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Oxyanion flux characterization using passive flux meters: Development and field testing of surfactant-modified granular activated carbon

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Abstract

We report here on the extension of Passive Flux Meter (PFM) applications for measuring fluxes of oxyanions in groundwater, and present results for laboratory and field studies. Granular activated carbon, with and without impregnated silver (GAC and SI-GAC, respectively), was modified with a cationic surfactant, hexadecyltrimethylammonium (HDTMA), to enhance the anion exchange capacity (AEC). Langmuir isotherm sorption maxima for oxyanions measured in batch experiments were in the following order: perchlorate>>chromate>selenate, consistent with their selectivity. Linear sorption isotherms for several alcohols suggest that surfactant modification of GAC and SI-GAC reduced (~30–45%) sorption of alcohols by GAC. Water and oxyanion fluxes (perchlorate and chromate) measured by deploying PFMs packed with surfactant-modified GAC (SM-GAC) or surfactant-modified, silver-impregnated GAC (SM-SI-GAC) in laboratory flow chambers were in close agreement with the imposed fluxes. The use of SM-SI-GAC as a PFM sorbent was evaluated at a field site with perchlorate contamination of a shallow unconfined aquifer. PFMs packed with SM-SI-GAC were deployed in three existing monitoring wells with a perchlorate concentration range of ~2.5 to 190 mg/L. PFM-measured, depth-averaged, groundwater fluxes ranged from 1.8 to 7.6 cm/day, while depth-averaged perchlorate fluxes varied from 0.22 to 1.7 g/m^2/day. Groundwater and perchlorate flux distributions measured in two PFM deployments closely matched each other. Depth-averaged Darcy fluxes measured with PFMs were in line with an estimate from a borehole dilution test, but much smaller than those based on hydraulic conductivity and head gradients; this is likely due to flow divergence caused by well-screen clogging. Flux-averaged perchlorate concentrations measured with PFM deployments matched concentrations in groundwater samples taken from one well, but not in two

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other wells, pointing to the need for additional field testing. Use of the surfactant-modified GACs for measuring fluxes of other anions of environmental interest is discussed.

Keywords: Perchlorate; Selenate; Chromate; Groundwater fluxes; Anionic contaminants; Groundwater contamination; HDTMA

1. Introduction

1.1. Oxyanion contamination of groundwater

Examples of oxyanion contamination of groundwater include perchlorate, borate, arsenate, selenate, chromate, and molybdate (Puls et al., 1999; EPA, 2002, 2005; Doherty et al., 2006). Other oxyanions found in groundwater are nitrate, sulfate, carbonates, and phosphate. Here, scenarios involving groundwater contamination with perchlorate are of primary interest, with secondary attention given two other oxyanions (chromate and selenate). Perchlorate salts are used in solid propellants (in rockets and missiles), munitions, commercial explosives, fireworks, and flares. Perchlorate compounds are also used in a number of other manufacturing operations (e.g., electroplating, pharmaceutical production; paints and enamels) and agricultural uses (EPA, 2005; ITRC, 2005a). Detection of perchlorate in soils, groundwater, and drinking water wells has been confirmed in several states throughout the United States (Urbansky, 1998, 2000; Motzer, 2001; Tan et al., 2004; EPA, 2005). For example, in an EPA survey of 2800 large public water systems and a representative 800 small public water systems, perchlorate was detected in 153 systems in 25 states (ITRC, 2005a).

Perchlorate salts are highly soluble in water and the perchlorate anion has little sorption affinity for most geologic materials except various oxides (Motzer, 2001; Urbansky and Brown, 2003; ITRC, 2005a). In addition, perchlorate neither complexes nor precipitates with common cations found in natural water bodies, including groundwater (Long, 2000). These characteristics result in rapid and long-range transport of perchlorate in both groundwater and surface water systems. Perchlorate releases – both as brine and solid – are known to produce source zones that can sustain dissolved plumes in groundwater for extended periods (Flowers and Hunt, 2000; ITRC, 2005a).

1.2. Measurement of contaminant fluxes

With a growing recognition of the need to measure contaminant fluxes as a component of site assessment (Rao et al., 2001; Einarson and Mackay, 2001; EPA, 2003; API, 2003; NRC, 2004; Falta et al., 2005a,b; ITRC, 2005b), innovative methods for flux measurement have been developed (Bockelmann et al., 2001, 2003; Hatfield et al., 2004). Development and field applications of the Passive Flux Meter (PFM) approach have been described in several recent papers (Hatfield et al., 2001, 2002, 2004; Annable et al., 2005; Basu et al., 2006). PFM deployment allows for simultaneous measurement of cumulative fluxes of contaminants and groundwater.

A PFM consists of a tight-mesh, tubular-shaped, nylon fabric sock packed with a permeable sorbent pre-loaded with “resident” tracers. A PFM sock is deployed in a screened well for a target period of time and the depletion of resident tracers and accumulation of contaminants of interest are determined. (see Annable et al., 2005 for details). The types of sorbent matrix, the suite of resident tracers used in a PFM, as well as the deployment period, are pre-selected based on the assessment of site-specific needs. In general, deployment periods can vary from as little as 1 week to 10 days at sites with high contaminant concentrations (e.g., near source zones) and/or large Darcy fluxes, or up to several weeks at sites with low contaminant concentrations (e.g., within plumes) and/or small groundwater fluxes (e.g., 1–3 cm/day). To date, the contaminants of concern in field-scale tests of PFMs have been limited to chlorinated DNAPL constituents (PCE, TCE, DCE, VC, etc.) and fuel hydrocarbons (BTEX, MTBE, TBA, etc.) (Annable et al., 2005; Basu et al., 2006). However, no field tests have been reported in which the PFM technology was evaluated at sites contaminated with anionic species.

1.3. Sorbents for passive flux meters

In this study, development and assessment of new sorbents for PFMs to measure oxyanion fluxes comprised of the following groups of activities: (1) batch studies on surfactant modification of GAC; (2) development and implementation of oxyanion extraction and ion-chromatography protocols; (3) batch studies to measure sorption of methylated alcohols used as tracers; (4) batch experiments to evaluate sorption of oxyanions and their selectivity; and (5) laboratory and field studies to examine the utility of the surfactant-modified GAC for measuring groundwater and oxyanion fluxes.

Selection of the new PFM sorbents was based on having a permeable solid matrix with large anion exchange capacity (AEC) and a highly selective functional group (here, a quaternary amine). This criterion ensures that all perchlorate (and other oxyanions) in groundwater passing through the device is “captured” even in the presence of other competing background anions (e.g., sulfates, carbonates, nitrate, etc.) typically found in groundwater. In addition, stable AEC on the modified sorbent is ensured by strong sorption of the modifier to the sorbent (i.e., minimal losses by desorption during the deployment period), and recalcitrance to microbial or chemical degradation.

Laboratory-scale application of the PFM approach to measuring oxyanion contaminant fluxes has been limited, and no field-scale studies of PFM application to examine anion fluxes have been reported. In recent laboratory experiments, Clark et al. (2005) and Campbell et al. (2006) evaluated activated alumina, anion exchange resins (AERs), and granular activated carbon (GAC) as PFM sorbents to measure anion fluxes. Arsenate fluxes measured with activated alumina as the PFM sorbent agreed well (within 4% of accuracy) with the imposed fluxes, but groundwater fluxes could not be simultaneously determined because alumina did not sorb alcohol tracers and use of other types of tracers was not investigated (Clark et al., 2005). Use of organic acids, such as benzoate as a resident tracer, was explored by Campbell et al. (2006) in their laboratory scale studies where AERs were used as the PFM sorbent for measuring chromate fluxes. However, sorption of hydrophobic contaminants to AERs has not yet been reported. These early applications of PFM technology for measuring oxyanion fluxes show promise, but they also revealed the difficulties in finding appropriate permeable sorbents specific for targeting both anionic contaminants as well as resident tracers.

Granular activated carbon (GAC), with and without impregnated silver, has been used in water treatment processes and in other industries (Etris, 1991; Hassler, 1963; Bayati, 1997; Jennings, 2005; Bansal and Goyal, 2005). Silver-impregnated GAC (SI-GAC), which has a high sorption capacity for the methylated alcohols (used as “resident tracers”), and for the hydrophobic constituents of LNAPLs (light nonaqueous phase liquids) and DNAPLs (dense nonaqueous phase liquids), has also been successfully used as a PFM sorbent to measure groundwater and contaminant fluxes (Hatfield et al., 2004; Annable et al., 2005; Basu et al., 2006).

1.4. Study objectives

The primary objective of this study was to develop and evaluate new PFM sorbents to measure perchlorate and other oxyanions (chromate and arsenate) fluxes. Granular activated carbon (GAC), with and without impregnated silver, and modified with a cationic surfactant, HDTMA, was evaluated in this study. Surfactant modification of GAC was intended to generate the required anion exchange capacity (AEC) for sorption of perchlorate and other oxyanions. The trimethyl amine “head” group of HDTMA is known to have high affinity for perchlorate (Gu et al., 2001). Sorption of oxyanions (perchlorate, chromate, and selenate) as well as a suite of methylated alcohol tracers was examined in laboratory batch studies. PFMs, packed with SM-GAC or SM-SI-GAC, were deployed in laboratory flow chambers to measure oxyanion (perchlorate and chromate) and groundwater fluxes. PFMs with SM-SI-GAC were then tested at a field site (Indian Head, Maryland) contaminated with perchlorate; limited access to the site, however, precluded extensive field evaluation and the results reported here are preliminary in scope.

2. Materials and methods

2.1. Chemicals

Standard-grade ammonium perchlorate (Sigma-Aldrich, purity >99%) was used in all laboratory experiments and for preparing analytical standards for instrument analysis. Alcohol tracers (methanol, ethanol, *iso*-propanol, *tert*-butyl-alcohol) were purchased from Fisher Scientific, while 2,4-dimethyl-3-pentanol was obtained from Sigma-Aldrich, all with purities >98%. Extraction solvents/solutions were: *iso*-butyl alcohol (IBA) for the alcohol tracers, and potassium nitrate (KNO_3) for the oxyanion contaminants; both were purchased from Fisher Scientific at purities >98%. HDTMA-Br (solid) was obtained through Alfa Aesar (99+% purity), while HDTMA-Cl (25 wt.% solution) and *p*-toluenesulfonic acid monohydrate (98% purity) were purchased from Sigma-Aldrich. Calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) used as a background electrolyte and sodium borate ($Na_2B_4O_2$) used as an analytical eluent (HPLC) were both purchased (with >99% purity) from Fisher Scientific.

2.2. Granular activated carbon

GAC and SI-GAC used in this study were purchased from Barnaby & Sutcliffe Co. (Columbus, OH), and used without further treatment. SI-GAC had been loaded with 0.026% silver using an electroplating method (Bayati, 1997). Both the GAC and SI-GAC were manufactured from coconut shells treated at high temperature. Based on the information provide by the supplier (Barnaby & Sutcliffe Co., Columbus, OH), the following GAC properties are summarized as being representative of a typical production lot number. The pore-size distribution of both GAC and SI-GAC was: 62% micropores (0–20 Å); 22% micropores (20–500 Å); and 16% macropores (>500 Å). The specific surface area is 1100–1200 m^2/g, and the ash content is 2–3%. Iodine Number (mg/g), Hardness Number (%), and bulk density (g/cm^3) are 1050, 98 and 0.48, respectively.

2.3. Batch sorption studies

2.3.1. HDTMA-Br sorption on GAC and SI-GAC

Batch experiments were conducted to examine the sorption of HDTMA-Br on GACs. Predetermined amounts of GAC (0.12 g) and aqueous solution (~40 mL) of HDTMA-Br at a known concentration (0.04 to 5.2 mM) were placed in pre-weighed 40-mL VOA vials and sealed with Teflon-lined screw-caps. Control samples containing the same amount of GAC and DI water were also prepared. All combinations were duplicated. The samples were loaded on a rotator (Glas-Col), equilibrated at 30 rpm for 24 h at 25 °C, and then allowed to settle for 24 h. Clear supernatant was sampled for analysis (see Section 2.6 for details). The sorbed mass of $HDTMA^+$ and Br^- (counter-ion) on SI-GAC was determined from the difference between initial and equilibrium concentrations in the supernatant solution.

2.3.2. Perchlorate sorption on SM-SI-GAC

A batch-equilibration method was used to measure sorption of perchlorate by SM-SI-GAC. Three grams of SM-SI-GAC and 12 mL of a known concentration of perchlorate aqueous solution was placed in a pre-weighed 20-mL glass VOA vial and sealed with Teflon-lined screw-cap. Initial perchlorate concentrations, in dilute electrolyte (0.005 M $CaCl_2$) aqueous solution, ranged from 0 to 107 mmol/L. It is recognized that concentrations and composition of groundwater background electrolytes at contaminated sites will be different, and might influence perchlorate ion exchange. Each sorption experiment was performed in duplicate. The vials were placed on a Glas-Col rotator set to 30 rpm for 24 h at room temperature (25 °C). Samples were then stored for a further 24 h to allow suspended particulates to settle. Then, a clear supernatant aliquot was subsampled and diluted (1:200 ratio) with de-ionized (DI) water prior to perchlorate analysis by Ion Chromatography (IC) (see Section 2.6).

2.3.3. Oxyanion sorption on SM-GAC

Sorption of three oxyanions (perchlorate, chromate, and selenate), was examined using GAC modified with HDTMA-Cl by surfactant loading at ~189 mmol/kg. All oxyanions salts were used as received and dissolved in reagent grade water (18 $M\Omega\ cm^{-1}$ from a NANO pure water system; Barnstead) with a 0.005 M $CaCl_2$ matrix. Batch sorption experiments were carried out using a 1:4 mass to volume ratio in 40-mL VOA vials. Initial oxyanion concentrations ranged from 0.03 to 120 mM. The samples were equilibrated for 48 h on a Glas-Col rotator set at 30 rpm. After 48 h, the vials were centrifuged (Jouan CR4-22 Centrifuge) for 10 min at ~1700×*g* and 20 °C. Clear supernatant was then decanted into 20-mL scintillation vials for overnight storage (~14 h) to facilitate settling out of residual particulate matter. Sorbed concentrations for each oxyanion were calculated by difference between initial and equilibrium solution concentrations.

2.3.4. Alcohol tracers sorption on SM-SI-GAC

Alcohols evaluated as candidates for "resident tracers" for PFM applications were: methanol (MEOH); ethanol (ETOH); *iso*-propanol (IPA); *tert*-butanol (TBA); and 2,4-dimethyl-3-pentanol (2,4DMP). These alcohols have been previously used as resident tracers in both laboratory (Hatfield et al., 2004) and field testing of PFMs (Annable et al., 2005; Basu et al., 2006).

Batch experiments were conducted to measure alcohol tracer sorption on SM-SI-GAC. The concentration range of each of the alcohols was 4 to 1900 mg/L. All solutions were prepared in DI water with 0.005 M $CaCl_2$ as a background electrolyte. A known amount of SM-SI-GAC (4 to 4.5 g) and 10 mL of an aqueous alcohol tracer solution were placed in a pre-weighed 40-mL VOA vial and sealed with a Teflon-lined screw-cap. The vials were then rotated for 24 h at 25 °C on a Glas-Col rotator. After allowing the GAC in the vials to settle for 24 h, the clear supernatant was sampled for analyses using a gas chromatograph (GC) (see Section 2.6). Sorbed amount of the alcohol tracers was estimated by the difference between initial and final supernatant concentrations.

2.3.5. Sorption data analysis

Isotherms for sorption of the oxyanions, HDTMA and bromide on modified and unmodified GACs were fitted to the Langmuir isotherm model:

$$C_s = \frac{C_{\max} k_L C_w}{1 + k_L C_w} \tag{1}$$

and/or the Freundlich model,

$$C_s = K_F C_w^N \tag{2}$$

where C_s is the sorbed perchlorate concentration at equilibrium (mmol/kg), $C_{\max}$ is the maximum sorption capacity (mmol/kg), C_w is the equilibrium aqueous concentration of perchlorate (mmol/L), k_L is the Langmuir coefficient (L/mmol), which represents the affinity of the sorbate to the sorption sites; K_F is the Freundlich sorption constant ($mmol^{1-N}\ L^N\ kg^{-1}$), and N is an empirical constant, with $0<N<1$ representing nonlinear isotherms. With $N=1$ for linear isotherms, K_F is the sorption coefficient, K_d (mL/g).

2.4. Oxyanion flux measurements in laboratory flow chambers

Laboratory experiments in flow chambers were conducted to evaluate HDTMA-modified GAC performance as a PFM sorbent for measuring groundwater and perchlorate and chromate fluxes. Experimental methods used were similar to those described by Hatfield et al. (2001). Commercial-grade (Quikerete, Atlanta, GA) medium sand packed in a rectangular flow chambers was used as the analog of a confined, homogeneous aquifer for these experiments. A plastic tub was used for chromate experiments (30 × 30 × 19 cm in length, height, and width, respectively) and a larger glass aquarium tank was used for the perchlorate experiments (75 × 30 × 30 cm in length, width, and height, respectively). In both chambers, ~ 5-cm long section on both ends was packed with gravel (> 10 mesh; Quikerete, Atlanta, GA), and stainless screen implants (AT-86-SW12; Geoprobe Systems, Salinas, KS) were installed for injection and extraction of fluids. The chamber was packed with sand (to a height of 15 cm for chromate; 12.5 cm for perchlorate), and a 10-cm layer of bentonite clay (Geoprobe system ®, Salina Kansas) capped the sand and gravel. PVC slotted well (one 2.54 cm diameter well for chromate; two 5-cm diameter wells for perchlorate) was placed near the middle of the flow chamber (~ 15 cm from the outlet end for chromate; ~ 35 cm from outlet for perchlorate). Constant heads were maintained at the inlet and outlet ends to achieve steady water flow and an imposed Darcy flux (q_0) of 9.1 cm/day for chromate, and 9.6 cm/day for perchlorate. Throughout the experiments, the inlet solution concentration was maintained at 25 mg/L for chromate, and at 78 mg/L for perchlorate. Thus, the imposed contaminant flux (J_0) for chromate was 2.3 g/m^2/day, and 7.5 g/m^2/day for perchlorate flux. PFMs packed with SM-GAC (chromate) or SM-SI-GAC (perchlorate) were deployed in the PVC wells for a specific time period (97 and 138 h for chromate; 275 h for perchlorate) before recovering the PFMs, and sampling the sorbent for quantifying the sorbed oxyanions and remaining tracer alcohols (see Section 2.6). These data were used to estimate groundwater and oxyanion fluxes (q_D and J_D) as described in Hatfield et al. (2004), and compared with the imposed fluxes (q_0 and J_0).

2.5. Field-scale evaluation of SM-SI-GAC

2.5.1. Site description

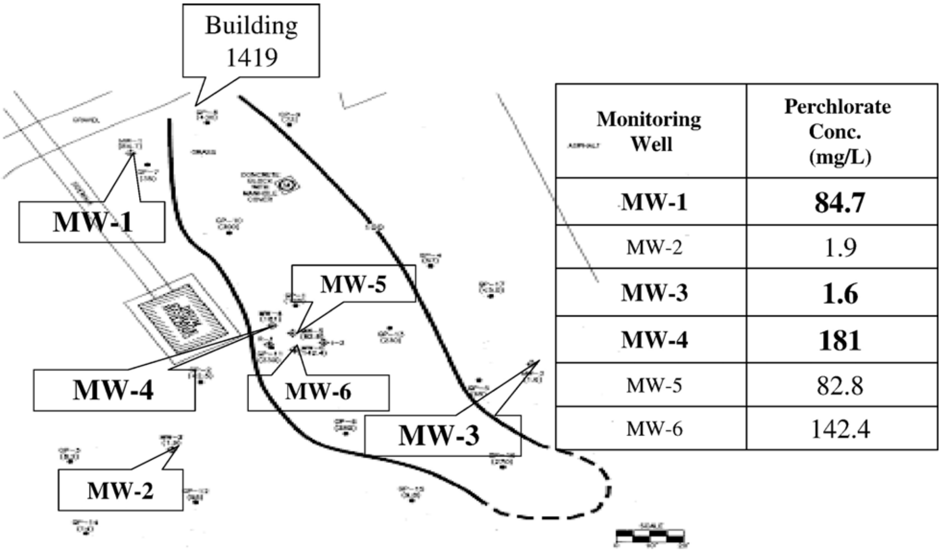
The perchlorate contaminated site is located at Indian Head, Maryland. The site is on an active Navy base, the Indian Head Division (IHDIV) of the Naval Surface Warfare Center (NSWC), located on a 3500-acre peninsula surrounded by the Potomac River and the Mattawoman Creek. Residual solid propellants and exhausted devices containing ammonium perchlorate were cleaned in a “Hog Out” facility, located in Building 1419 Wastewater was discharged from 1982 to 1994 at a permitted facility, under the National Pollution Discharge Elimination System (NPDES), but since 1995 the waste water has been recycled within Building 1419 (Cramer et al., 2004). The wastewater disposal/transfer and cleaning activities in the Hog Out facility caused perchlorate contamination of the shallow aquifer. Cramer et al. (2004) conducted a site investigation as a prelude to an in-situ perchlorate bioremediation study in an area southeast of Building 1419, and the following summary is based on the data from that report.

The site geology comprises of fill material (top 1.2 m), and sandy silt to clayey silt with fine-grained sand seams to a depth of 5 m. A continuous, 30–50 cm thick sand–gravel layer is found at the 5-m depth, underlain by a confining clay layer (likely the Potomac Group) that extends at least to 7 m depth (Cramer et al., 2004). At the time of PFM deployments the water table was at ~1.2 m below ground surface (bgs), but in this shallow, unconfined aquifer can rise and fall by ~1 m in response to recharge events, especially during the spring and summer seasons. Saturated hydraulic conductivity (K_s), measured using pump and slug tests in monitoring wells MW4, MW5, and MW6, ranged from 5 to 20 m/day (Cramer et al., 2004). Groundwater flows in the south–southeast direction towards the Mattawoman Creek, a tributary of the Chesapeake Bay, located at ~100 m from the suspected source area (Hog Out building).

Cramer et al. (2004) sampled groundwater from 17 Geoprobe borings and 6 monitoring wells, and analyzed for perchlorate, nitrate, sulfate, pH and dissolved oxygen (DO). Groundwater samples taken from the monitoring wells were also analyzed for perchlorate, pH and DO (Cramer et al., 2004). Groundwater pH ranged from 4.2 to 5.6, DO concentrations ranged from ~1 to 6.6 mg/L, the average redox potential was 0.91 mV, while perchlorate concentrations ranged from 1.6 to 430 mg/L within the plume (Cramer et al., 2004). The spatial extent of the perchlorate plume, as delineated by Cramer et al. (2004) using the 100 mg/L perchlorate concentration contour as the outer boundary, is shown in Fig. 1.

2.5.2. Groundwater and perchlorate flux measurements

Three existing wells, MW1, MW3, and MW4, were selected for PFM deployments; locations of these and three other wells are shown in Fig. 1, along with representative perchlorate concentrations detected in groundwater samples collected in early February 2002 (Cramer et al., 2004). The wells were constructed according to ASTM: D-1586 protocols using 2-inch i.d., 10-ft PVC screens (0.010-inch slots) and Schedule 40 PVC risers. The bottom of the screens was set about 30-cm into the confining clay layer and a bentonite plug was placed above the sand pack to prevent surface water flowing into the well screen (Cramer et al., 2004).



Monitoring Well	Perchlorate Conc. (mg/L)
MW-1	**84.7**
MW-2	1.9
MW-3	**1.6**
MW-4	**181**
MW-5	82.8
MW-6	142.4

Fig. 1. Perchlorate plume distribution (adapted from Cramer et al., 2004) and location of three monitoring wells (MW1, MW3, and MW4) used for PFM deployments at the Indian Head, Maryland site. Perchlorate concentrations in these and three other wells (MW2, MW5, and MW6), as measured in February 2002 by Cramer et al. (2004), are shown in the inset table. The line is the plume boundary defined by the 100 mg/L perchlorate concentration contour. The scale shown in the figure is 20 feet (~7 m).

Two sets of flux measurements were made; an initial short-term PFM deployment for 21 days (Nov. 20, 2004 to Dec. 13, 2004), and a second for a longer term of 44 days (Dec. 13, 2004 to Jan. 26, 2005). For both deployments, PFMs were pre-packed in the laboratory, secured in large wooden crates containing frozen blue ice, and transported to the site by van. Two 150-cm long PFMs were deployed in each well to cover the screen interval of ~3 m (10 feet). In general, the protocols for constructing PFMs, and the techniques for their field deployment and retrieval, were similar to those outlined in previous field studies (see Annable et al., 2005; Basu et al., 2006).

For both PFM deployments, the sampling protocol was as follows. A retrieved PFM sock was cut into 30-cm sections, homogenized in a plastic bowl and 10 g of wet SM-SI-GAC was then transferred into separate 40-mL VOA vials containing 20 mL of IBA for extraction of alcohol tracers. For perchlorate extraction, the remaining SM-SI-GAC from each homogenized section was transferred into plastic Ziploc bags. In addition, for the second deployment, both PFMs in MW1 and the bottom PFM in MW4 were sub-sampled at a higher resolution (5-cm sections) to provide a more detailed characterization of the vertical distribution of groundwater and contaminant fluxes within the respective screened intervals. All other PFM socks for the second deployment set were sampled at 30-cm intervals. All samples were stored in coolers packed with frozen blue ice and shipped back to the laboratory for extraction and analyses.

2.6. Extraction and analytical methods

2.6.1. Extraction methods

Extraction of the GAC samples and analysis for the alcohol tracers remaining on PFM sorbents (SM-GAC or SM-SI-GAC) was completed using protocols similar to those described by Annable et al. (2005) and Basu et al. (2006). For the alcohol tracer extraction, the 40-mL VOA vials containing field samples of SM-SI-GAC were rotated for 24 h on a Glas-Col rotator and then allowed to settle refrigerated for a further 24 h. A sample of the clear supernatant was taken for GC analysis to determine the concentrations of the alcohol tracers (see below). These tracer concentrations, expressed as a ratio of the initial amounts loaded on the PFM sorbent, were used to estimate the groundwater fluxes (q_D), as described by Hatfield et al. (2004) and Annable et al. (2005).

For extraction of the perchlorate field samples, 1.5 g of wet SM-SI-GAC was transferred into pre-weighed 40-mL VOA vials. A volume (~40 mL) of hot (~95 °C) 1 M KNO_3 aqueous solution was added and the vial was sealed with a Teflon-lined screw-cap. The vials were re-weighed and gently shaken (to minimize breakdown of the GAC particles) for 5 min. About 35 mL of supernatant quantified gravimetrically was removed and ~20 mL of additional hot KNO_3 solution was added for the second extraction. Extracting solution was diluted (1:200 ratio) using DI water to minimize IC analytical interferences due to the high nitrate concentration. Total extracted mass was obtained by summation of extracted oxyanion mass at each extraction stage. In control studies, the extraction efficiency was determined as the ratio of total oxyanion mass extracted (sum of two extractions) and the total oxyanion mass applied.

For laboratory experiments with perchlorate, a 10 g (wet) sample of GAC was extracted, first with 40 mL and then with 20 mL, hot (90–98 °C) 1 M KNO_3. The vials were gently shaken for ~5 min to minimize breakdown of the GAC particles. For chromate, 2 g of wet SM-GAC was extracted with 40 mL of 0.1 M KNO_3 solution. Vials were rotated for 48 h on a Glas-Col Rotator set at 30 rpm. An aliquot of supernatant from each extraction protocol (perchlorate, chromate, and selenate) was decanted into separate 40-mL VOA vials and allowed to cool to room temperature before dilution (1:200) in DI water. Extracts were stored refrigerated until Ion Chromatography analysis (see below). QA/QC controls of known concentrations of contaminants were extracted along with each batch of laboratory and/or field samples. Extracted blanks were also included to monitor for other potential background interferences. Extraction efficiencies ranged between 70% and 90%.

2.6.2. Analytical methods

Contaminant analysis was performed using a Dionex DX600 Ion Chromatograph, equipped with an ECD ElectroChemical Detector in Conductivity Mode, an AG40 Potassium Hydroxide (KOH) Eluent Generator, AS50 solvent pump and an AS50 Autosampler. Perchlorate separation was accomplished on a guard column (Ion Pac 4 × 50 mm AG16) in tandem with an analytical column (Ion Pac 4 × 250 mm AS16). Analysis for chromate and selenate was carried out on an IonPac 4 × 50 mm AG11 guard column connected in tandem with an IonPac 4 × 250 mm AS11 analytical column. An external water suppression mode of the ASRS Ultra II Suppressor was used to counter the high potassium nitrate matrix (0.005 M, post dilution) in the sample extracts, and to provide an instrument working detection limit of 6 µg/L for perchlorate, and 10 µg/L for chromate and selenate. Eluent concentrations were 35 mM KOH for perchlorate and 5 to 10 mM KOH for chromate and selenate, with respective flow rates of 1.2 mL/min. To meet low level detection limits dictated by necessary method dilution factors, a 1-mL sample loop was used to enable a sample loading capacity of 990 µL on-column. High KNO_3 concentration in the sample extracts tended to stress the analytical columns and ASRS Suppressor after approximately 150 samples. The IC required cleaning/rinsing/regeneration more frequently to maintain a standard instrument background operating condition of 2 to 3 µS (micro Siemens).

Alcohol tracer analysis was completed on a Varian 3800 CX Gas Chromatograph, equipped with a Flame Ionization Detector (FID). Compound separation was accomplished on a J&W Scientific DB624 column (30 m long; 0.53 mm i.d., 3 μm film thickness) with a temperature program initiating at 40 °C, held for 6 min, ramped to 235 °C at 40 °C per minute, and held for a final 2 min period. Detector and injection port temperatures were held at 235 °C and 230 °C, respectively. A 1-μL aliquot of the *iso*-butanol extracts was injected in split-less mode for a 0.25 min sampling time. Detection limit for all alcohol tracers was 1 mg/L.

A Shimadzu VP-HPLC (High Pressure Liquid Chromatography) system equipped with an ultraviolet (UV) detector (wavelength set to 254 nm) and a Nucleosil CN (Alltech Co., 150 mm long; 4.6 mm i.d.) column was used to analyze for HDTMA. A mobile phase of 5 mM *p*-toluenesulfonate and methanol (45:55, v/v) was set at a flow rate of 1 mL/min. HDTMA eluted at 3.5 min, similar to that reported by Li and Bowman (1997). HDTMA detection limit was 28 mg/L. Bromide was analyzed by Shimadzu HPLC using UV detection and a wavelength set at 210 nm. An Ion Pac AG14 guard column (50 mm long; 4 mm i.d.) in tandem with an IonPac AS14 analytical column (250 mm long; 4 mm i.d.) was used for compound separation. The eluent was 0.02 M sodium borate with a detection limit of 5 μg/L.

3. Results and discussion

3.1. HDTMA and bromide sorption on SI-GAC and GAC

Sorption of HDTMA-Br on SI-GAC and GAC was investigated to assess the generation and stability of AEC due to the surfactant modification. Batch isotherms for sorption of $HDTMA^+$ and Br^- (counter ion) by SI-GAC and GAC (Fig. 2) were fitted to Langmuir sorption model (Eq. (1)) to estimate sorption maxima (C_{max}, mmol/kg) and sorption affinities (k_L, L/mmol) for $HDTMA^+$. The C_{max} for $HDTMA^+$ sorption by SI-GAC was 624 ± 38 mmol/kg, contrasted to 403 ± 23 mmol/kg for sorption on GAC. This indicates that SM-SI-GAC can produce a larger AEC than SM-GAC. Sorption affinity parameter, k_L, was 5.7 ± 1.8 L/mol and 9.8 ± 3.7 L/mol, respectively, for SI-GAC and GAC. These values indicate that $HDTMA^+$ sorption is more favorable than desorption, and suggests the stable nature of the sorbed HDTMA on the GACs.

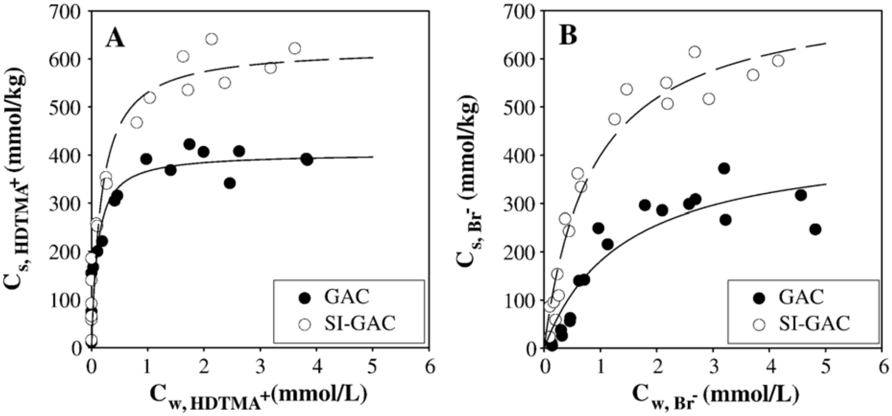


Fig. 2. (A) Isotherms for sorption of $HDTMA^+$ by GAC and SI-GAC. (B) Isotherms for sorption of Br^- as a counter ion by GAC and SI-GAC. Solid lines are Langmuir isotherm fits to the measured data.

$HDTMA^+$ is expected to be adsorbed on GACs predominantly by hydrophobic interactions between the hexadecyl tail group and the surface of GACs. The quaternary amine groups should be oriented out into the bulk aqueous solution and interacting with anions such as Br^- and the oxyanions. Thus, if Br^- sorbs as a counter ion on the quaternary amine head of $HDTMA^+$, the sorption characteristics of Br^- would reflect the configuration of the surfactant sorbed on the GAC. Fitted values of C_{max} determined from Br^- sorption isotherms (Fig. 2B) were 739±45 mmol/kg (SI-GAC) and 435±59 mmol/kg (GAC), and the corresponding k_L values were 1.2±0.2 L/mol (SI-GAC) and 0.71±0.3 L/mol (GAC). Note that sorption maxima for $HDTMA^+$ and Br^- are similar, suggesting that Br^- is the counter ion for the sorbed $HDTMA^+$. Similar trends in Br^- and $HDTMA^+$ sorption isotherms support the case for a monolayer configuration of HDTMA sorbed on SI-GAC.

3.2. Oxyanion and alcohol tracer sorption on GACs

3.2.1. Perchlorate sorption on GAC

Nonlinear isotherms for perchlorate sorption, measured for SI-GAC modified with different loading rates of HDTMA-Br (0, 51, 103 and 285 mmol/kg), were fitted to the Freundlich model (Eq. (2)) with $R^2 > 0.93$ (Fig. 3A; Table 2). The increase in K_F for HDTMA sorption was linearly proportional to the nominal surfactant loading at the two lower loading rates (51 and 103 mmol/kg), but became distinctly nonlinear, appearing to reach a plateau at the higher loading rate (285 mmol/kg) (Fig. 3B). Note that unmodified SI-GAC had sorption maxima of ~100 mmol/kg and ~10 mmol/kg, respectively, for perchlorate and chromate. Selenate was not sorbed by either GAC or SI-GAC to a measurable level (data not shown). The total AEC for the modified GAC and SI-GAC would be the sum of the background AEC plus that generated by sorption of HDTMA.

The data in Fig. 3B and Table 1 suggest that HDTMA loading rates of 51 and 103 mmol/kg are more effective in generating AEC accessible to perchlorate. At higher surfactant loading rates (~285 mmol/kg), however, efficiency of the quaternary amine sites might have decreased by limited accessibility to perchlorate. Thus, surfactant configuration on SI-GAC at the highest loading capacity is deemed sub-optimal in terms of generating additional AEC.

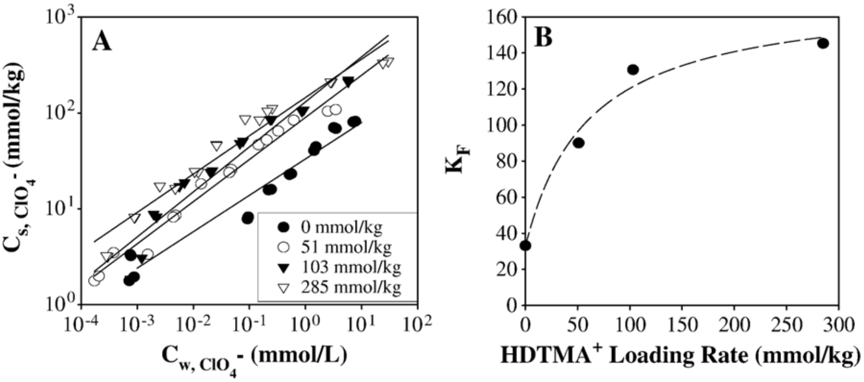


Fig. 3. (A) Freundlich isotherms for perchlorate sorption by SM-SI-GAC at different HDTMA loading rates; (B) dependence of the Freundlich isotherm parameter, K_F, for perchlorate sorption on SI-GAC modified with different HDTMA loading rates.

Table 1
Freundlich isotherm parameters for sorption of perchlorate on surfactant-modified SI-GAC for data shown in Fig. 3

Freundlich isotherm parameters	HDTMA loading rate (mmol/kg)			
	0	51	103	285
K_F	33	90	131	145
N	0.38	0.44	0.47	0.40
R^2	0.95	0.98	0.93	0.95

3.2.2. Oxyanion sorption on SM-GAC

Isotherms for sorption of the three oxyanions by SM-GAC were fitted to the Langmuir model (Fig. 4), with C_{max} of ~370 mmol/kg for perchlorate, 182 mmol/kg for chromate, and 40 mmol/kg for selenate. The k_L values ranged from 1.3 to 2 L/mmol. This ordering of C_{max} for the three oxyanions is reflective of the higher selectivity of the quaternary amine head group for perchlorate. The measured perchlorate C_{max} of ~370 mmol/kg contrasted to an expected maximum of ~290 mmol/kg suggests that either the actual HDTMA loading on the SM-GAC sample exceeded the target 189 mmol/kg loading rate, or that the perchlorate C_{max} for the unmodified GAC was underestimated.

3.2.3. Alcohol tracers sorption on modified GACs

Alcohol sorption isotherms were all linear, regardless of HDTMA loading on GAC, and SI-GAC had larger K_ds for alcohol sorption than GAC (Table 2). Given that both GAC and SI-GAC are produced using the same source material, it is unclear as to how the silver-impregnation treatment leads to increased sorption of both the cationic surfactant HDTMA (Fig. 2) and the alcohol tracers (Table 2). Linear correlation between alcohol K_d and octanol–water partition coefficients, K_{ow} (Fig. 5), shows that alcohol tracers were sorbed predominantly by a hydrophobic sorption mechanism and that the modification with HDTMA did not alter the linearity of the sorption isotherms. HDTMA modification did reduce K_d for all the alcohol tracers, by ~44% for SM-SI-GAC and by ~31% for SM-GAC. Note that ~40% of the pores in GAC are classified as being macro- and meso-pores (>20 Å diameter). The trimethylamine "head" of HDTMA has a diameter of ~7 Å, and the hexadecyl

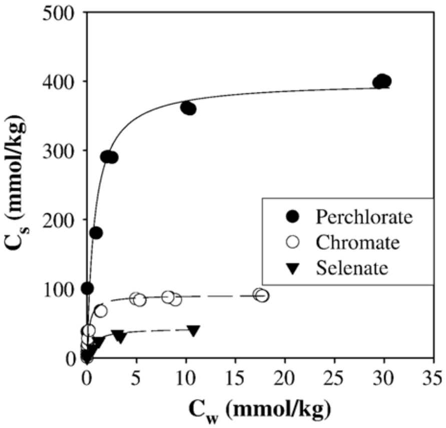


Fig. 4. Sorption of three oxyanions on surfactant-modified GAC (HDTMA-Cl surfactant loading was targeted at 189 mmol/kg). Solid lines are the Langmuir isotherm model fit to the data.

Table 2
Sorption coefficients, K_d (L/kg), for sorption of four alcohol tracers by unmodified and HDTMA-modified GACs

Linear sorption coefficient, K_d (L/kg)	MEOH[a]	ETOH	IPA	TBA
GAC	2.6 (0.1)[b]	18.1 (0.7)	109 (5)	228 (10)
SM-GAC	0.9 (0.1)	7 (0.4)	34.4 (2)	69.8 (4)
SI-GAC	2.7 (0.04)	25.6 (0.5)	198 (8)	509 (23)
SM-SI-GAC	1.6 (0.2)	14.4 (0.6)	92.7 (5)	221(12)

[a] MEOH: methanol; ETOH: ethanol; IPA: *iso*-propyl alcohol; TBA: *tert*-butyl alcohol.

[b] Values in parentheses are standard errors.

"tail" length is ~26 Å. It is likely that the HDTMA is excluded from the micro-pore regions (diameter <20 Å). Thus, the reduction in K_d (L/kg) for tracer sorption on SM-GAC and SM-SI-GAC is probably the result of attached surfactant blocking access to macro- and meso-pores of GAC.

3.3. Evaluation in laboratory flow chambers

3.3.1. Chromate fluxes

Flow chamber experiments to evaluate SM-GAC as the sorbent for measuring chromate fluxes were conducted at an imposed Darcy flux (q_0) of 9.1 cm/day, and with a constant inflow chromate concentration of 25 mg/L. This represents an imposed chromate flux (J_0) of 2.3 g/m^2/day. Darcy fluxes measured (q_D) using PFMs with SM-GAC as the sorbent were: 9.8 cm/day (97 h deployment) and 8.3 cm/h (138 hr deployment), yielding an average of 9.1 cm/day that matches the imposed water flux. This result suggests that the flow convergence factor ($\alpha = q_D/q_0$) was ~1 (for further discussion, see Hatfield et al., 2004; Annable et al., 2005; Klammler et al., in press). The measured chromate fluxes (J_D) for the two deployments were: 2.64 g/m^2/day (97 h deployment) and 1.96 g/m^2/day (138 h deployment), with an average of 2.3 g/m^2/day, in agreement with the imposed chromate flux (J_0).

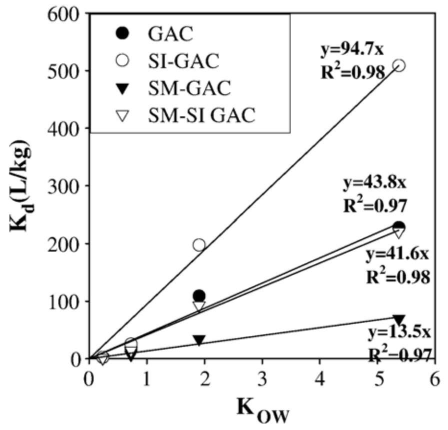


Fig. 5. Correlation of K_{ow} and K_d for alcohol sorption by unmodified and surfactant-modified GACs. Solid fitted lines are based on linear regression. The K_{ow} values are 0.23, 0.72, and 5.4 for methanol, ethanol, and *tert*-butyl alcohol, respectively.

3.3.2. Perchlorate fluxes

Flow chamber experiments to evaluate SM-SI-GAC as the PFM sorbent were conducted with an influent perchlorate concentration of 78 mg/L, and a q_0 of 9.6 cm/day, with a corresponding J_0 of 7.5 g/m^2/day. PFM deployments yielded q_D estimate of 10.9 cm/day, suggesting that the flow convergence factor (α) in this case was 1.1. The estimated perchlorate flux (J_D) was 8.7 g/m^2/day. After correcting for flow convergence ($J_0=J_D/\alpha$), the measured perchlorate flux is 7.9 g/m^2/day, close to the imposed perchlorate flux.

3.4. Field-scale test of SM-SI-GAC

3.4.1. Groundwater flux measurements

The average groundwater fluxes (q_D, cm/day) measured in three wells for the first and second PFM deployments were similar for MW1 (1.8 cm/day) and MW4 (2.8. and 2.1 cm/day), but were within a factor of two (7.6 and 4.9 cm/day) in MW3. Groundwater fluxes estimated using the depletion of two alcohol tracers during the PFM deployments compare well (Fig. 6), with a regression slope of 1.2 and most of the q_D values falling within a factor-of-two error bounds. Borehole dilution test (BHT) conducted in a well near MW4 yielded a groundwater flux estimate of 3.5 cm/day.

Using a geometric mean hydraulic conductivity (K_s) of 10 m/day, based on the slug and pump tests conducted by Cramer et al. (2004) at this site, and an average hydraulic gradient (i) of 0.017 measured during the period of PFM deployments, average Darcy flux ($q_0=K_s i$) is estimated to be ~17 cm/day. All of q_D values estimated from the two PFM deployments and the BHT are considerably smaller than this q_0 estimate. To match the PFM- or BHT-measured flux values with the estimated q_0 value, α values ranging from 0.1 to 0.5 would be required, suggesting that divergence of groundwater flow may have occurred around the PFMs. Independent estimates of α, based on approaches suggested by Hatfield et al. (2004) and Klammler et al. (in press), yield α values in the range of 1 to 1.5 for this site. Limited access to the site precluded the option of developing the wells prior to PFM deployments or to conduct follow up investigations. The wells

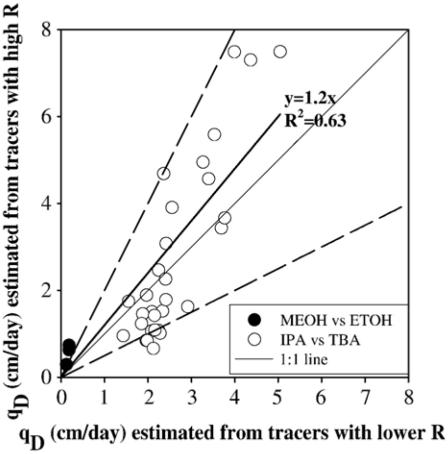


Fig. 6. Comparison of groundwater flux (q_D, cm/day) values estimated using the depletion of two alcohol tracers during PFM deployments at the Indian Head, MD site. Solid lines representing a 1:1 relationship and linear regression are shown along with dashed lines bounding a factor-of-two deviation from the 1:1 line.

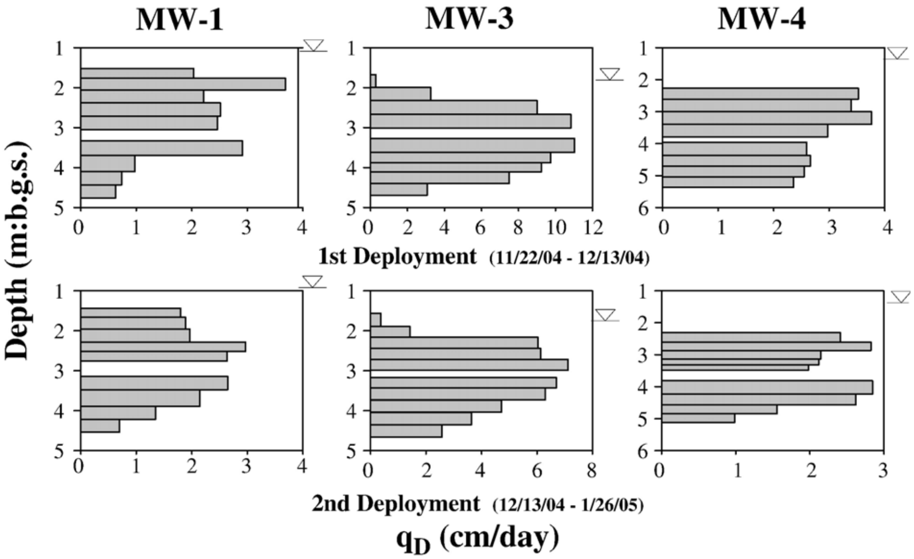


Fig. 7. Comparison of groundwater flux ($q_{D,}$) distributions measured using PFM deployments in MW1, MW3 and MW4 for two time periods at the Indian Head, MD site.

had not been developed since the Cramer et al. (2004) study and the well screens could have become clogged with silt, which would result in significant flow divergence ($\alpha < 1$). It should be recognized also that the q_0 estimates are subject to uncertainties from incorrect estimation of the hydraulic gradient (e.g., average value used instead of time-varying gradients during the period of PFM deployment) and possible errors associated with estimating K_s from pump and slug test data.

The depth-distribution of groundwater fluxes for the two PFM deployments was similar in the three wells, showing reproducibility of PFM measurements (Fig. 7). Groundwater fluxes (q_D) in monitoring wells for the two deployments seem to be quite uniform, except for the smaller fluxes at the bottom of this unconfined, shallow aquifer, perhaps reflecting the presence of the clay confining layer.

3.4.2. *Perchlorate flux measurements*

Depth-averaged perchlorate fluxes (J_D) for the first and second PFM deployments were: 1.7 and 1.4 g/m^2/day in MW1; 1.0 and 0.9 g/m^2/day in MW3; and 0.43 and 0.22 g/m^2/day in MW4, respectively. Perchlorate fluxes in MW1 and MW3 are of similar magnitude, while that in MW4 is lower by a factor of 4 to 6 (see Table 3). Note that even though MW1 is closer to the source zone compared to MW3, its location is outside the 100 mg/L plume boundary as delineated by Cramer et al. (2004) (see Fig. 1). Lower perchlorate fluxes in MW4 were not expected since this well is located within the perchlorate plume. However, this well is also within the area where an enhanced bioremediation study was conducted in 2002 and involved lactate injection in recirculation wells (Cramer et al., 2004), which may have imposed hydrologic changes (recirculation pumping) and biogeochemical alterations (lactate injection) that could still have a residual impact on the perchlorate flux measurements.

A comparison of the depth-distribution of perchlorate fluxes measured in the three wells, determined from two PFM deployments, is shown in Fig. 8, while groundwater flux (q_D) and perchlorate flux (J_D) distributions determined from two sampling resolutions (5 and 30 cm sections) are shown in Fig. 9. Measured perchlorate fluxes generally match well between the two deployments in MW1 and MW3, but not for MW4 (Fig. 8). High-resolution sampling of the two PFMs deployed in MW1 showed that perchlorate fluxes were larger near the water table (see Fig. 9) suggesting the possibility of a vadose zone source. Given that the source zone was from the result of perchlorate brine disposal near MW1, higher perchlorate fluxes were expected near the bottom of the well; however, this conclusion cannot be tested since previous work (Cramer et al., 2004) at this site did not include a detailed source-zone characterization.

For MW3, perchlorate fluxes estimated from PFM deployments were larger in the middle of aquifer compared at the top and bottom, similar to the trends in the vertical distribution of groundwater fluxes in this well. For the first deployment, higher perchlorate fluxes existed in the upper layers, while the lower layers had higher fluxes for the second deployment. These observations suggest that perchlorate fluxes in MW4 are more transient, perhaps as a result of the previous bioremediation study (Cramer et al., 2004).

3.4.3. Flux-averaged perchlorate concentrations

Observed groundwater and perchlorate fluxes were used to estimate flux-averaged concentrations (C_F) using:

$$C_F = \frac{\int J_i \cdot \mathrm{d}z}{\int q_i \mathrm{d}z} \tag{3}$$

where J_i and q_i are, respectively, the *local* values for perchlorate and groundwater fluxes corresponding to the ith depth increment of sampling by PFM, and the averaging is done over the entire length of the well screen interval. The resulting flux-average concentration, C_F, is comparable to the concentration measured in a groundwater sample taken using traditional methods (e.g., bailing, pumping).

Perchlorate concentrations in groundwater sampled on November 22, 2004, and also in February 2002 (by Cramer et al., 2004), are shown in Table 3 for comparison with the estimates based on two PFM deployments in three wells. Note that PFM estimates of C_F are averaged over the duration of the deployment (21 and 44 days) while the groundwater sampling provides a perchlorate concentration estimate at a specific time. Two successive PFM deployments produced

Table 3

Summary of depth-averaged groundwater fluxes (q_D)[a], perchlorate fluxes (J_D)[b], and flux-averaged perchlorate concentrations (C_F)[c] measured with two PFM deployments in three wells (MW1, MW3, and MW4) at the Indian Head, Maryland site

Method	Dates		MW1			MW3			MW4		
	Deployed	Retrieved	q_D	J_D	C_F	q_D	J_D	C_F	q_D	J_D	C_F
First PFM	November 22, 2004	December 13, 2004	1.8	1.7	94.1	7.6	1.0	12.9	2.8	0.44	15.4
Second PFM	December 13, 2004	January 26, 2005	1.8	1.4	79.1	4.9	1.1	21.7	2.1	0.23	10.9
Groundwater sampling	November 22, 2004				74.7			2.5			95.2
	February 5 and 6, 2002[d]				84.7			1.6			181

[a] q_D, PFM-measured, depth-averaged Darcy flux, cm/day.

[b] J_D, PFM-measured, depth-averaged perchlorate flux, g/m^2/day.

[c] C_F, Flux-averaged perchlorate concentrations, mg/L.

[d] As reported by Cramer et al. (2004).

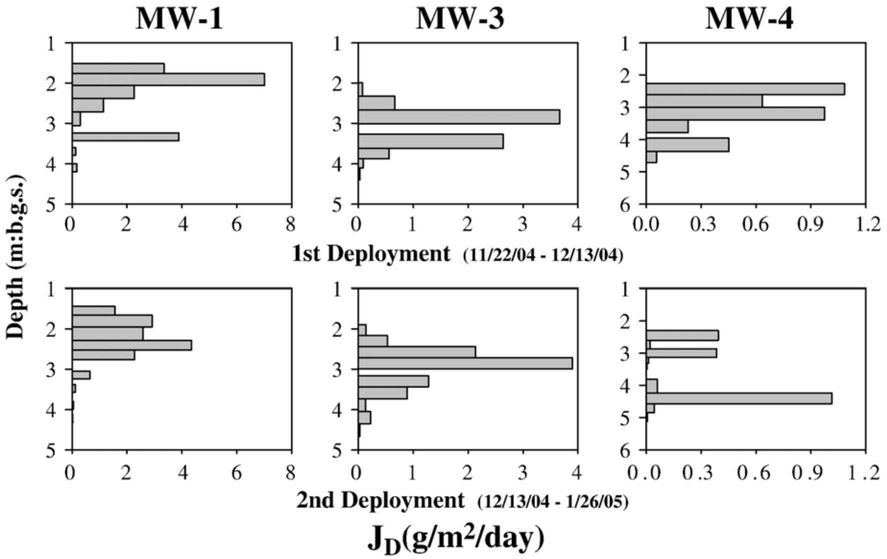


Fig. 8. Comparison of perchlorate flux (J_D) distributions measured using PFM deployments in MW1, MW3 and MW4 for two time periods at the Indian Head, MD site.

similar average groundwater and perchlorate flux values and yielded similar estimates of C_F values. However, perchlorate concentrations based on PFM deployments and groundwater sampling are in reasonable agreement in one well (MW1) but not in the other two wells (MW3 and MW4). C_F values estimated from PFM in MW4 are about an order-of-magnitude smaller than those based on groundwater sampling, while in MW3 PFM-based estimates of C_F are about an order of magnitude larger (Table 3). This result is at variance with the agreement found between the two methods under controlled conditions of the laboratory flow chambers (see Section 3.3).

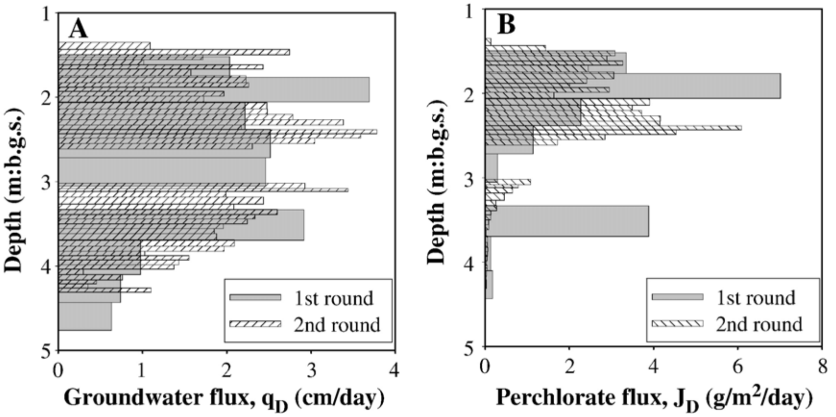


Fig. 9. Comparison of (A) groundwater flux, q_D, and (B) perchlorate flux, J_D, distributions determined from PMFs deployed in MW1, with standard sampling (30-cm sections) in the first PFM deployment and high-resolution sampling (5-cm sections) of PFMs for the second deployment.

Given the inconsistency of the results from three wells, systematic errors or bias do not offer an explanation. Note that the flux-averaged concentration is simply the ratio of the depth-averaged contaminant and groundwater fluxes ($C_F = J_D/q_D = J_0/q_0$), and as such flow convergence/divergence is not an issue for C_F estimation using PFM deployments. Geochemical factors, including the effects of other anions competing with perchlorate for sorption sites on the SM-SI-GAC, need to be explored in additional field work.

3.5. Extension to other anions and other modifiers

We reported here on the use of PFMs for measurement of oxyanion fluxes in laboratory and field experiments. The surfactant-modified GACs can also be used in PFM application to monitor fluxes of a number of other anions of environmental interest, such as various electron acceptors and donors (nitrate, sulfate, lactate, pyruvate, etc. at bioremediation sites), nutrients (nitrate, phosphate, etc. in agricultural settings), and other anionic contaminants (e.g., arsenate, borate, etc. at coal–ash sites). For example, K_d values for acetate and citrate sorption by SM-GAC, estimated from single-point adsorption measurements, were ~20 and 11 L/kg over an equilibrium concentration range of 0.1 to 0.3 mmol/L. The sorption isotherms for these and other organic acids are expected to be nonlinear (Langmuir type), and selectivity or sorption maxima have not been estimated; but, large K_d values do suggest that HDTMA-modified GAC can be used to estimate electron donor fluxes (e.g., lactate, acetate, citrate, and other organic acids resulting from biodegradation) at DNAPL source zones where lactate, ethanol, ethyl lactate or other organic substrates are injected to enhance reductive dehalogenation of chlorinated solvents (e.g., Fennell et al., 1997; Carr and Hughes, 1998; Rodriguez et al., 2004). Similarly, the surfactant-modified GACs can be used for *simultaneously* measuring the fluxes of groundwater, fuel hydrocarbon constituents (e.g., BTEX, TPH), and electron acceptors (e.g., nitrate, sulfate) to provide corroborative flux data in support of natural attenuation assessments at LNAPL sites.

Use of organic acids as resident tracers, instead of the methylated alcohols, to measure groundwater fluxes is also feasible, as shown in laboratory tests conducted with benzoate by Campbell et al. (2006). However, as discussed above, such organic acids can serve as electron donors for microbial consortia and thus may be readily degraded under field conditions, making them unsuitable as PFM tracers. But, fluorobenzoates may be ideal candidates as a suite of PFM resident tracers, and their use as reliable water tracers in soils and groundwater has already been demonstrated (Bowman and Gibbens, 1992; Benson and Bowman, 1994; Jaynes, 1994).

We used the cationic surfactant HDTMA as a modifier of GAC to produce sorbents with AEC enabling the measurement of oxyanion fluxes. Parette and Cannon (2005) have demonstrated that activated carbon modified with HDTMA and three other cationic surfactants (dicocodimethylammonium, chloride, tallowtrimethylammonium chloride, and cetylpyridinium chloride) can be an excellent sorbent for treatment of groundwater contaminated with perchlorate (at 75 μg/L); other anions present were sulfate and nitrate at ~30 μg/L. Appropriate selection of other modifiers and sorbents extends the possibility for the measurement of fluxes for other ionic contaminants. Recent efforts have demonstrated other modifications to zeolite and GAC. Iron oxide impregnation within GAC microporosity generated the sorption capacity for arsenic (Gu et al., 2005). Powdered activated carbon (PAC) was modified with cationic and anionic surfactants (Basar et al., 2003); surfactant modification changed the zeta potentials and generated sorption capacities for ions. Modification of activated coir pith carbon with $ZnCl_2$ enhanced sorption of molybdate (Namasivayam and Sangeetha, 2006). Natural zeolite, alumina and Canadian River Alluvium modified with three anionic surfactants (DOWFAX-8390; STEOL-

CS330; Aerosol-OT) and a cationic surfactant (HDTMA) were shown to have significant sorption capacity for nonpolar organic contaminants; HDTMA modification was reported to be more stable than the three anionic surfactants (Karapanagioti et al., 2005). Agricultural byproducts (corn husk, soybean shells, etc.) treated by cross-linking of dimethyloldihydroxyethylene urea (DMDHEU) and the quaternary amine, choline chloride, served as high-capacity and inexpensive anion exchange resins for removal of chromate, selenate, and arsenate from water (Wartelle and Marshall, 2005). This may offer yet another strategy for modifying GACs or zeolite to produce PFM sorbents.

4. Conclusions

1. Laboratory studies showed that modification of micro-porous, granular activated carbon (GAC) with a cationic surfactant, HDTMA, can generate a suitable sorbent for applications involving the Passive Flux Meter. The anion exchange capacity (AEC) of the modified sorbent can be adjusted with the loading rate of the surfactant, but a surfactant loading rate of about 150–200 mmol/kg appears to be optimal in producing maximum AEC on the GAC we used.
2. The modified GAC had significant sorption capacity for several oxyanions of environmental interest, and the Langmuir isotherm sorption maxima were in the following order: perchlorate >> chromate > selenate, consistent with their selectivity. Preliminary results suggest that the modified sorbent can also sorb other inorganic anions (e.g., nitrate, bromide) and organic acids (e.g., lactate, acetate, citrate).
3. For all methylated alcohol tracers, sorption isotherms were linear and SI-GAC had larger sorption K_d values than GAC. HDTMA-modification of SI-GAC reduced (~30–40%) tracer K_d values, possibly as a result of sorbed surfactant blocking tracer access to meso- and macro-pores (>20 Å).
4. Laboratory studies in flow chambers to evaluate the performance of the modified GAC sorbents for PFM applications were successful. PFM-measured water and oxyanion (perchlorate and chromate) fluxes matched those imposed during the study.
5. Performance of the modified GAC as a sorbent was examined in PFM deployments at a field site contaminated with perchlorate. Groundwater fluxes (q_D) and perchlorate fluxes (J_D) measured in three existing monitoring wells allowed the characterization of depth-distributions of q_D and J_D.
6. Depth-averaged q_D estimates from two sequential PFM deployments were consistent, varying by no more than a factor of two. However, groundwater fluxes (q_0) estimated using reported saturated hydraulic conductivities (K_s) and hydraulic gradients (i) were much larger than the depth-averaged q_D estimates from both PFM deployments. This suggests that flow divergence around the well screens could have occurred, possibly as a result of silt build up.
7. PFM-based flux-averaged perchlorate concentration ($C_F = J_D/q_D$) was in agreement with the perchlorate concentrations in groundwater samples taken from one well (MW1), but was either underestimated (MW4) or overestimated (MW3) in two other wells. Limited access to the site precluded identification of specific factors contributing to such variable results. These results suggest that comprehensive testing of PFM with surfactant-modified SI-GAC is necessary at other perchlorate sites and at field sites with other oxyanions.
8. GAC modification with other surfactants and extension of PFM applications are discussed for measuring fluxes of electron donors and acceptors in volatile organic contaminants (VOCs) plumes in groundwater at sites contaminated with fuel hydrocarbons or chlorinated solvents to

simultaneously characterize hydrologic and biogeochemical processes governing contaminant attenuation (natural or enhanced remediation).

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