass discharge. A spatial integration was used in which each 20-cm-long PFM sample interval was assigned a representative area  $20\text{ cm} \times \pi r/4$  ( $550\text{ cm}^2$  area for each PFM segment). This integration of Darcy fluxes over the total area of the cylinder produced a total flow rate of  $258 \pm 60\text{ mL/min}$ . This compares well with the applied flow rate of  $255 \pm 20\text{ mL/min}$ . The integrated mass flux data for PCE produces a total mass discharge of  $102 \pm 26\text{ mg/h}$ , which compares well with the measured mass discharge at the extraction well,  $96 \pm 7.9\text{ mg/h}$ . For TCE the integrated mass discharge is  $79 \pm 20\text{ mg/h}$ , which compares to  $110 \pm 9.1\text{ mg/h}$ . The magnitudes of PCE and TCE mass discharge based on the integrated PFM data are within 30% of the mass discharge measured at the extraction well. This supports the PFM approach as a passive method to obtain spatially discrete local fluxes that integrate to produce total mass discharge.

**Subsurface Flow Channel Flux Assessment.** The subsurface flow channel experiment was also conducted to assess field performance of the PFM. In this experiment, the Darcy flux results were compared to flow at the extraction well and mass flux results were compared to estimates based on the multilevel samplers. In addition, two types of well packing were compared.

A steady flow of water,  $203 \pm 6.8\text{ mL/min}$ , was pumped from the extraction well located at the closed end of the channel during the experiment. This produced a calculated Darcy flux at the flux meter wells and multilevel samplers of  $10.5 \pm 0.4\text{ cm/day}$  based on a saturated thickness of  $1.39 \pm 0.02\text{ m}$ . This saturated thickness does not include the capillary

fringe. If an estimated capillary fringe of 20 cm is included as part of the flow field, the Darcy flux is  $9.2 \pm 0.35\text{ cm/day}$ . The PFMs were installed in the down-gradient row of wells (FB1–FB3) first for a period of 5 days. PFM tests in the second set of wells (FA1–FA3) were initiated just prior to extraction of the downstream PFMs. This approach was used to avoid tracer interference between PFMs. During this period of time, the MLSs were sampled four times to collect concentration data in order to calculate mass discharge through the channel and produce a spatial distribution of contaminant mass flux for comparison with the PFMs.

The groundwater flow pumped from the channel can be compared to the flow estimated from the PFMs. Like the previous single pumping well problem, the spatial Darcy fluxes estimated from the PFMs must be integrated over the cross section of the channel. A simple averaging approach was taken. The average velocity for the wells with no sand pack was  $8.7 \pm 1.7\text{ cm/day}$ , while the sand pack well was  $9.5 \pm 2.0\text{ cm/day}$ . These values take into account the convergence calculated on the basis of the measured hydraulic conductivities of the materials used:  $\alpha_{\text{no sand}} = 0.83$ ;  $\alpha_{\text{sand}} = 1.05$ . These estimated water flux values compare reasonably well, suggesting that PFMs can be designed to function in a variety of well types (note the channel application used 2-in. wells while the pumping test used 1.25-in.). Note that if the capillary fringe estimate is included when the Darcy flux is calculated, the estimated values are within 5%. Vertical profiles of Darcy flux are provided in the Supporting Information. In general, Darcy flux was reasonably uniform in both the FA and FB well profiles with coefficients of variation of about 0.35.

Flux of MTBE was also evaluated in the channel experiment. Vertical profiles of local mass flux were compared between the MLSs and the PFMs (Figure 7). The results suggest that the PFM deployed in the wells with no sand pack does capture the contaminant flux behavior (vertical trend) supporting the assumption of minimal vertical flow

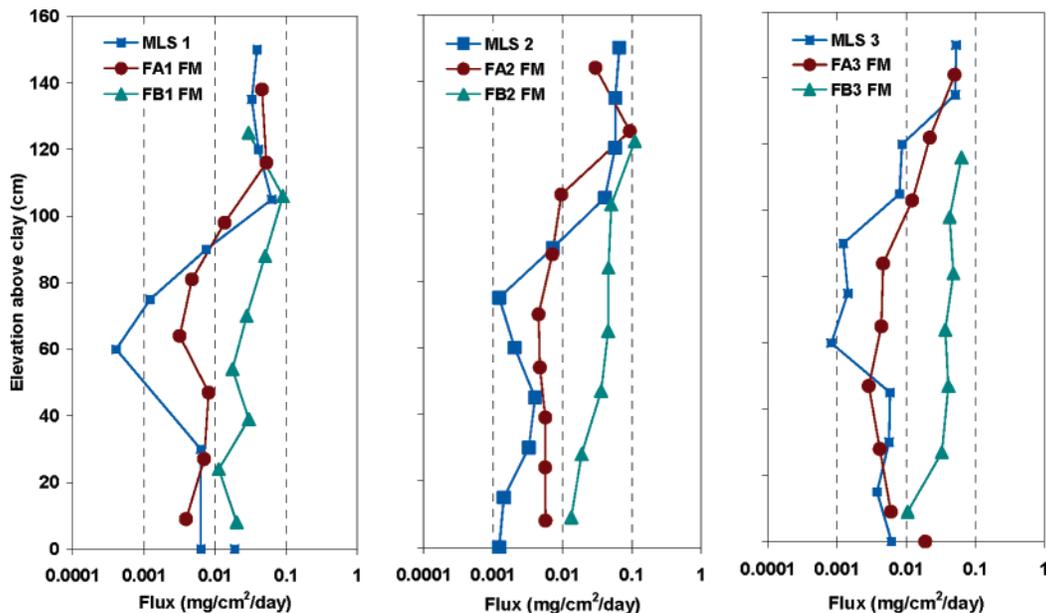


FIGURE 7. Comparison of mass flux profiles for flux meters and multilevel samplers in the flow channel.

within the PFM. In the wells with sand packs, it was apparent that the flux was higher in the lower zone where little MTBE is present, based on the MLS data. This suggests that the sand pack may provide movement of MTBE deeper in the profile. The assessment here focused only on the general trends observed. Local flux comparisons, between point measurements, are difficult due to the physical separation of two measurements (such as MLS versus PFM) and the fact the both methods integrate differently over space and time. Further work is warranted in higher density sampling networks to assess spatial statistics of flux fields.

Integrated mass discharge, based on point measurements, was also evaluated. The total integrated MTBE mass discharge within the flow channel based on the MLSs was  $0.54 \pm 0.12$  g/day, which is in good agreement with the integrated PFM-based mass discharge of  $0.47 \pm 0.08$  g/day in the wells without a sand pack (FA). The MTBE mass discharge reported in wells FB with a sand pack are significantly higher at  $1.1 \pm 0.2$  g/day. The fact that the FB wells report higher mass discharge compared to the MLSs is consistent with the observation of an increasing MTBE concentration gradient toward the channel extraction well. This is likely the result of discontinuing the injection of MTBE at the up-gradient end of the channel during previous experiments (15). Groundwater samples collected at the extraction well show a decreasing trend from 19 to 13 mg/L of MTBE during the experiment. Water samples collected at the flux wells prior to PFM deployment had average concentrations of MTBE of 2.5 and 5.8 mg/L in the FA and FB wells, respectively. These data also supports the observation of increasing concentration of MTBE down-gradient within the channel although these wells were of different construction. The ratio of MTBE concentration in water samples from the FA and FB wells ( $5.8/2.5 = 2.32$ ) is very similar to the ratio of mass discharge measured by the PFMs ( $1.1/0.47 = 2.34$ ). This observation indicates that the PFMs are consistent with water samples collected from these wells. While the existing trend of MTBE concentration within the channel complicated the data interpretation, the observed fluxes are consistent with conditions in the channel and support the method for estimating MTBE flux. Additional testing of the PFMs concurrent with other methods including MLSs and integral pump tests (5, 6) are needed at controlled field sites with imposed and confirmed mass injection and discharge.

The two tests conducted at the Borden site demonstrate the application of the PFM for estimating groundwater and contaminant mass fluxes. Both tests support the PFM concept and demonstrate that reasonable values can be obtained by this method of site characterization. While more rigorous testing of the device is needed in a range of hydrogeologic settings and with different well construction and quality, such as currently underway, the method shows promise as a new tool to assess groundwater contamination at hazardous waste sites. The approach may have utility for assessing remedial performance, evaluating natural and enhanced bioremediation, and for quantifying risk to humans and ecosystems.

### Acknowledgments

This research was funded by the Environmental Security Technology Certification Program (ESTCP), U.S. Department of Defense (DoD), Project CU-0114. This paper has not been subject to DoD review and accordingly does not necessarily reflect the views of the DoD.

### Supporting Information Available

Additional details on the methods used to measure the well screen hydraulic conductivity in the presence of Borden sand, along with the PFM data for the two field sites. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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*Received for review January 13, 2005. Revised manuscript received July 3, 2005. Accepted July 7, 2005.*

ES050074G