TITLE: Expanded application of the Passive Flux Meter: In-situ Measurements of 1,4-dioxane, Sulfate, Cr(VI), and RDX

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Abstract

Passive flux meters (PFMs) have become invaluable tools for site characterization and evaluation of remediation performance at groundwater contaminated sites. To date, PFMs technology has been demonstrated in the field to measure low - to midrange hydrophobic contaminants (e.g., chlorinated ethenes, fuel hydrocarbons, perchlorate) and inorganic ions (e.g., uranium and nitrate). However, flux measurements of a low partitioning contaminant (e.g., 1,4-dioxane, hexahydro-1,3,5-trinitro-s-triazine (RDX)) and reactive ions-species (e.g., sulfate (SO$_4^{2-}$), Chromium(VI) (Cr(VI))) are still challenging because of their low retardation during transport and quick transformation under highly reducing conditions, respectively. This study comprises the first application of PFMs for the in-situ mass flux measurements of 1,4-Dioxane, RDX, Cr(VI) and SO$_4^{2-}$ reduction rates. Laboratory experiments were performed to model kinetic uptake rates and extraction efficiency for sorbent selections. Silver impregnated granular activated carbon (GAC) was selected for capture of 1,4-Dioxane and RDX, whereas Purolite 300A was selected for chromium and SO$_4^{2-}$. PFM field demonstrations measured 1,4-Dioxane fluxes ranging from 13.3 to 55.9 mg/m$^2$/day, an RDX flux of 4.9 mg/m$^2$/day, Cr(VI) fluxes ranging from 2.3 to 2.8 mg/m$^2$/day, and SO$_4^{2-}$ consumption rates ranging from 20 to 100 mg/L/day. These data suggest other low-partitioning contaminates and reactive ion-species could be monitored using the PFM.

1. Introduction

The freely dissolved concentrations of contaminants and metals in sediment pore water are critical measurements for assessing their fate and transport in groundwater systems. However, accurate measurement of metals and organic contaminates using
traditional groundwater sampling methods (e.g., low flow point sampling) is challenging due to difference in solubility and solid phase partitioning behavior. Concentrations of compounds in groundwater withdrawn from wells are controlled partly by the transfer of mass to flowing water from other phases: (1) mass sorbed to aquifer solids; and/or (2) mass trapped in immobile pockets. Transfers of masses can result in extracted groundwater concentrations being underestimated because this traditional method cannot account for vertical or horizontal spatial variability in the distribution, nor can it account for how concentrations may change over time due to seasonal variability (e.g., increased rainfall, tidal changes, etc.) [1]. However, passive sampling approaches have emerged as a promising method since they allow for both temporally and spatially averaged concentrations.

Diffusion-based samplers inhibit advective transport processes through porous casing material and are usually deployed for a limited exposure time due to variations in environmental conditions (e.g., water level, groundwater flow rates) [2]. Examples of diffusion-based samplers currently used include ceramic dosimeters, bag samplers, dialysis membrane samplers, polyethene samplers, peepers, polymer-based samplers [3-9]. However, such samplers have difficulty reaching equilibrium between the pore water and sorbent material due to mass transfer limitations through the depletion layer and the absence of active mixing [10-12]. Permeation-based passive samplers rely on groundwater flow to control advective transport processes as it passes through the sampler, while Passive Flux Meters have proven to be the only sampler that is able to effectively measure mass fluxes near source groundwater [2]. Additionally, PFM's and
the integral pump tests were reported to produce similar estimates of mass flux, demonstrating the accuracy of the device [13,14].

The standard PFM is a self-contained permeable sorbent-filled cartridge installed in wells and boreholes that provides simultaneous in-situ time-average measurement of mass flux ($J$) and water flux ($q_o$) with depth under ambient hydraulic gradients in saturated porous media [15,16]. The sorbent material (e.g., granular activated carbon (GAC), anionic exchange resin, etc.) is impregnated with water soluble tracers that elute at proportional groundwater flow rates. The sorbent material also serves to intercept and retain any aqueous phase compounds present in groundwater flowing through a well [17,18]. This design has been adapted and modified for measurements of $J$ and $q_o$ at fractured-rock sites, the hyporheic zone, streams, rivers and lakes [19-22]. To date, PFMs have been shown to measure chlorinated ethenes (e.g., Perchloroethene (PCE), Trichloroethene (TCE), cis-dichloroethene (cis-DCE), vinyl chloride (VC)), brominated ethenes (e.g., tetrabromoethane (TBA), tribromoethene (TBE)), methyl tert-butyl ether perchlorate, arsenic, chromate, chromium(VI), uranium, phosphate, and nitrogen [16,23-30]. However, this technology has not yet proven its ability to measure low partitioning compounds (e.g., Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 1,4-Dioxane) and reactive ion species in field sites with highly reducing conditions (e.g., sulfate ($SO_4^{2-}$), chromium).

1,4-dioxane are ubiquitous contaminants commonly found at current and former military installations and industrial sites. 1,4-dioxane is used as a stabilizer in chlorinated solvents, and it relative high solubility in water ($C_s = 4.31 \times 10^5 \text{ mg/L}$) produces rapid dissolution into groundwater and very low retardation during transport.
Thus, the release of 1,4-dioxane behaves similar to release of a non-reactive tracer from the DNAPL source zone, resulting in transport of 1,4-dioxane ahead of chlorinated ethenes. This can produce an extensive 1,4-dioxane plume disconnected from the source zone. 1,4-dioxane has a very low retardation factor, signifying the challenge of capturing it using sorbents typically used in PFMs. The partitioning between the GAC typically used in PFMs and 1,4-dioxane is estimated to have a retardation value (R) of about 10-20, which is based on a reported log $K_{\text{ow}}$ of -0.27 [34].

A field study was conducted at McClellan Air Force Base comparing rigid polypropylene (RPP) diffusion-based passive sampler concentrations of 1,4-Dioxane to low-flow purge grab sample concentrations [35]. RPP passive samplers detected 1,4-dioxane, but appeared to under predict aqueous phase concentrations in comparison to the low flow method [35]. To the best of the authors’ knowledge, permeation-based passive samplers for either RDX or 1,4-dioxane have not been reported in the literature.

RDX is a high energy explosive found at numerous military installation and artillery ranges [36]. RDX has been in production since World War Two (Urbanski). The U.S. EPA has classified RDX as a possible contaminant. RDX has a moderate solubility ($C_s = 37.5$ mg/L at pH 6.2 and $20^\circ$C) and a low affinity for carbon ($K_{OC} = 6.26$ to 42 L/kg), suggesting it is fairly mobile and difficult to capture from the aqueous phase [37,38]. However, several methods have been developed to detect RDX in groundwater systems. Jar aquifer tests, assessing RDX uptake into a polyethene diffusion-based passive sampler using different soils (e.g., sandy loam soil, silty loam soil, sand), have shown that organic carbon content impacts the uptake behavior and may not accurately reflect the amount of RDX present in the soil [39]. Polar organic chemical integrative
samplers (POCIS), a diffusion-based sampler, have recently been developed and deployed at underwater munitions sites and have detected concentrations of RDX ranging from 4.3 to 11.0 μg/L [40]. GAC has also shown to be a useful material for the removal of RDX from aqueous phase solutions [41-43].

The biological formation of iron-sulfide minerals has been shown to dramatically enhance rates of reductive dechlorination of chlorinated ethenes [44-51]. Factors that are important in the promotion of these biogeochemical transformations include SO$_4^{2-}$ concentration, hydraulic residence time, electron donor availability and presence of iron oxides [52,53]. The optimal combination of these factors promotes a high volumetric SO$_4^{2-}$ consumption rate and a high rate of reactive iron sulfide generation (Evans et al. 2014). However, few monitoring tools exist to quantify these in-situ transformation rates. Currently, biogeochemical reaction rates are monitored by measuring the groundwater concentration in suit microcosm, soil core analysis, or calorimetrically [33,54,55]. Although groundwater concentrations can provide an approximation of the rate, it often underestimates the rate [56]. Microcosms are often used to estimate biodegrading rates but are not representative of the environment since they are often manipulated in the lab [33,57,58]. No device currently exists to directly and spatially determine in-situ biogeochemical transformation rates.

Chromium, a wide spread toxic metal contaminant, has been used for industrial processes since 1816 [59]. Chromium (Cr(VI)) is relatively soluble, more toxic and highly unstable in a reducing environmental than trivalent chromium (Cr(III)) [60]. Beside monitoring aqueous phase concentration, several passive samplers have been developed to monitor Cr(VI). These include passive capillary samplers, suction
cup/zero tension lysimeters and NALGENE® polyethylene diffusion-based passive samplers [61,62]. The complex chemistry of Cr(VI) in groundwater makes interpretation of field based transport data difficult to understand, implying diffusion-based samplers may have high uncertainties associated with them [63]. Lysimeters and capillary passive samplers are more qualitative than quantitative, as they sample an undefined volume, do not provide flux data, and macroporous flow can cause mass transfer issues with the devices [62,64]. Depending on the environmental conditions, the NALGENE® passive sampler may only provide semi-quantitative results as equilibrium between the sampler and aqueous phase may never be reached, as has been previously described [10]. Campbell et al. (2006) conducted box-aquifer tests on the PFM and obtained average measurement errors for mass flux of Cr(VI) of 12%, suggesting this permeation-based passive sampler can overcome the limitation of the diffusion-based samplers as previously described. However, in-situ PFM field measurement of Cr(VI) has not yet been reported in the literature, to the best of our knowledge.

The PFM technology was expanded and demonstrated in both laboratory studies and in field trials to measure fluxes of RDX, Cr(VI), 1,4-Dioxane, and in-situ biogeochemistry transformation rates of $\text{SO}_4^{2-}$. Anionic exchange resin and granular activated carbon have been demonstrated to be effective at removing Cr(VI) and GAC, respectively, from water [24,41]. A multilayered-PFM (ml-PFM) of alternating layers of Purolite 300A and GAC were deployed at a DOD Contaminated nuclear site for post-remedial flux monitoring of Cr(VI) and RDX. Standard and modified versions of the PFM were assessed in laboratory batch and aquifer tests for capture of 1,4-Dioxane. The standard version performed well in laboratory studies and was deployed at three
different chloroethene contaminated sites undergoing remediation (confidential sites) to measure 1,4-dioxane mass fluxes. The first application, to the best of our knowledge, of a PFM using anionic exchange resin for measuring both $\text{SO}_4^{2-}$ reduction rates and water fluxes is presented here. Laboratory batch equilibrium studies and column studies were used to assess the sorbent materials ability to uptake $\text{SO}_4^{2-}$. The PFM was then deployed at Altus Air Force Base (AFB) to monitor biowalls remediation performance for removal of chlorinated solvents by assessing volumetric $\text{SO}_4^{2-}$ consumption rates.

2. Material and Methods

2.1 Passive Flux Meter Technology

The experimental basis, theoretical basis and field performance data validating the PFM have been previously described and the reader is referred to these for more detail [14-17]. Briefly, the PFM is a self-contained permeable active carbon cartage installed in wells and bore holes that provides simultaneous in situ time-averaged measurements of contaminant mass flux ($J_c$) and water flux ($q_o$) under ambient hydraulic gradients (Annable et al., 2005; Hatfield et al., 2004). The activated carbon serves to intercept and retain dissolved hydrophobic organic contaminants present in groundwater flow through the well. The activated carbon is also impregnated with known amounts of four water soluble tracers. These tracers are leached from the sorbent at rates proportional to the fluid flux.

After a specified period of exposure to groundwater flow, the PFM is removed from the well screen. Next, the sorbent is extracted to quantify the mass of all organic contaminants intercepted by the PFM and the remaining masses of all resident tracers. The contaminant masses are used to calculate time-averaged contaminant mass fluxes.
(C_f) or contaminant mass fluxes (J_c), while residual resident tracer masses are used to calculate time-averaged water flux. Depth variations of fluxes can be measured by vertically segmenting the exposed sorbent at specified depth intervals. Retardation factors for soluble tracer impregnated onto GAC are presented in Annable et al. (2005).

The cumulative, time-average Darcy flux, \( q_d \) (L\(^3\)/L\(^2\)/T), and the contaminant flux, \( J_d \) (M/L\(^2\)/T) are given by equations (1) and (2) [15-17]:

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

\[
J_d = \frac{1.67m_c}{\pi rb t} \quad (2)
\]

where \( r \) is the radius of the PFM cylinder, \( \theta \) is the water content in the PFM, \( R_d \) is the retardation factor of the resident water-soluble tracers on the sorbent, \( M_R \) is the relative mass if resident tracer remaining on the PFM sorbent at a particular well depth, \( t \) is the sampling time, \( m_c \) is the mass of the contaminant sorbed onto the tracer, \( b \) is the length of the sorbent matrix segment.

The PFM flux data can then be used to estimate the flux-averaged contaminant concentration, \( C_f \) (M/L\(^3\)), over the well screen interval/PFM sorbent section given by equation (3) (Basu et al., 2005):

\[
C_f = \frac{\int J_d dz}{\int q_d dz} \quad (3)
\]

\( C_f \) is independent of groundwater fluxes, meaning it is not subject to effects of flow convergence towards or divergence around the PFM. \( C_f \) represents a time averaged contaminant concentration estimate over the deployment period, whereas traditional groundwater sampling techniques yield an instantaneous contaminant concentration that is estimated only at the time the groundwater samples were collected [13,65].
2.2. Sorbent Materials

Numerous sorbents have been created and utilized for removal of both organic and inorganic compounds from wastewater and groundwater. Silver impregnated coconut-based 12x40 mesh GAC, Amberlite XAD16, Amberlite XAD4 and Superlite DAX8 were investigated as possible sorbent materials for capture of 1,4-dioxane. Coconut-based GAC was considered because GACs from pecan and walnut shells have shown higher levels of adsorption than other GACs [66,67]. In previous laboratories studies, Amberlite XAD16, Amberlite XAD4 and Superlite DAX8 were proven to be effective at removing aromatic carbon from water and wastewater effluent [66,68,69]. Batch-equilibrium studies were conducted on each sorbent material to determine the adsorption capacity. Those showing promise for capture of 1,4-Dioxane were subjected to column studies and box aquifer tests for further analysis.

GAC has been shown to effectively absorb RDX in column studies, pump and treat systems, and fluidized bed reactors to remove RDX from aqueous phase liquids despite its relatively high solubility and low affinity for organic carbon [41,70,71]. However, GAC has a finite adsorption capacity. GAC was only examined for extraction efficiency since previous literature studies have already proven its effectiveness at adsorption/desorption of RDX.

Both GAC and Purolite A300 were used as sorbent materials in the PFM to remove Cr(VI) from aqueous phase solutions. Cr(VI) occurs in the environment as either chromate (CrO$_4^{2-}$) or dichromate (Cr$_2$O$_7^{2-}$) anionic complex that are relatively mobile in soil [72]. GAC has been shown to effectively absorb Cr(VI) in batch-equilibrium studies and ex-situ filtration systems [73-79]. Purolite A300 has never been tested, to the best of
our knowledge, to remove Cr(VI) from aqueous solutions. However, Purolite A300 has been used to effectively remove nitrate (NO$_3^-$) from aqueous phase solutions, which has a weaker charge than Cr(VI) species [80,81]. Thus, it is likely that Cr(VI) species may be even more strongly sorbed to Purolite A300 since it has a more negative charge than NO$_3^-$. Screening extraction experiments (data not shown) showed recovery of Cr(VI) was possible from both GAC and Purolite A300, which has been described in Extraction and Analytical Procedures section of this paper.

Purolite A300 and 500A were assessed for the removal of SO$_4^{2-}$ from aqueous phase solutions. Purolite A300 was shown in both batch studies and column studies to effectively remove SO$_4^{2-}$ from aqueous phase solutions, suggesting it is a good candidate for sorbent selections [82]. Fix-bed experiments assessing the ability of Purolite 500A to remove SO$_4^{2-}$ from wastewater effluent showed that it had a loading capacity of 25 to 30 mg SO$_4^{2-}$/L, making this an excellent candidate for possible use as a sorbent material in the PFM [83]. Both Purolite A300 and A500 underwent batch equilibrium studies to determine adsorption capacity and column loading tests to estimate retardation factors and dynamic sorption capacities. Note, Table 1 shows a comparison of the resin properties used.

2.3 Extraction and Analytical Procedures

The deployment and retrieval of the PFMs and analyses of the silver-impregnated granular activated carbon (SI-GAC) sorbent were done following the protocol outlined in Hatfield et al. (2004). As part of the analysis, a pre-weighed amount of PFM-deployed GAC sample was briefly placed in 10 mL of extraction solution and allowed to rotate for up to 24 hours on a Glass-Col Rotator. 1,4-dioxane, chlorinated
ethenes, ethene and five “resident” tracers [methanol; ethanol; isopropyl alcohol; tert-butyl alcohol; and 2,4-dimethyl-3-pentanol] were extracted with dichloromethane and then analyzed using a gas chromatograph (GC) equipped with a flame ionization detector and auto sampler (Perkin-Elmer). Cr(VI) was extracted from sorbent material using 1 M sodium chloride (NaCl) solution and analyzed by UF/IFAS Analytical Service Laboratory (Gainesville, FL) using HPLC/ICP-MS. This extraction technique was found to give Cr(VI) recoveries of 87 ± 5% (data not shown). Cr(VI) ra RDX was extracted from sorbent material using acetonitrile and analyzed by the U.S. Department of Energy Pantex Plant Labs (Amarillo, Texas) using a high-performance liquid chromatography – ultraviolet (UV) detector. This extraction technique was found to give RDX recoveries of 14 ± 2% (data not shown). SO\textsubscript{4}^2− was extracted from sorbent material using 1 M NaCl solution and was analyzed using ion chromatographed as previously described by Cho et al. (2007) and Lee et al. (2007).

2.4 Batch Adsorption Isotherms and Recovery

Batch adsorption isotherms were developed for SO\textsubscript{4}^2− and 1,4-dixoane using method described elsewhere [15,24,28,30]. 2 g of Purolite A500 and Purolite A300 were added 30 mL SO\textsubscript{4}^2− solutions ranging from 0 to 8,200 mg/L. 0.1 to 10g of GAC and 0.1 to 5 grams of nonionic exchange resin (e.g., Purolite XAD16, Purolite XAD4, Superlite DAX8) were added to 1,4-dixoane solution of 1,030 mg/L. The mixtures were then rotated for a minimum of 24 hours and then filtered through a 0.45-μm glass filter. Sorbed contamination was recovered from drained resin using extraction solvents and rotated for 24 hours. Filtered and sorbent recovery solutions were analyzed using the methods as described in the Extraction and Analytical Procedures section. Note, batch
studies were not performed on Cr(VI) and RDX since previously mentioned literature studies showed GAC was a good sorbent for capture of these materials.

2.5 Column Studies

Column studies were only conducted for SO$_4^{2-}$ and 1,4-dioxane using Purolite A300 and GAC, respectively, as previously described [15,24,28,30]. As previously mentioned, column studies were not performed on RDX and Cr(VI) since previously discussed literature supported the use of GAC and anionic exchange resin as sorbent material in the PFM. Small glass columns (2.5 cm i.d. and 5 cm long, Kontes Co. Vineland, NJ) were wet-packed with GAC and Purolite A300. GAC packed columns were then flushed with a contaminant solution consisting of 65 mg/L 1,4-dioxane, 68 mg/L methylene chloride (CH$_2$Cl$_2$), 57 mg/L cis-DCE, and 36 mg/L methanol (CH$_3$OH) at a steady solution flow of 1.7 ml min$^{-1}$. CH$_2$Cl$_2$ CH$_3$OH, and cis-DCE served as controls for performance and to see how multiple contaminants may impact breakthrough times since 1,4-dixoane is rarely the only contaminant found at chlorinated compound contaminated sites [84]. The Purolite A300 packed column was flushed with 3000 mg/L SO$_4^{2-}$ solution at a steady solution flow of 0.5 ml min$^{-1}$. Effluent samples were analyzed for contaminants and tracers as described in the Extraction and Analytical Procedures.

2.6 Bench-scale aquifer testing of 1,4-Dioxane PFM

Bench-scale aquifer model experiments were conducted as previously described by Cho et al. (2007). A rectangular stainless-steel box (38 cm x 30.7 cm x 12 cm) was packed with commercial grade sand (Sunniland Corporation, Longwood, FL). One-cylinder PVC well screen (16 cm long, 3.2 cm inner diameter, 4.2 cm outer diameter) was placed upright at the center of the chamber [28]. Teflon tape was placed over the
top part of the well screen to minimize loss of 1,4-Dioxane and to create a screen well of 10 cm. The water table was set to a height of 10 cm [28]. Coarse gravel was packed at the injection and extraction ends to facilitate uniform flow through the model [28]. A 1-inch layer of bentonite clay was used to cover the sand to minimize contaminant loss from volatilization. A 4-L aspirator bottle (Kimax Co. Vineland, NJ) was used to contain a 1,4-dioxane solution and maintain a constant head [28]. The flushing experiments were conducted with an injection solution of 1.8 mg/L 1,4-dioxane.

The standard PFM was constructed using sewn fabric socks (10 cm long and 3.2 cm inner diameter) filled with GAC. Before packing, the GAC was pre-equilibrated with an aqueous solution of alcohol tracers consisting of methanol, ethanol, isopropyl alcohol (IPA), tert-butyl alcohol (TBA), and 2,4-dimethyl-3-pentanol (2,4-DMP) [15,28]. The PFM was packed as previously described by Cho et al., (2007). Briefly, a GAC-filled fabric sock was placed in the PVC packing tube [28]. Mechanical vibration was then used to compact the resin into place. During packing, the GAC was subsampled to measure the initial concentrations of resident tracers [28]. The PFM was then slipped into the model aquifer well screen [28]. Upon termination of the experiment, the model standard PFM was retrieved, homogenized, and then subsampled for 1,4-dioxane and tracer loss analysis as has been previously described [28]. Six PFMs were constructed and deployed in the model aquifer under flow rates ranging from 2.2 to 18 mL min\(^{-1}\).

2.7 Field Studies

2.7.1 RDX and Cr(VI) Measurements

A U.S. Department of Energy nuclear weapons facility (confidential site) located in the continental U.S. has been a storage site for both conventional and nuclear
weapons for the last 65 yr. Pre-1980s industrial waste disposal activates included on-site disposal of high explosive industrial waste water into unlined ditches. Runoff from these ditches into a perched aquifer recharging playa has caused contamination of the groundwater below. The aquifer has been contaminated with RDX, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (2,4-DNT), 1,2-dichloroethane (1,2-DCA), TCE, PCE and Cr(VI). The groundwater is approximately 90 m below the surface, 30 m above an uncontaminated drinking water source, and the saturated thickness of the contaminated aquifer is less than 4.5 m. The stated objective of the deployment at this site was to demonstrate the PFM technology and identify were fluxes of contaminants were greatest so future remediation efforts could be target to prevent migration of both RDX and Cr(VI) off site. Of these, considerable attention was focused on the high explosive RDX and Cr(VI) because they were the most widespread and prevalent at the site.

In-situ bioremediation downgradient of the suspected source zone was conducted from 2008 to 2016 to prevent migration of RDX and Cr(VI) off site through the stimulation of native microorganism. A total of five injections of lactic acid and soybean oil occurred with the most recent injection occurring in September 2016. After the most recent injection, eight PFMs were installed in wells (confidential) within, upgradient, and downgradient of the treatment zone. Each deployed PFM was constructed with alternating segments of GAC and Purolite A300. PFMs 1-5 were installed within the treatment zone (shown in Figure 1), PFM 6 was installed upgradient of the treatment zone, and both PFM 7 and 8 were installed downgradient of the treatment zone.
2.7.2 1,4-Dioxane Measurements

PFMs were deployed at 3 chlorinated solvent contaminated sites being remediated by a large U.S. based environmental remediation firm (confidential sites) that will be referred to as Site 1, Site 2, and Site 3. All sites had 1,4-dioxane as a priority contaminant for remediation. Site 1 is a former industrial site where chlorinated ethene was likely discharged from 3 above ground tanks. At Site 1, PFMs were deployed on August 5th, 2014 in four different wells and retrieved on August 8th, 2014. Contaminants also present at Site 1 are vinyl chloride (VC), trichloroethene (TCE), cis-1,2-dichloroethene, 1,1-dichloroethene (1,1-DCE), 1,1-dichloroethane (1,1-DCA). Site 2 is a former chemical plant that has been in operation since 1923 but was subsequently decommissioned. Contamination was determined to be from areas where drums, sludge, boiler ash and other wastes were landfilled or buried. At Site 2, PFMs were deployed February 2013 in 13 wells containing benzene, chloroform flux, and carbon tetrachloride (Figure 3-2). Site 3 is a former industrial facility contaminated with 1,1-DCA, cis-DCE, TCE, 1,2-dichloroethane (1,2-DCA), 1,1,1-trichloroethane (1,1,1-TCA). PFMs were deployed in September 2014 at Site 3.

2.7.3 Sulfate Measurements

PFMs were deployed at biowalls OU-1 (Figure 3) and SS017 (Figure 4) in Altus Air Force Base, Oklahoma in order to determine volumetric SO\(_4^{2-}\) consumption rates as part of a performance remediation study. The volumetric SO\(_4^{2-}\) consumption rate was calculated from SO\(_4^{2-}\) flux data using the following equation:

\[
R_{SO_4} = \frac{(F_{SO_4}^{upgradient} - F_{SO_4}^{biowall})}{W_{biowall}}
\]  

(4)
$R_{SO_4}$ is the volumetric $SO_4^{2-}$ consumption rate, $F_{SO_4}^{\text{upgradient}}$ is the $SO_4^{2-}$ flux in a well upgradient of the biowall, $F_{SO_4}^{\text{biowall}}$ is the $SO_4^{2-}$ flux in the biowall, and $W_{\text{biowall}}$ is the width of the biowall parallel to groundwater flow.

SS17 site is located in the southwest portion of Altus AFB and contains a VOC plume comprised mostly of TCE and reductive dechlorination products. Groundwater is characterized by high $SO_4^{2-}$ concentrations ranging from 1,000 to 2,000 milligrams per liter (mg/L). The biowall was installed in 2005 and material used for construction included 42% mulch, 32% sand, 15% gravel and 11% cotton gin waste materials. The section of the biowall where the PFMs were deployed (Part B for Reference) was spiked with magnetite at the time of construction to increase the iron content from 1,600 mg/kg to 120,000 m/kg to promote biogeochemical reduction of chlorinated ethenes present at the site. Emulsified vegetable oil (EVO) injections occurred in 2008 to promote $SO_4^{2-}$ reduction so that iron-sulfur cluster could be formed. PFMs were deployed upgradient of the biowall (Well BB04U) and in the wall (Well BB04W). PFMs were deployed in November 2011 and May 2012.

The OU1 site in the vicinity of Landfill 3 contains a TCE plume that has $SO_4^{2-}$ concentrations similar to SS17. The biowall was installed in 2002 and was constructed with 50% tree mulch, 10% composted cotton gin waste, and 40% river sand. The biowall was amended in 2011 with EVO, lactate, ferrous lactate and hematite. PFMs were deployed in upgradient wells (EPAU108, EPAUMP01, EPAU105) and in wall wells (EPA107, EPA106, EPA104). PFMs were deployed in May 2011 and October 2011.

3. Results

3.1 RDX and Cr(VI)
PFMs were deployed in September 2016 right after cessation of active biostimulation occurred. RDX was only detected in PFM 4 (Figure 5) with average mass flux of 4.9 mg/m²/day, which equates to a Cr of 174 μg/L. Groundwater samples taken just before deployment of PFM4 were in good agreement since an RDX concentration of 180 μg/L was measured, which is a 3.4% difference from the PFM Cr value. RDX was not detected in any of the other PFMs deployed, suggesting the PFM 4 is the only hotspot and may be undergoing degradation prior to leaving the site since it was not detected in any downgradient samples. Cr(VI) was detected in PFMs 4, 6 and 7, but not in PFMs 1, 2, 3, 5 and 8. Average Cr(VI) mass fluxes from PFM 4, 6, and 7, based on recovery of Cr(VI) from Purolite A300, were determined to be 2.3, 2.3 and 2.8 mg/m²/day (Figure 5). Average Cr(VI) mass fluxes from PFMs 4 and 7, based on recovery of Cr(VI) from GAC, were determined to be 1.0 and 0.77 mg/m²/day. Note, no Cr(VI) was detected off GAC samples from PFM 6. Groundwater samples, obtained prior to PFM deployment, were only available for PFM 4 and was determined to be 82 μg/L. PFM Cr values based on Purolite A300 and GAC were 83 and 38 μg/L, respectively, which are 1.2% and 74% differences from groundwater sample data. Thus, Purolite A300 appeared to perform better than GAC at the capture of Cr(VI) in aqueous phase environmental samples. Additionally, these data suggest that Cr(VI) fluxes are relatively stable both within and downgradient of the treatment zone, and Cr(VI) poses on ongoing risk at both leaving the site and contaminated the aquifer. Thus, more target injections in and around these wells may be needed to stimulate the bacteria necessary to reduce Cr(VI) to an insoluble form.

3.2 1,4-Dioxane
Adsorption capacity and recovery efficiency of GAC, XAD16, XAD 2 and DAX8 for 1,4-dioxane were evaluated. Adsorbed 1,4-dioxnae mass is shown as a function of the equilibrium aqueous 1,4-dioxane concentration (Figure 6). Adsorption capacity of each sorbent is assessed by fitting data with a Freundlich isotherm model [28,75]:

\[ C_s = K_f C_e^{1/n} \]

where \( C_s \) (M/M) is the equilibrium value of SO\(_4^{2-}\) mass absorbed per unit mass of sorbent, \( C_e \) (M/L\(^3\)) is the equilibrium 1,4-dioxnae concentration in the aqueous phase, \( K_f \) and \( n \) are empirical fitting parameters where \( n>1 \). The Freundlich isotherm model fit for GAC was determined to be \( K_f = 3.15 \) and \( n = 2.11 \) with a Nash-Sutcliffe model efficiency (E) coefficient of 0.99. The Freundlich isotherm model fit for XAD 16 was determined to be \( K_f = 0.50 \) and \( n = 2.37 \) with a \( E = 0.87 \). The Freundlich isotherm model fit for XAD 4 was determined to be \( K_f = 0.23 \) and \( n = 1.7 \) with a \( E = 0.99 \). No fit could be determined for DAX8. The observed sorption capacity for GAC for 1,4-dioxane (73 mg g\(^{-1}\) at 838 mg L\(^{-1}\) \( C_{eq} \)) was much higher than the other resins used in these batch test (8.8 mg g\(^{-1}\) at 862 mg L\(^{-1}\) \( C_{eq} \) for XAD 16; 12.3 mg g\(^{-1}\) at 822 mg L\(^{-1}\) \( C_{eq} \) for XAD 4).

1,4-dioxane flux measurement using the PFM is based on the cumulative 1,4-dioxane mass retained on the sorbent over the test period. However, solute loss over the test period can lead to significant errors in flux estimations [15,24,28,30]. The 1,4-dioxane breakthrough loss through the PFM was assessed by a multispecies column elution test conducted at steady water flow using GAC as a sorbent material (Figure 7). Retardation (R) values were determined using the following equation [15]:

\[ R = \frac{m_c}{\pi r^2 b A_{RC} \theta C_F} \]
where $m_c$ is the mass retained by the PFM, $r$ is the radius of the column [M/M], $b$ is the thickness of the column [L], $A_{RC}$ is the dimensionless fraction of sorptive matrix containing contaminants, $C_F$ is the flux-averaged concentration of the contaminant of the aqueous phase [M/L$^3$], and $\theta$ is the dimensionless volumetric water content of the sorptive matrix. $\theta$ for wet-packed GAC was determined to be 0.55. The bulk volume of the wet-pack GAC in the column, equaling $\pi r^2 b A_{RC}$, 25.3 cm$^3$. The amount of contaminant per gram of GAC passed through the column at initial breakthrough, 50% breakthrough, and 100% breakthrough and R values for each breakthrough are summarized in Table 2. The R values determined for 1,4-dioxane was 57 time higher than that estimated for methanol, 2 and 7 time lower than $\text{C}_2\text{H}_2\text{Cl}_2$ and cis-DCE, respectively, suggesting GAC is sufficient to retain the 1,4-dioxane over a typical PFM deployment and multiple contaminants in the aqueous phase did not significantly affect the capture of 1,4-dioxane during a typical deployment period. Additionally, the R values calculated on 50% breakthrough were used to estimate water fluxes from the PFM in the bench-scale aquifer model test discussed below.

A series of bench-scale aquifer model studies were conducted to evaluate the PFM for measuring simultaneous time-averaged water and 1,4-dioxane fluxes in porous media as previously described [15,28]. Flux-measurements were performed with a PFM deployed in a single screen well during each test. After deployment, PFM$s were sampled and data from the resulting samples were averaged and compared with applied water and solute flux as similarly described by Cho et al. (2007) and Hatfield et al. (2004). Figure 8A provides a comparison of measured actual versus measured cumulative water flux based on the ethanol tracer. A high correlation ($R^2 =0.99$)
between measured and true cumulated fluxes. Measured water fluxes averaged 6% higher than true values. Figure 8B compares the measured and true cumulative 1,4-dioxanes fluxes. A high correlation ($R = 0.96$) was obtained between measured and true cumulative contaminant fluxes. Measured fluxes averaged 8% greater than true values. These plots show that the standard PFM works well for measuring 1,4-dioxane flux while simultaneously measuring water flux at low concentrations of 1,4-dioxane. If breakthrough in the PFM had occurred then the measured 1,4-dioxane flux would be lower than the actual flux, however in this test the measured 1,4-dioxane flux was similar to the applied 1,4-dioxane mass flux.

PFMs were deployed at three different 1,4-dioxane contaminated sites (confidential sites) undergoing remediation monitoring by U.S. based environmental remediation services company (confidential client). PFMs were deployed at Site 1 in August 2014. 1,4-dioxane was measured in two of the four wells (Figure 9). Figure 9A shows the vertical distribution of 1,4-dioxane mass flux and volumetric water flux with 1,4-dioxane flux corresponding to increase with water flux. The resulting flux-averaged concentration for this well was 456 μg/L. This is 1824 times higher than the most conservative recommendation of 0.25 μg/L set by the state of New Hampshire. VC, 1,1-DCE, 1,1-DCA, cis-DCE and TCE were also simultaneously measured in the same wells where 1,4-dioxane was detected (Figure 9B). Traditional groundwater sampling data was not available to make comparisons with PFM derived $C_f$.

PFMs were deployed at Site 2 in February 2013. 1,4-dioxane was detected in 9 of the 13 wells with mass fluxes ranging from 1.2 to 295 mg/m$^2$/day (Figure 10). Figure 10A is similar to the one described for Site 1, and the resulting flux-averaged
concentration for this well was 2195 μg/L. This is 8780 times higher than the value recommended for safe drinking by the state of New Hampshire. The flux-averaged TCE and DCE concentration, estimated from the PFM results, were compared with groundwater data obtained in 2013-2014 (Table 3) and estimates ranged from 2 to 133 percent differences with all $C_f$ being much greater than traditional groundwater data. Basu et al., (2006) made similar comparisons and noted that $C_f$ estimation are likely to be more representative of in-situ contaminant concentration than transitional groundwater modeling samples. These PFM measurements suggest that contaminant levels are higher than may have been previously thought and that there could be a source of 1,4-dioxane upgradient or a DNAPL source zone that has not yet been discovered. Chloroform, carbon tetrachloride, and benzene were also detected at this site (Figure 10B).

PFMs were deployed at Site 3 in September 2014. 1,4-dixoane was detected in both wells (Figure 11) with average mass fluxes of 76 and 3 mg/m²/day. Figures 11A and B are similar to the ones described for Site 1 and Site 2 and the resulting flux-averaged concentration for this well was 68 and 599 μg/l, respectively, which are 275 and 2396 times higher than the safe drinking water standard suggested by New Hampshire, respectively. The profiles generally indicated increasing mass flux with depth which is consistent with a region with clean water recharge thus driving the 1,4-Dioxane plume deeper. 1,1-DCE, cis-DCE, 1,2-DCA, TCE, and 1,1,1-TCA were also simultaneously detected by PFMs in these wells (Figure 11C). However, 1,4-dioxane was much higher than the other contaminants, suggesting that a DNAPL source may be upstream and the many other chlorinated ethenes may eventually migrate in greater
concentrations to these wells. Traditional groundwater sampling data was not available to make comparisons with PFM derived $C_t$.

3.3 In-situ biogenic $SO_4^{2-}$ reduction rates

Equilibrium batch tests for selection of an appropriate sorbent were conducted using Purolite A500 and Purolite A300 (Figure 12). Adsorption capacity of each sorbent is assessed by fitting data with a Freundlich isotherm model as was previously described and done for 1,4-dioxane [28,75]. The Freundlich isotherm model fit for the Purolite A500 were $K_f = 7.65$, $n = 5.31$, and $E = 0.98$. The Freundlich isotherm model fit for the Purolite A500 acid form were $K_f = 7.10$, $n = 5.1$, and $E = 0.97$. The Freundlich isotherm model fit for the Purolite A300 were $K_f = 10.46$, $n = 5.31$, and the Nash-Sutcliffe model efficiency coefficient $E = \text{Both forms of Purolite A500 performed similarly, but Purolite A300 showed the strongest affinity of the sorbent for } SO_4^{2-}. \text{ Based on these data, Purolite A300 was used in column studies.}$

To assess the performance of Purolite A300 under dynamic conditions, 1D column tests were conducted. The column elution experiment generated resident chloride concentration data as a function of column pore volumes (PV) of eluted solution (Figure 13). The amount of contaminant per gram of Purolite A300 passed through the column at initial breakthrough, 50% breakthrough, and 100% breakthrough and $R$ values for each breakthrough are summarized in Table 4. These retardation values were estimated to range from 15 to 37, suggesting Purolite A300 is sufficient to entrap sulfate during the typical deployment of a PFM.

PFMs were constructed and deployed at Altus AFB. They were packed with alternating individual segments of Ag-GAC impregnated with water soluble tracers and
Purolite A300. The reason for the alternating layers was to test the individual capability of Purolite A300 to capture $\text{SO}_4^{2-}$ under field conditions. GAC data was used to estimate groundwater flux. The PFMs were deployed at Altus AFB for about 2-3 weeks between 2011 and 2012 to monitor biowall performance at two chloroethene contaminated sites. The individual PFM profiles were too numerous to display, but Figure 14 shows the vertical distribution of $\text{SO}_4^{2-}$ mass flux and volumetric water flux. Greater water flux results were observed with higher $\text{SO}_4^{2-}$ fluxes. These data suggest that contaminant fluxes varied through the sampling, suggesting that seasonal effect (e.g., rainfall) likely caused increases and decreases of $\text{SO}_4^{2-}$ flux at the site. However, these data show that $\text{SO}_4^{2-}$ mass fluxes can be measured in-situ. These data were used to calculate volumetric $\text{SO}_4^{2-}$ reduction rates as a performance measure of the biowall as an ongoing remediation project at Altus Air Force Base.

Figure 15 presents the relationships among VOC removal, sulfide generation, and $\text{SO}_4^{2-}$ consumption in the four biowall sections as previously described. Sulfide concentrations in the SS17 biowall were less than 10 mg/L (Figure 15A). Sulfide concentrations in the OU1 biowall sections prior to amendment ranged from 90 mg/L in the organic amended section and 260 mg/L in the organic/iron amended section, were more than ten-fold greater; they varied between 90 (organic-amended section) and 260 (organic/iron-amended section) mg/L. Sulfide concentrations in the OU1 unamended biowall section remained elevated, ranging from 140 to 200 mg/L. However, sulfide concentrations decreased in the OU1 amended biowall sections. Sulfide concentrations in the OU1 organic-amended and organic/iron-amended biowall sections decreased to minimum values of 13 and 1.6 mg/L, respectively (data not shown). Percent total molar
VOC removal was high in the SS17 biowall section throughout the study, demonstrated no discernible trends, and ranged from 93 to 100 percent (Figure 15B). VOC removal in the OU1 organic/iron-amended biowall section was also high with VOC increasing from 90-93% to 97-98%. VOC removals were initially low in the OU1 organic amended biowall but increased simultaneously with the decrease in sulfide concentrations. VOC removals were low in the OU1 unamended biowall section, which had consistently high sulfide concentrations. This data demonstrates a relationship between high sulfide concentration and an inhibition of VOC removal. This data also indicates that OU1 biowall amendment reduced sulfide concentrations, which facilitated VOC removal.

An unexpected observation is the high sulfide in the OU1 organic/iron-amended biowall section prior to amendment (260 mg/L) and the lack of significant inhibition of biotic reductive dechlorination (total VOC removal was 90 to 93 percent). A possible explanation is that biogeochemical transformation was occurring at a greater rate in this section relative to the other OU1 biowall sections prior to amendment. Nevertheless, amendment with organic/iron led to improved performance with respect to total VOC destruction, which increased to 97 to 98 percent.

The use of passive flux meters demonstrated that volumetric SO$_4^{2-}$ consumption in the biowalls was lower in the OU1 unamended biowall section relative to the other biowall sections (Figures 15C). This lower consumption rate correlated with lower VOC removal (Figure 15D). Electron donor limitation may partially explain the lower VOC removal. However, sulfide generation was still high in the unamended biowall, suggesting that a lack of electron donor was not completely limiting biological activity. While volumetric SO$_4^{2-}$ consumption was lower in the OU1 unamended biowall section,
it was not sufficiently low to preclude the observed generation of high sulfide concentrations. Thus, a combination of high sulfide concentrations and lower volumetric \( \text{SO}_4^{2-} \) consumption prevented biogeochemical transformation, complete biotic reductive dechlorination, and complete VOC removal in the OU1 unamended biowall section.

4. Discussion

This work, based on the results obtained from Cr(VI) and RDX standard PFMs deployed in the field, confirms the laboratory results discussed by Campbell et al. (2006) for measuring in-situ Cr(VI) flux. The field deployment of this PFM was able to sorb both RDX and Cr(VI) onto GAC, suggesting that competitive sorption does not undermine the ability of the PFM to capture and retain low partitioning target contaminants. Because RDX is an explosive and should not be allowed to accumulated to large quantities, caution must be taken during measurement. Although this work is preliminary for RDX, more work is needed to understand the sorption mechanism under different pH and geochemical conditions. Additionally, flux-averaged concentrations should be compared with aqueous phase concentrations to validate the measurement of the PFM. This demonstrates that more explosive and inorganic compounds can be detected using the standard PFM.

The laboratory experiments and the field demonstrations show that the PFM can effectively measure both water and 1,4-dioxane contaminant mass fluxes. These data suggest that other low partitioning compounds such as perfluorooctanesulfonic acid or ibuprofen could be better tracked in groundwater systems. Since 1-4 dioxane is predominantly associated with dilute plumes that are often detached from the original source zone, measurement of the flux distribution within the aquifer could become an
early detection system of further contamination and would allow for better identification of source zones in upgradient wells where 1,4-dioxane has been detected.

The biowalls at Altus AFB SS17 and OU1 provided a unique opportunity to evaluate monitoring tools for biogeochemical transformation. The SS17 biowall was demonstrated to be functioning with a biogeochemical transformation pattern based on a consistently high total molar VOC destruction without accumulation of reductive dechlorination and with a high $SO_4^{2-}$ consumption rate as determined by the passive flux meters. These results contrast to the low total molar VOC destruction observed in the unamended OU1 biowall section. Unlike the SS17 biowall, this biowall section had very low volumetric $SO_4^{2-}$ consumption rates. High dissolved sulfide concentrations also probably inhibited complete biotic reductive dechlorination of TCE to ethene. Thus, high dissolved sulfide concentration was an important indicator of ineffective biotic and biogeochemical transformation processes of VOC destruction. Injection of organics into the organic-amended OU1 biowall section resulted in activation of passivated iron oxides as shown by decreased dissolved sulfide concentrations even though volumetric $SO_4^{2-}$ consumption rates were high.

The PFM was demonstrated in the field to measure both water fluxes and biogeochemical transformation rates in porous media. Passive flux meters have the potential to fill the gap in measuring biogeochemical transformation rates of other electron acceptors in groundwater remediation systems. Quantifying biogeochemical transformation rates in groundwater systems is an essential step to further evaluating remediation performance. In the future, biogeochemical transportation rates, as obtained by the PFM, have the possibility of being incorporated into a transport model to
understand geochemical cycling in some systems. We anticipate further improvement in and increased use of passive flux meter approaches to advance conceptual models of biogeochemical cycling in groundwater systems undergoing active remediation. We demonstrated modifications which extended the PFM application from mass flux measurement to measurement of biogeochemical rates. Further applications will likely focus on measuring of other biogeochemical transformation rates such as Fe-reduction.

Overall, this study demonstrates the versatility of passive flux meter technology for monitoring biogeochemical rates, low partitioning contaminants (RDX and 1,4-dioxane) and toxic metals. Thus, this technology can be used to measure remedial performance and potentially quantify in-situ degradation/removal rates of both chemical and inorganic compounds.
Table 1. Comparison of sorbent material tested. Information was obtained for manufacture fact sheets, except for DAX8, which was determined for Sigma-Aldrich website available information.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Polymeric Structure</th>
<th>Appearance</th>
<th>Functional Group</th>
<th>Exchange Capacity (eq/L)</th>
<th>Ionic Form (as shipped)</th>
<th>Water Content (%)</th>
<th>Specific Gravity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-GAC</td>
<td>Activated carbon</td>
<td>Granular</td>
<td>Type I Quaternary Ammonium</td>
<td>1.15</td>
<td>Chloride</td>
<td>53-58</td>
<td>1.08</td>
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<tr>
<td>Purolite A500</td>
<td>Macroporous polystyrene crosslinked with divinylbenzene</td>
<td>Spherical beads</td>
<td>Type I Quaternary Ammonium</td>
<td>1.4</td>
<td>Chloride</td>
<td>40-45</td>
<td>1.09</td>
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<tr>
<td>Purolite A300</td>
<td>Gel polystyrene crosslinked with divinylbenzene</td>
<td>Spherical Beads</td>
<td>Type II Quaternary Ammonium</td>
<td>NA</td>
<td>Free-form</td>
<td>62-70</td>
<td>1.02</td>
</tr>
<tr>
<td>Amberlite XAD16</td>
<td>Macrotetrical aliphatic crosslinked polymer</td>
<td>White translucent beads</td>
<td>styrene-divinylbenzene</td>
<td>NA</td>
<td>Free-form</td>
<td>54-60</td>
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<tr>
<td>Amberlite XAD4</td>
<td>Macrotetrical crosslinked aromatic polymer</td>
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<td>styrene-divinylbenzene</td>
<td>NA</td>
<td>Free-form</td>
<td>N/A</td>
<td>1.0</td>
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<tr>
<td>Amberlite DAX8</td>
<td>N/A</td>
<td>White translucent beads</td>
<td>styrene-divinylbenzene</td>
<td>NA</td>
<td>Free-form</td>
<td>N/A</td>
<td>1.0</td>
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Figure 1. Trihydro, Inc. (Laramie, Wyoming) managed site at U.S. Department of Energy nuclear weapons facility. Adapted from a confidential EnviroFLUX Personal Communication (2016).
Figure 2. 1,4-dioxane contaminated Site 2 (confidential site) with identified PFM deployment locations. Adapted from a confidential EnviroFLUX Personal Communication (2015).
**Figure 3.** OU-1 Biowall study site in Altus Air Force Base in Jackson County, Oklahoma. Adapted from Whiting et al. (2014).
Figure 4. SS017 Biowall study site in Altus Airforce Base in Jackson County, Oklahoma. Adapted from Whiting et al. (2014).
**Figure 5.** Average mass flux for each well measured at DOD Nuclear Facility managed by Trihydro, Inc. (Laramie, Wyoming).
Figure 6. Adsorption isotherm of 1,4-Dioxane on (A) GAC, (B) XAD4, (C) XAD16, and (D) DAX8.
Figure 7. Breakthrough curves for (A) Methanol, (B) 1,4-dioxane, (C) methylene chloride, and (D) cis-dichloroethene for the 1-D multispecies column test.
**Table 2.** Methanol, 1,4-dioxane, methylene chloride, cis-DCE properties determined from 1D column test with GAC.

<table>
<thead>
<tr>
<th></th>
<th>Methanol</th>
<th>1,4-dioxane</th>
<th>Methylene Chloride</th>
<th>cis-DCE</th>
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<tr>
<td></td>
<td>Mass retained by GAC</td>
<td>Retardation factor</td>
<td>Mass retained by GAC</td>
<td>Retardation factor</td>
</tr>
<tr>
<td>Initial Breakthrough (mg/g)</td>
<td>0.04</td>
<td>1</td>
<td>6.4</td>
<td>62</td>
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<tr>
<td>50% breakthrough (mg/g)</td>
<td>0.12</td>
<td>3</td>
<td>13.3</td>
<td>192</td>
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<tr>
<td>100% breakthrough (mg/g)</td>
<td>0.4</td>
<td>5</td>
<td>19.8</td>
<td>235</td>
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Figure 8. (A) Actual versus measured Darcy velocity with a standard PFM. (B) Actual vs measured 1,4-dioxane flux in box aquifer tests on the standard PFM.
Figure 9. Mass flux measurements at ARCADIS managed Site 1 (confidential site). (A) Mass flux profile for PFM-2 and (B) Average mass flux of contaminations for each well at Site 1.
Figure 10. Mass flux measurements at ARCADIS managed Site 2 (confidential site). (A) Mass flux profile for PFM-7 and (B) Average mass flux of contaminations for each well at Site 2.
Table 3. Comparison of PFM Results (August 2015) with traditional groundwater data (2013-2014).

<table>
<thead>
<tr>
<th>Well</th>
<th>PFM Flux-averaged concentration (μg/L)</th>
<th>Measured aqueous phase concentration (μg/L)</th>
<th>Percent Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFM 1</td>
<td>N.D.</td>
<td>2.3</td>
<td>NA</td>
</tr>
<tr>
<td>PFM 2</td>
<td>N.D.</td>
<td>330</td>
<td>NA</td>
</tr>
<tr>
<td>PFM 3</td>
<td>18</td>
<td>8.6</td>
<td>68</td>
</tr>
<tr>
<td>PFM 4</td>
<td>ND</td>
<td>1.9</td>
<td>ND</td>
</tr>
<tr>
<td>PFM 5</td>
<td>5932</td>
<td>1600</td>
<td>115</td>
</tr>
<tr>
<td>PFM 6</td>
<td>1663</td>
<td>1700</td>
<td>2</td>
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<tr>
<td>PFM 7</td>
<td>2195</td>
<td>990</td>
<td>76</td>
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<tr>
<td>PFM 8</td>
<td>1675</td>
<td>480</td>
<td>111</td>
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<tr>
<td>PFM 9</td>
<td>55</td>
<td>46</td>
<td>18</td>
</tr>
<tr>
<td>PFM 10</td>
<td>20</td>
<td>N/A</td>
<td>NA</td>
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<tr>
<td>PFM 11</td>
<td>ND</td>
<td>2.3</td>
<td>NA</td>
</tr>
<tr>
<td>PFM 12</td>
<td>1384</td>
<td>280</td>
<td>133</td>
</tr>
<tr>
<td>PFM 13</td>
<td>602</td>
<td>310</td>
<td>64</td>
</tr>
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</table>

Figure 11. Mass flux measurements at ARCADIS managed Site 3 (confidential site). (A) Mass flux profile for PFM-1, (B) Mass flux profile for PFM-2, and (C) Average mass flux of contaminations for each well measured at Site 3.
Figure 12. Adsorption isotherm of SO$_4^{2-}$ on Purolite A500 and Purolite A300 resins with a Freundlich model fit.
Figure 13. Breakthrough curves for $\text{SO}_4^{2-}$ for Purolite A300 from 1D column test.

Table 4. Sulfate properties determined from 1D column test with Purolite A300.

<table>
<thead>
<tr>
<th>Sulfate</th>
<th>Breakthrough (mg/g)</th>
<th>Retardation factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Breakthrough</td>
<td>50.5</td>
<td>27</td>
</tr>
<tr>
<td>50% breakthrough</td>
<td>68</td>
<td>15</td>
</tr>
<tr>
<td>100% breakthrough</td>
<td>70.4</td>
<td>37</td>
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</table>
Figure 14. Mass flux measurements at Altus Air Force Base Oklahoma.
Figure 15. Comparison of VOC removal, sulfide production, and \( \text{SO}_4^{2-} \) consumption. Biowall sulfide concentrations (A), percent VOC removal trends (B), average volumetric \( \text{SO}_4^{2-} \) consumption rate for T2 through T7 (C), and average percent VOC removal for T2 through T7 (D). Positive error bars represent one standard deviation.
**Author Contribution:** M.D. Annable was responsible for obtaining funding, designing experiments and aided in writing the manuscript. Meghan Thiemann conducted 1,4-dioxane column and batch shake test on 1,4-dioxane. Patrick Evans deployed PFMs for sulfate analysis and interpret sulfate-based field data. Jaehyun Cho was responsible for building PFMs for deployment, conducting sulfate batch studies, conducting 1D sulfate column test and measuring contaminants. Alexander Haluska was responsible analyzing/interpreting data and preparing the manuscript for publication.

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