FINAL REPORT

Development of a Passive Flux Meter Approach to Quantifying 1-4 Dioxane Mass Flux

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14. ABSTRACT

The Passive Flux Meter (PFM) was developed at the University of Florida in 2001 to obtain direct measurements of contaminant mass flux and Darcy flux at contaminated sites. Increased error may occur in this technology when low-partitioning contaminants are involved. The objective of this study was to develop a modified PFM approach to quantifying contaminant flux of low-partitioning contaminants while simultaneously measuring Darcy flux with a acceptable measurement error. Modifications were proposed based on past studies such as the Passive Surface Water Flux Meter (PSFM) and low-density polyethylene (LDPE) passive diffusion samplers.

15. SUBJECT TERMS

passive sampler, groundwater, contamination, contaminant flux, Darcy flux, contaminants, low-density polyethylene, LDPE, diffusion

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Abstract

The Passive Flux Meter (PFM) was developed at the University of Florida in 2001 to obtain direct measurements of contaminant mass flux and Darcy flux at contaminated sites. Increased error may occur in this technology when low-partitioning contaminants are involved. The objective of this study was to develop a modified PFM approach to quantifying contaminant flux of low-partitioning contaminants while simultaneously measuring Darcy flux with a acceptable measurement error. Modifications were proposed based on past studies such as the Passive Surface Water Flux Meter (PSFM) and low-density polyethylene (LDPE) passive diffusion samplers. Designs incorporating modified permeability were tested in box aquifer setups. The low partitioning contaminants used in the experiments were 1,4-dioxane and methanol. While the modified design produced significant error with the very low partitioning methanol flux measurements, the error in 1,4-dioxane measurements was acceptable at 21% in contrast to 41% for the standard PFM application when contaminant breakthrough occurred. A second approach considered in this study was the incorporation of a diffusion domain in a PFM configuration. A diffusion passive sampler was constructed using LDPE and filling it with granular activated carbon (GAC). The diffusion sampler was surrounded by sand to produce a similar configuration to a standard PFM and was tested in a laboratory aquifer model. The results were compared to samplers filled only with deionized water. Contaminants tested in this evaluation included 1,4-dioxane, methylene chloride, 1,1-dichloroethylene (1,1-DCE), and cis-1,2-dichloroethylene (1,2-DCE). This approach does not work for all types of contaminants due to the diffusion characteristics of the LDPE. Based on experiments conducted in this study the modified design may work well for chlorinated contaminants such as methylene chloride, but would require alternate diffusion membranes to function for methanol or 1,4-dioxane.

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1. Objectives

The objective of this project was to develop a method for the simultaneous in situ measurement of 1,4-dioxane and water flux. Measurement of flux is critical to both the design and evaluation of remedial strategies that rely on injection of stimulants to promote biological or abiotic reactions to degrade 1,4-dioxane. 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 becomes critical to successful and economical implementation of in-situ remedial efforts.

2. Background

Groundwater is a high value resource that can be endangered by contaminant spills. Groundwater contamination is a significant problem, making site cleanup a high priority. In order to determine the risk of contamination and efficiently cleanup a site, contaminant mass flux and Darcy flux are needed (Einarson and Mackay, 2001,Goltz et al., 2007,Li et al., 2007). Contaminant mass flux provides a more relevant measurement at groundwater contaminated sites than contaminant concentration. Flux is linked to the risk from both the contaminant source and plume, providing more accurate determinations of the amount of contaminant that may end up in a critical location near the site such as a water supply well (Goltz et al., 2007). Due to its importance, accurate measurement of contaminant flux is crucial in site risk assessments and when determining remedial strategies (Goltz et al., 2007,Verreydt et al., 2013). There are three major mass discharge field measurement technologies currently in use, the Multilevel Sampling Method (MLS), the Integral Pumping Test (IPT), and the Passive Flux Meter

(PFM) (Li et al., 2007). A common method of determining flux profiles at a contaminated site is to perform individual measurements and calculations based on Darcy’s Law using hydraulic conductivity, gradients, and contaminant concentration. This method is indirect and also only provides an instantaneous measurement, so error can be high (Verreydt et al., 2013).

The PFM developed at the University of Florida is a tool used to measure both the contaminant flux and water flux, and was validated by both lab and field tests (Annable et al., 2005,Basu et al., 2006,Hatfield et al., 2004). The PFM is able to measure the mass flux of dissolved contaminants provided that the sorbent in the PFM captures and retains the contaminant (Hatfield et al., 2004). One source of error in this method increases with the measurement of low partitioning compounds, since the PFM may not retain all the mass after extended deployment durations. This suggests that the standard PFM would require a short deployment duration to measure low partitioning contaminant mass. Short durations are not ideal, however, because there can be a significant increase in the amount of error associated with the PFM Darcy flux measurements. Darcy flux is measured in the PFMs through tracer loss. The PFM is impregnated with multiple water soluble tracers, and the rate at which the tracers leave the PFM is proportional to the water flux (Hatfield et al., 2004). In a typical deployment of a standard PFM there is tracer loss when the flux meters are both installed and removed from the well. During long duration deployments, the amount of tracers lost during installation and retrieval is negligible compared to the amount lost due to water flow (Hatfield et al., 2004). If the flux meters were to be deployed for only a few days, then the amount of tracer loss due to PFM deployment and retrieval would be significant compared to the amount of tracers lost due to groundwater flow assuming typical Darcy flux. This means that while contaminant flux of low partitioning compounds could be measured with a short duration deployment, the water flux might not be simultaneously measured accurately. One option to avoid this challenge is to first apply a standard PFM at sites contaminated with low partitioning compounds only to measure contaminant mass flux. A second deployment of longer duration could then be used only to measure water flux. This can increase the cost and time required, and may not be the most efficient use of the technology. It is also important to consider that there may be increased error when measuring contaminant flux with a shorter PFM deployment. A modification to the PFM design may allow the PFM to retain low partitioning compounds so that both the contaminant flux and the water flux can be accurately measured over the same PFM deployment.

One particular low partitioning contaminant of interest is 1,4-dioxane. The U.S. EPA has classified 1,4-dioxane as a probable human carcinogen (Mahendra et al., 2013,Stepien et al., 2014). While drinking water regulations currently do not contain a maximum contaminant level for 1,4-dioxane, a water health advisory has been established, stating that at a concentration of 0.3 mg/L there is an estimated cancer risk of 1 in 10,000. Water quality standards for 1,4-dioxane have been added for some States (Abe, 1999,Zenker et al., 2003).

The structure of 1,4-dioxane, cyclic with two symmetric ether linkages opposite each other, makes it a difficult compound to remove from the environment. 1,4-dioxane is miscible with water, has a low Henry’s constant, a low partitioning coefficient, and is highly resistive to biodegradation (Zenker et al., 2003). It is also considered one of the most mobile contaminants in groundwater. These properties are significant because it makes 1,4-dioxane difficult to detect and clean up in groundwater (Zenker et al., 2003). While 1,4-dioxane is commonly found in sites contaminated with 1,1,1-trichloroethane (TCA), it's high mobility causes the 1,4-dioxane plume to spread and become larger than the associated TCA plume (Otto and Nagaraja, 2007). It has been a difficult contaminant to analyze in the past, causing some sites to have already been remediated for TCA without managing the 1,4-dioxane, which can be problematic (Otto and Nagaraja, 2007).

In this project, methods to quantify contaminant flux of low partitioning compounds while simultaneously measuring water flow with a passive flux meter were investigated. The primary contaminant of interest in this study was 1,4-dioxane, however other compounds, such as methanol and methylene chloride, were examined. In an effort to determine a suitable method for measuring both the 1,4-dioxane and water flux, modifications to the current PFM method were made. Modified PFMs were developed and tested using a laboratory aquifer model. The box aquifer is a 3D chamber simulating groundwater contaminant movement. Modified PFMs were developed and tested in the model using a similar approach as employed in the development of the PFM (Hatfield et al., 2004) as well as other flux meter modifications (Cho et al., 2007,Lee et al., 2007). The applied mass flux was compared to the PFM measured mass flux to determine the measurement error in both the standard and modified PFMs for the contaminants selected.

Two methods were proposed to allow retention of the low partitioning contaminants in a PFM. Both methods involve lowering the amount of water passing through either the entire PFM or a section of it. One modification is to change the permeability of the PFM by changing the PFM materials or by adding a separate media layer around the PFM. The other proposed method considered in this study was to create a diffusion domain within the PFM.

The early stage of this project focused solely on the capture of 1,4-dioxane as a low-partitioning contaminant. It was determined that at low concentrations of 1,4-dioxane contaminant mass flux can be measured accurately using the standard PFM designs. At high 1,4-dioxane concentrations breakthrough occurs in the PFM leading to increased errors. To further test the modified PFM capability, methanol, a well-known low partitioning compound on granular activated carbon (GAC) (Annable et al., 2005), was used as a contaminant surrogate in the aquifer model. Methanol breakthrough occurs very rapidly. It is typically used as a tracer in standard PFMs and is the first to elute from the GAC. Methylene chloride was also used as a contaminant for comparison. Methylene chloride is considered a low-partitioning contaminant when compared to other chlorinated compounds, but breakthrough should not occur rapidly in standard PFMs. In later tests based on creating a diffusion PFM, 1,1-DCE and 1,2-DCE were used for comparison as well. These contaminants were used in the diffusion tests for comparison because they are chlorinated contaminants and partition favorably through a diffusion domain.

3. Methods for Evaluating Low Partitioning Contaminants

A batch test was completed to determine the best sorbent material to use in the flux meters for capturing low partitioning contaminants (Cho et al., 2007,Lee et al., 2007,Stucker et al., 2011). In standard PFMs GAC is used. Changing the media in the PFM was successful in developing a PFM for measuring chromium mass flux, thus this approach was used here to determine if this is a suitable method for 1,4-dioxane capture (Campbell et al., 2006). Different sorbents as well as silver impregnated coconut-based 12x40 mesh GAC were tested to compare retentions of 1,4-dioxane. The three nonionic resins selected were XAD16, DAX8, and XAD4. A Freundlich adsorption isotherm was developed for each sorbent, allowing for determination of the maximum capacity for 1,4-dioxane. While many studies predict that GAC is not suitable for treatment of 1,4-dioxane because of 1,4-dioxane's low adsorptive capacity, there have been applications where it has been shown to be efficient for the capture of 1,4-dioxane (Otto and Nagaraja, 2007).

Different sorbent masses were tested, ranging from 0.1 g to 10 g for GAC, and 0.1 g to 5 g for the three resins. A total of 15 vials for GAC and 8 vials for each of the resins were used. 40 mL EPA vials with Teflon-lined caps were used and weighed to get an accurate weight of the sorbent. A solution with a 1,4-dioxane concentration of 1,030 ppm was added and the vials were then put on the rotator for 24 hours. The equilibrium solution was then sampled and analyzed on the gas chromatograph with a flame ionization detector (GC-FID). From this the mass adsorbed onto the sorbents was calculated. In Figure 2-1 a sorption isotherm for all the sorbents is displayed. GAC had the highest 1,4-dioxane mass adsorbed, while DAX 8 had almost no adsorption. Freundlich isotherms were developed for all sorbents except DAX8 and were used to determine the maximum capacities on each of the sorbents (Dada et al., 2012). The maximum capacity for 1,4-dioxane on GAC was 10 times higher than that on XAD16 and 7 times higher than on XAD4, so it was determined to be the best sorbent. This negated the need for using a different media. Powdered activated carbon was not considered due to the extremely low hydraulic conductivity. While there is another sorbent, Ambersorb 563 (Environmental Protection Agency, 1995), which may have a higher capacity than GAC, as indicated by The Emerging Technology Bulletin, this sorbent is far too expensive to use in this application because of the relatively large quantities needed (compared to those used in analytical applications).

a. Column Tests

A column test was conducted to estimate retardation factors as well as dynamic sorption capacities for contaminants used in this study and to predict optimal deployment times (Cho et al., 2007,Hatfield et al., 2004). The column was packed with GAC, the selected sorbent material. Breakthrough curves for 1,4-dioxane, methylene chloride, methanol, and 1,2-DCE were determined. Concentrations in the injection solution were 36 ppm for methanol, 65 ppm for 1,4-dioxane, 68 ppm for methylene chloride, and 57 ppm for 1,2-DCE. In this column test, competition between contaminants may lead to a slightly shorter breakthrough time than with only a single contaminant applied. A column test with contaminant competition is best for predicting the breakthrough of 1,4-dioxane in the environment because many studies indicate that 1,4-dioxane is rarely the only contaminant present.

A 4 L Mariotte bottle was used to for the injection solution. This system maintained a constant head at the container effluent. A 2.5 by 5 cm Kontes glass column was used with a dry mass 13.9 g GAC. The contaminant solution flowed through the column with samples taken of the effluent. A flowrate of 1.7 mL/min was used. The column test setup is displayed in Figure 3-2. Effluent samples collected were analyzed on the GC-FID to generate breakthrough curves (BTCs) shown in Figure 3-3. 1,2-DCE has a high adsorption capacity for GAC, so this BTC can be compared to other contaminants, which breakthrough much faster. The BTCs for methanol, 1,4-dioxane, and methylene chloride are shown separately in Figures 3-4, 3-5, and 3-6. These BTCs display the effluent concentration over the amount of pore volumes passed through the column.

The retardation factors calculated are displayed in Table 3-1 below. 1,4-dioxane had a much higher retardation factor than anticipated. This would indicate that the standard PFM (Hatfield et al., 2004), which was discussed in the introduction, may work well when there are low 1,4-dioxane concentrations present at the site. Higher 1,4-dioxane concentrations will be later tested in laboratory aquifer tests, where the amount of error occurring at both low concentrations and at high concentrations of 1,4-dioxane will be examined. Retardation factors were calculated for each contaminant based on the amount of contaminant adsorbed to the GAC in the column when 50% breakthrough occurred. The amount of contaminant per gram of GAC passed through the column at initial breakthrough, 50% breakthrough, and 100% breakthrough are shown in Table 3-1. The column test was also used to predict how much error would occur as the maximum capacity for methanol and 1,4-dioxane on GAC was reached. The results of this analysis are displayed in Figure 3-7.

b. Aquifer Model Test

A 3D box was designed to simulate a well in a groundwater flow field. The aquifer was set up in a stainless steel box with dimensions of 40 x 30 x 13 cm. A commercial patio leveling sand produced by Sunniland was packed in the box. A 20 cm piece of well screen was used and placed upright in the center of the box. A piece of plexiglass was secured to the bottom of the well screen to ensure water would not enter through the bottom, as well as to help keep the well screen secured in place during packing. Teflon tape was placed over the top part of the well screen sealing the slots to create a screened section 10 cm long. The sand was packed around the well screen to a depth of 10 cm under standing water to keep saturated conditions and ensure that there were no trapped air bubbles. Coarse gravel was used at the box inlet for flow injection and at the box outlet for flow extraction. The gravel was able to provide a constant head across the inlet and outlet, as well as to create a uniform flow gradient over the width of the box. Wire mesh separated the gravel and sand to prevent mixing. About 1 inch of bentonite clay was used to cover the sand to minimize contaminant loss due to volatilization. The reservoir for the contaminant solution was a 20 L glass jar setup as a Mariotte bottle. The pump at the outlet controlled the flowrate. A photograph of the 3D box aquifer setup is displayed in Figure 3-8.

c. Standard Flux Meter Test

Box aquifer tests were completed on standard PFMs to determine the ability of the PFM to measure the flux of 1,4-dioxane at low concentrations. The contaminant solution used for these box tests only had a 1,4-dioxane concentration of 1.8 mg/L. Samples of the contaminant water solution entering and leaving the box were taken periodically to ensure that the contaminant concentration remained constant. From the column test results it was predicted that at this concentration the standard PFM will work well for measuring the 1,4-dioxane flux. The PFM consisted of wet GAC impregnated with tracers packed into the crinoline socks. The tracers used were methanol, ethanol, isopropyl alcohol (IPA), tert-butyl alcohol (TBA), and 2,4-dimethyl-3-pentanol (2,4-DMP). Six PFM tests were completed, each at a different flow rate. Flow rates ranged from 2.2 mL/min to 18 mL/min. For each of the six tests, around 8 to 9 L of the contaminant solution were passed through the model. The PFMs were packed using the same method as is used when packing standard PFMs for field deployments, with the only difference being the length of the PFM. Each PFM was about three inches in length. Figure 3-9 shows an image of the standard PFM in the clear PVC pipe before being deployed in the box aquifer.

Results from the standard PFM box tests are displayed in Figure 3-10 and Figure 3-11. Figure 3-10 shows a plot of the applied Darcy flux to the box aquifer and the PFM measured Darcy flux. Figure 3-12 shows the actual 1,4-dioxane mass flux applied in the box aquifer compared to the PFM measured 1,4-dioxane mass flux. 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. At sites contaminated with small amounts of 1,4-dioxane, the standard flux meter is a good approach for obtaining mass flux. If there were high concentrations of 1,4-dioxane with competition between other contaminants, however, the standard PFM may not last as long.

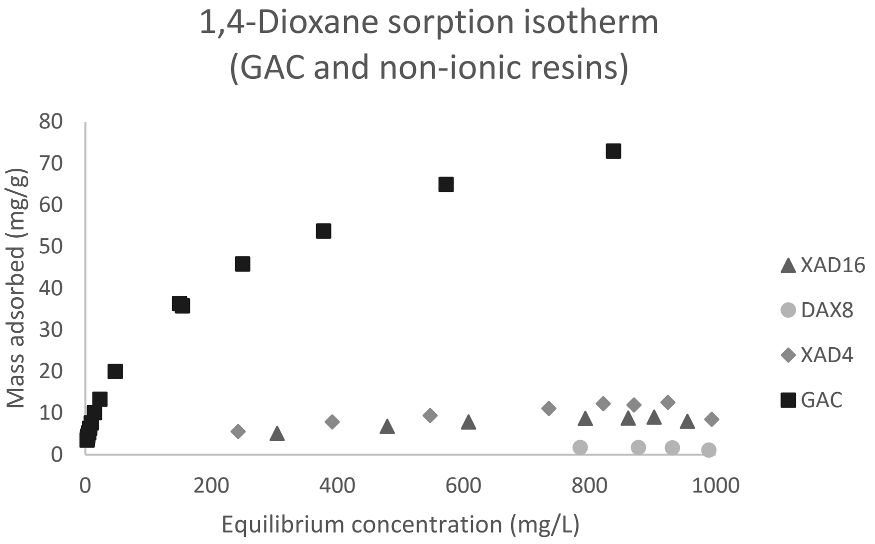


Figure 3-1. Isotherms for 1,4-dioxane on each sorbent tested in batch adsorption test.

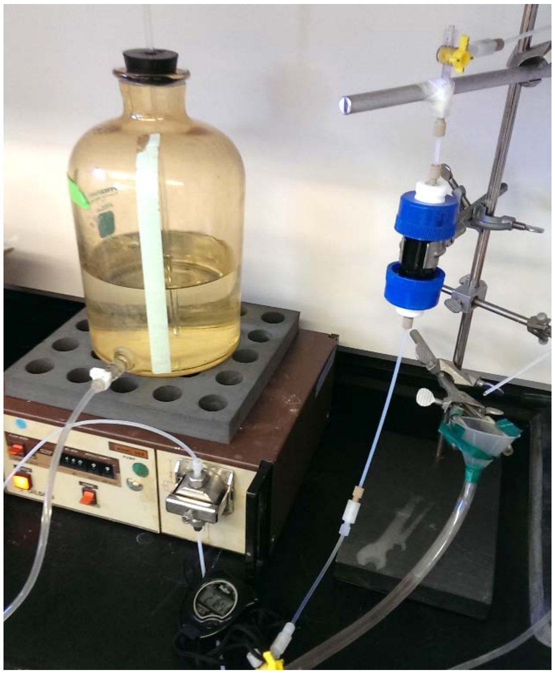


Figure 3-2. Column test setup.

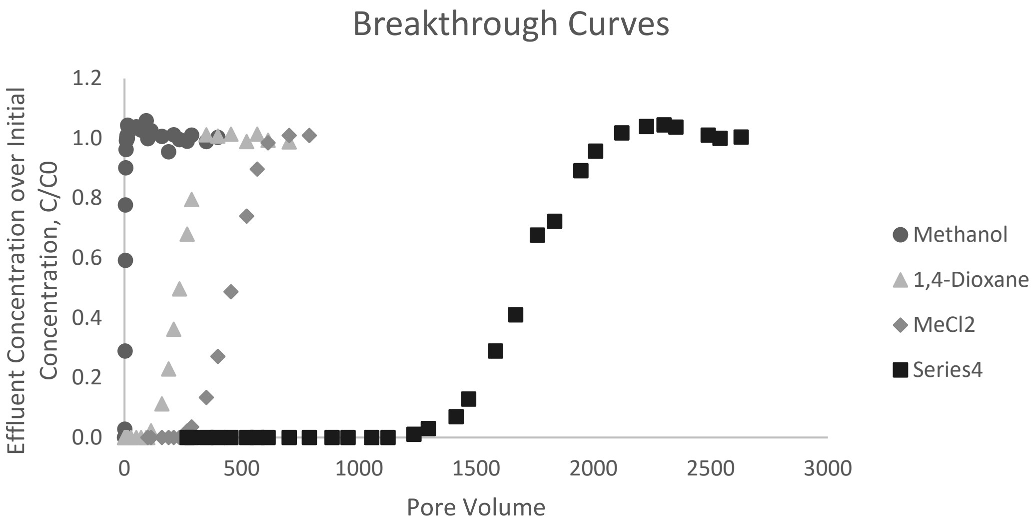


Figure 3-3. Breakthrough curves for all contaminants used in the 1-D column test.

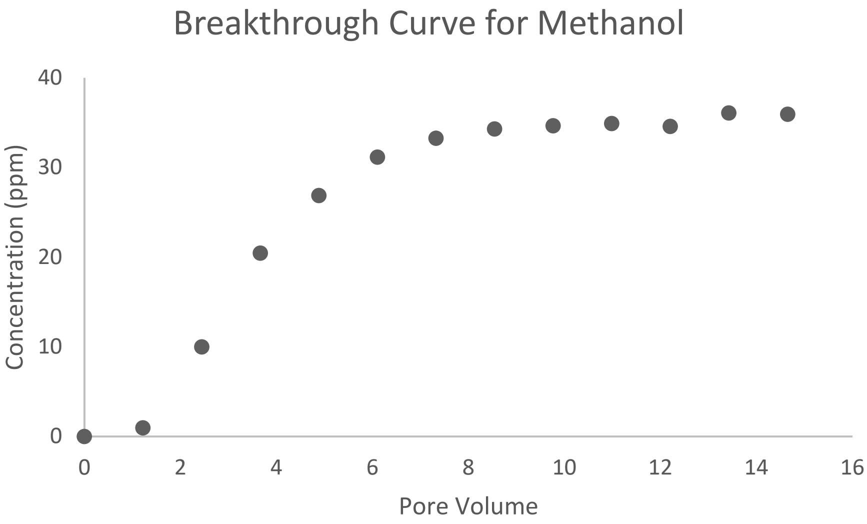


Figure 3-4. Breakthrough curve for Methanol from the 1-D column test.

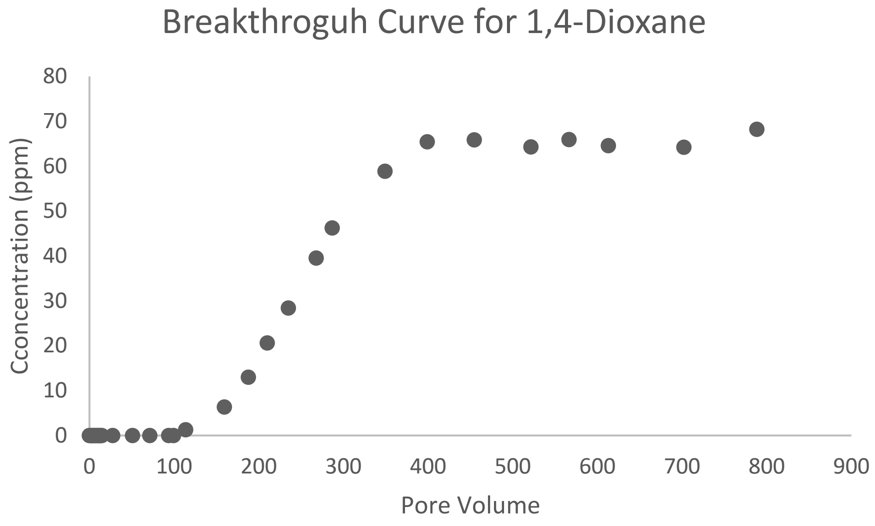


Figure 3-5. Breakthrough curve for 1,4-dioxane from the 1-D column test.

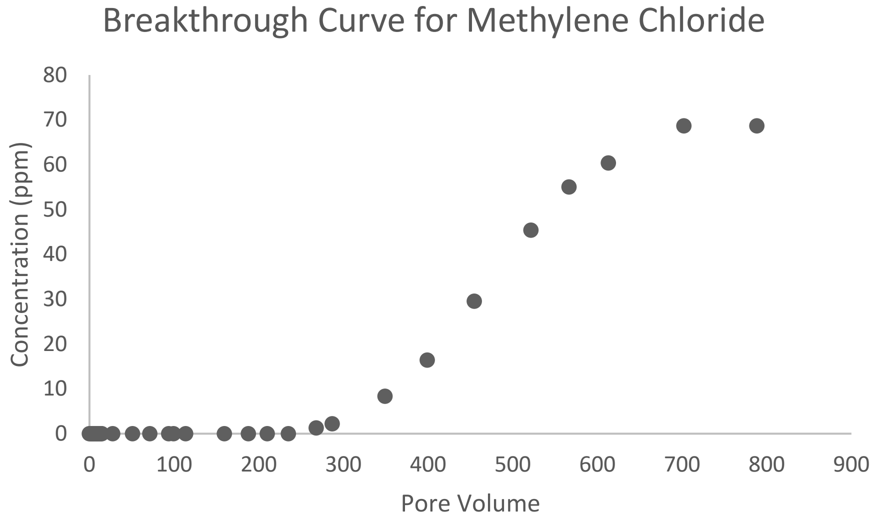


Figure 3-6. Breakthrough curve for methylene chloride from the 1-D column test.

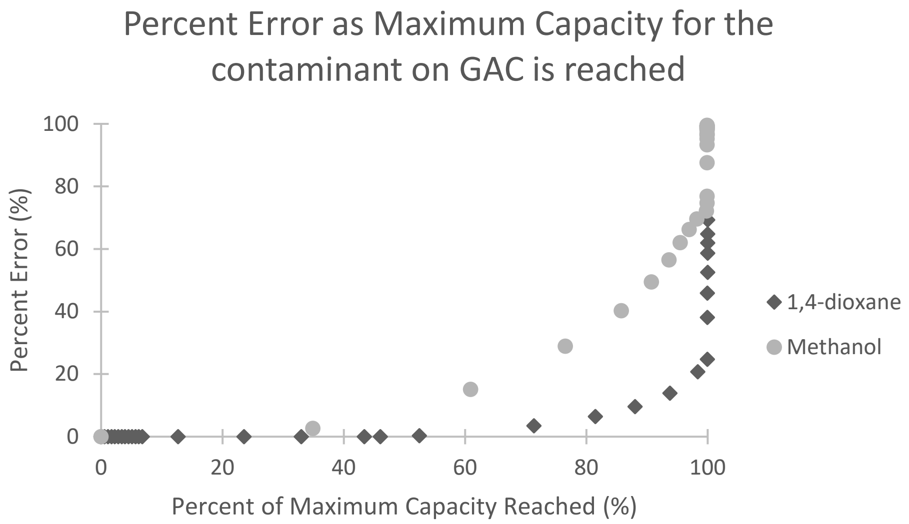


Figure 3-7. The percent error predicted by the amount of contaminant mass injected vs the amount of contaminant mass adsorbed plotted against the percent to which the maximum capacity on the GAC for each contaminant is reached.

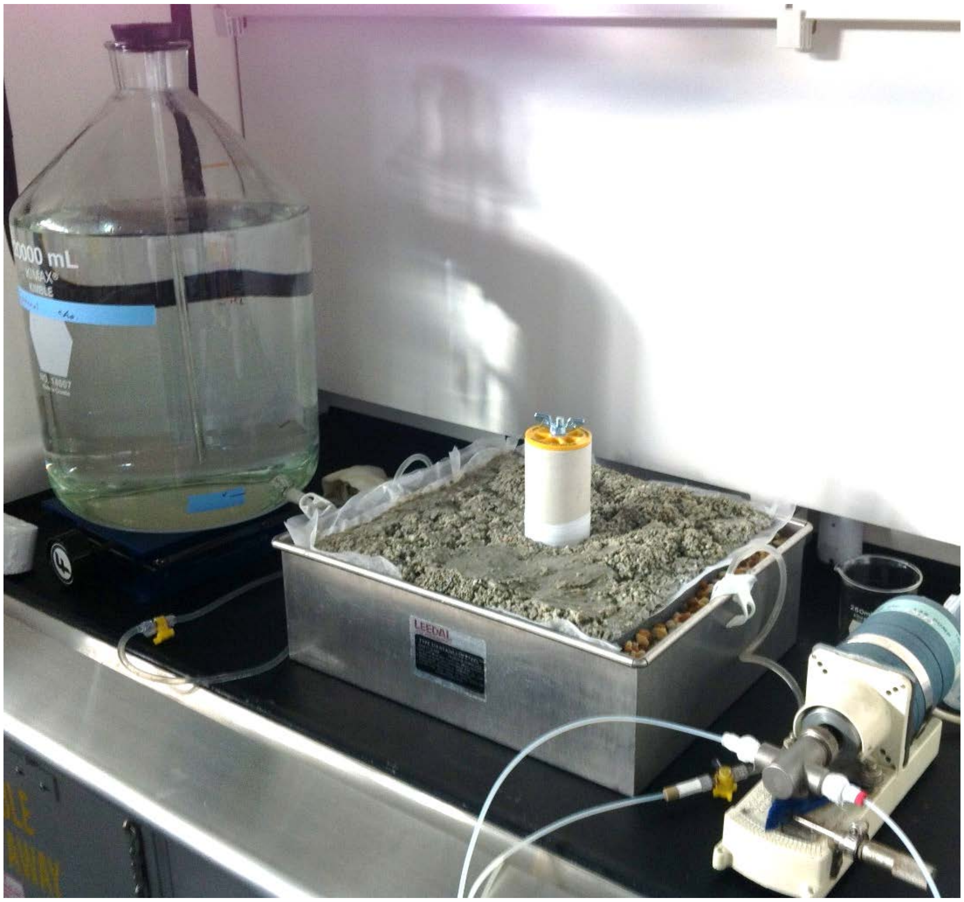


Figure 3-8. Box aquifer setup.

Figure 3-9. Laboratory tested passive flux meter.

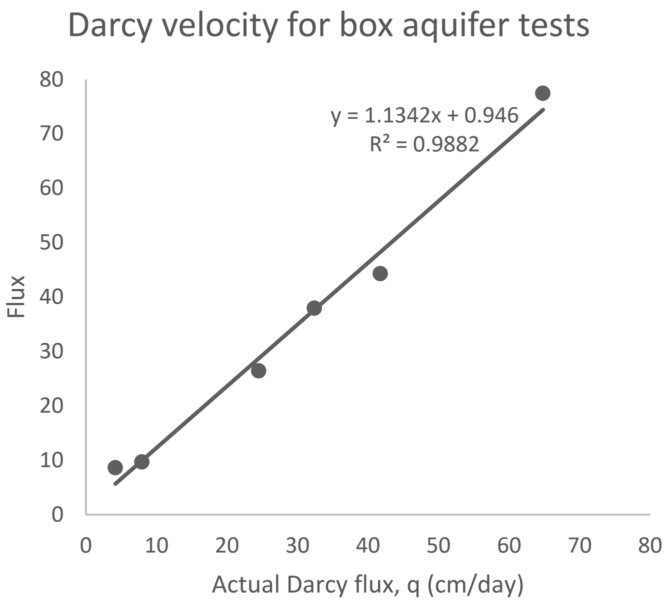


Figure 3-10. Actual versus measured Darcy flux with a standard PFM.

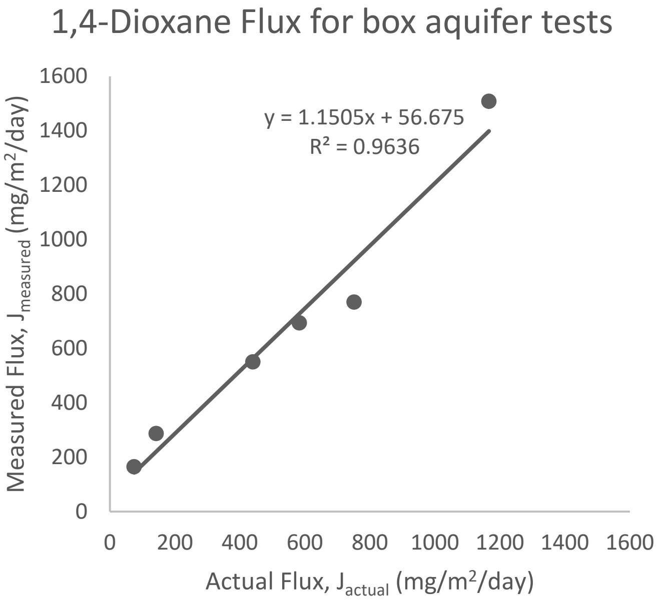


Figure 3-11. Actual vs measured 1,4-dioxane flux in box aquifer tests on the standard PFM.

Table 3-1. Properties determined for each contaminant from the column test

Property	Methanol	1,4-dioxane	Methylene Chloride	1,2-DCE
Retardation factor	3.30	235	455	1700
Initial Breakthrough (mg/g)	0.04	6	17	71
50% breakthrough (mg/g)	0.12	13	28	98
100% breakthrough (mg/g)	0.40	20	44	123

4. Modified PFM Configuration for Evaluating 1,4-Dioxane Flux

It is difficult to measure the flux of low partitioning contaminants since they typically breakthrough rapidly in standard flux meters. One way to extend the time in which the flux meter can be deployed is to control the amount of water flowing through the PFM. One way to do this is to adjust the permeability of the flux meter. By reducing the amount of water through the flux meter, there will be less contaminant flow, and therefore longer breakthrough times. In previous research, a Passive Surface Water Flux Meter was developed, and this approach involved the use of an impermeable shell to control the water flow through the PFM (Klammler et al., 2007b,Padowski et al., 2009). Similarly, use of different materials around the PFM were tested in order to reduce the water flow through the PFM. Hydraulic conductivity tests were performed on multiple sands, fabrics, and gravel and details for these tests can be found in Appendix A.

The modified PFM should provide contaminant mass flux and Darcy flux measurements much lower than the applied values due to reduced water flow. The modified PFMs were tested in a box aquifer model, and the measured fluxes were compared to the applied flux. Based on the Darcy flux measured from the modified PFM, a relationship between the measured flow and actual flow was determined.

One concern regarding this PFM design is the effect of flow divergence. The groundwater will diverge around the modified PFM significantly more than it will around the standard PFM, which could increase the error associated with the modified PFM. Flow fields were evaluated for each PFM modification and this is discussed in Appendix A. Convergence factors were calculated and will be applied to account for the error due to divergence. For the modifications on the PFM to be successful, the error due to divergence will need to be less than the error caused by contaminant breakthrough in a standard PFM.

a. Modified Configurations

i. High Hydraulic Conductivity

A proposed PFM modification includes the development of a zone of high hydraulic conductivity around the PFM. Since the standard PFM already has a relatively high conductivity of about 300 m/day, the surrounding media will need a higher hydraulic conductivity. By creating this zone, the water will most likely bypass the PFM since the majority of flow will be focused through this high hydraulic conductivity zone.

Two different modifications were used to create a zone of high hydraulic conductivity around the PFM. One modification was to create empty space between the well screen and the PFM. This involved a standard PFM with a diameter of one inch that was placed in a two inch well screen. Sponges of the same diameter as the well screen were used at the top and bottom of the PFM to keep it in place when deployed. Technically no modification has been made to this PFM. The creation of the open space is the characteristic modified from typical standard PFM installations. The flow divergence could not be directly calculated due to the essentially infinite hydraulic conductivity of the open water annulus. The second PFM with a high hydraulic conductivity zone was designed using a one inch PFM with a course gravel packed around the outside of the PFM, thus producing a two inch PFM. The gravel has a very high hydraulic conductivity and would work in a similar manner to the first modification. The advantage to this modification is that the PFM will not move laterally inside the well screen. Both of these modifications depend significantly on the flow field diverging around the PFM rather than complete bypassing of the GAC in the PFM. Figure 4-1 displays top view diagrams of these proposed designs. In Figure 4-1 the top down images display the different zones that can cause a change in the flow fields. Looking at the diagrams and comparing the modified configurations to a standard PFM, it would be expected that the flow would be much more divergent around the modified PFMs. Figure 4-1 (A) represents a standard PFM, with k_0 representing the hydraulic conductivity of the box aquifer sand, k_1 representing the hydraulic conductivity of the well screen, and k_2 representing the hydraulic conductivity of the PFM. In the standard PFM the image shows that once water passes through the well screen it will flow directly into and through the PFM. Figure 3-1 (B) represents the one inch PFM in a two inch well screen. In this case k_2 represents the zone with no media in it, so the hydraulic conductivity here would nearly infinite, and k_3 represents the hydraulic conductivity of the one inch PFM. In Figure 4-1 (C) k_2 represents the hydraulic conductivity of the gravel. Most of the water in both Figure 4-1 (B) and 4-1 (C) should flow around the PFM and stay in the zone with hydraulic conductivity k_2, which is much higher than hydraulic conductivity k_3, causing much of the water to bypass the PFM.

ii. Low Hydraulic Conductivity

An alternative approach to modifying a standard PFM is to create a zone of low hydraulic conductivity around the flux meter. This would cause fewer pore volumes to pass through the flux meter, which would allow the flux meter to be deployed a long enough period to both capture and retain low partitioning contaminants.

To create a PFM with low permeability, two different modifications were tested. One of these modifications involved using a one inch standard PFM and then packing a fine sand around the GAC to bring the total PFM diameter to two inches. The mesh of the sand to be used was 100 to 140 since this would provide a hydraulic conductivity difference of five times lower than the hydraulic conductivity of the surrounding box aquifer sand. For a standard flux meter, crinoline socks are used to hold the GAC around the center tube, but in this case a fabric with a finer mesh was needed since the fine sand particles can pass through the crinoline mesh. The fabric used was 97%/3% cotton/spandex. The second modification to create a low permeability PFM was to use a thicker fabric instead of the standard PFM crinoline socks. This is the only change from a standard PFM and would be easier and require less time constructing than the first low permeability modification. As mentioned previously, the hydraulic conductivities of multiple fabrics were tested. Three different fabrics were used in the box tests, including a 97%/3% cotton/spandex material, 100% polyester material, and duckcloth, which is a thick and tightly woven 100% cotton material. Figure 4-2 displays top view diagrams of each modification, Figure 4-2 (B) and Figure 4-2 (C), compared to the top down diagram of a standard PFM, Figure 4-2 (A). The zone of low hydraulic conductivity is significantly greater in the first low permeability modification, shown in Figure 4-2 (C), so it would be expected that this would lower the flow through the PFM more significantly than the second proposed low permeability modification shown in Figure 4-2 (B).

b. Modified PFM Box Aquifer Tests

The modified PFMs were tested using a 3D box setup as described earler. A 10 ppm contaminant solution of methanol, 1,4-dioxane, and methylene chloride was used in this box aquifer test. Only the 1,4-dioxane data was used in the initial PFM modification screenings, but the methanol and methylene chloride will create some competition for sorption on the GAC in the PFM.

The deployment duration and flow applied for each modified PFM test was kept constant. A standard PFM was tested as an initial check to verify that the water in the box was flowing uniformly, which was determined by an accurate measurement of the Darcy flux by a standard PFM. The flowrate for all the tests was set to 7.7 mL/min, which produced a Darcy flux of 27.6 cm/day. Approximately 12,000 mL of contaminated water was passed through the box during each test. The standard PFM was packed using the same method as was done for the first set of box tests. The remaining PFMs were packed similarly, with slight adjustments depending on the modification evaluated. For the one inch PFM standard construction design was followed to produce a one inch PFM. For the one inch PFM surrounded by gravel the GAC portion was packed to produce a one inch PFM and then a two inch PFM was created filling the annulus with gravel. The one inch PFM with sand packed around it followed the same procedures. The fabric used in place of the crinoline for the one inch PFM with sand was 97%/3% cotton/spandex. For the remaining modified PFMs, the same procedure for packing standard PFMs was used with different fabrics. Images of each PFM are shown in Figure 4-3 (A) through (E), with Figure 4-3 (A) being the standard PFM, Figure 4-3 (B) the one inch PFM, Figure 4-3 (C) the one inch PFM with gravel, Figure 4-3 (D) the one inch PFM with sand, and Figure 4-3 (E) the PFM with a different fabric material. Figure 4-3 (E) shows the PFM with polyester as the fabric material.

c. Results

Table 4-1 and Table 4-2 display the results of each PFM test, with Table 4-1 showing the Darcy flux measurements and Table 4-2 the 1,4-dioxane mass flux measurements. Table 4-3 displays the percent differences between the applied Darcy flux and 1,4-dioxane mass flux and the PFM measured values. Flow divergence has been accounted for in the values displayed in the Table 4-1 and Table 4-2 through use of the calculated convergence factors, with the exception of the one inch PFM since a convergence factor could not be calculated for this design. The low permeability PFMs appear to provide better results than the PFM's with the high hydraulic conductivity zone. The differences in Darcy flux and 1,4-dioxane flux for the one inch PFM with gravel was not large enough to extend PFM deployment so that contaminant breakthrough does not occur, since the difference between the actual flux and the measured 1,4-dioxane flux was only a factor of two. For the one inch PFM with open space, the difference in actual to measured flux is significant with a factor of 4. For this design the flow field was not considered. With the low permeability PFMs the difference in both actual and measured Darcy flux and actual and measured 1,4-dioxane flux is significant. For the one inch PFM with sand, the ratios of actual to measured Darcy flux and actual to measured 1,4-dioxane flux are not consistent, with the Darcy flux ratio being 14 and the flux ratio being 31. The same occurrence takes place with the two inch PFMs that use polyester and duckcloth over the crinoline socks. The two inch PFM with 97%/3% cotton/spandex, however, has an actual to measured Darcy flux ratio that is very similar to the actual to measured 1,4-dioxane flux ratio, which may make it the best design considered. This modification is also the quickest and easiest PFM to pack, which makes it more appealing.

Additional testing was done on two of the modified PFMs, one on the modification that involved a one inch PFM with sand packed around it and the other on the two inch PFM with the 97%/3% cotton/spandex fabric. In these tests, the PFMs were deployed for a duration of 6 days with a much slower flowrate of 1.4 mL/min, equivalent to a Darcy flux of 5 cm/day. The results from these tests are displayed in Table 4-4 and Table 4-5, with Table 4-4 containing the Darcy flux data and Table 4-5 the 1,4-dioxane mass flux data. While the difference in Darcy flux is almost equal to the difference in flux for the PFM with the 97% cotton fabric, the difference is only just above one, meaning there is almost no difference from the standard PFM for this modification at a very low flow rate. The low flow rate causes the cotton fabric to have almost no impact on the flow field. This may be caused by the low Darcy flux producing flow that is similar to plug flow, where diffusion becomes important (Hatfield et al., 2004). The one inch PFM packed with sand around it still has a difference greater than one in the measured Darcy flux and 1,4-dioxane mass flux, however as was seen in the previous tests the differences are not consistent, nor does there appear to be a direct relationship between the test with the high flow and the test with the low flow. Table 4-6 contains the percent differences for each of these tests between the applied and PFM measured values.

Based on the results provided, the relationships between actual and measured Darcy flux and actual and measured flux do not appear to be consistent, but rather change based on the applied flow rate. For the one inch PFM with sand there does not appear to be a direct relationship, which would make determination of a correction factor for this PFM design challenging. For the two inch PFM with the cotton fabric the difference in Darcy flux is equal to the difference in flux for both tests. This means that in developing a modified PFM that could accurately determine the contaminant flux, the relationship between the actual and measured Darcy flux could be used to correct the measured flux and obtain the actual flux. An approach that would allow measurement of actual Darcy flux, modified PFM measured Darcy flux, and modified PFM measured flux is to create a

PFM with alternating layers or segments in the vertical direction. One layer would serve as a standard PFM and the other layer would contain the modification. If the modification layer was the two inch PFM with the 97%/3% cotton/spandex fabric then the difference in the Darcy flux could be used to correct the measured flux, which would give an accurate value for the contaminant flux measured by the modified PFM. The modified layer would allow the standard layer to be deployed long enough to accurately measure Darcy flux through use of the tracers, while the modified layer would measure the contaminant flux since the standard layer would give error due to contaminant breakthrough. The only concern for this PFM would be if the Darcy flux was low enough that diffusion became an important flow component. It would be very difficult to alternate layers with any of the modified PFMs tested except for the ones that use the 97%/3% cotton/spandex fabric.

d. Extended Tests

Based on the box tests completed for testing PFMs with modified configurations, more tests were warranted for the two inch PFM with 97%/3% cotton/spandex fabric. Based on the initial screenings this modification provided the best results as well as ease of assembling. A further modification was made to more accurately measure Darcy flux while simultaneously measuring the contaminant flux. The new PFM was designed to have two layers, with one layer being the standard crinoline socks material, and the next being the 97%/3% cotton/spandex material. Two rubber washers would be placed between each GAC layer to prevent vertical flow of the water in the PFM and mixing of the layers. The layer with the crinoline socks was used to measure the Darcy flux, while the modified layer would was used to simultaneously measure the low-partitioning contaminant flux. The difference in the measured Darcy flux between the two layers will be used to correct the measured contaminant flux to give the actual flux. An image of this modified PFM is shown below in Figure 4-4.

The PFM was assembled following the same procedures for a standard PFM while adding the 97%/3% cotton/spandex fabric to the bottom half of the PFM. The images in Figure 4-4 show the alternate layer PFM after it has been transferred to the clear PVC tube and right before being deployed into the box aquifer. The length of the modified portion of the PFM was about 8 cm and the length of the standard PFM portion was about 7 cm. The space between the bottom of the PFM and the start of the GAC region was 2 cm due to the metal clamp, giving the PFM a total length of 17 cm.

e. Box Aquifer Tests

The design described above was tested using a series of box aquifer tests as described earlier. A box with dimensions of 29 x 23 cm on the top, 23.5 x 20 cm on the bottom, and 20 cm in height was used to provide the extra height needed to test the modified PFMs with alternate layers. The well screen used for this box aquifer was 30 cm in height with Teflon tape placed over the top part to create a screened section 17.5 cm long. The sand was packed to 17.5 cm in depth. An image of this box aquifer setup is displayed in Figure 4-5. Contaminants in this set of box aquifer tests includes methanol, 1,4-dioxane, and methylene chloride.

The first series of tests with this design were focused on Methanol capture. A contaminant solution of approximately 50 ppm methanol, 1,4-dioxane, and methylene chloride was used. Four of these tests were completed, each with the same flowrate and same concentration but with a different duration, or number of pore volumes, passed through the PFM. Durations were chosen based on the data from the column tests. A one hour deployment duration would be needed to test the PFMs before the expected methanol breakthrough. Durations were chosen based on percent breakthrough expected in the PFM based on the column test. It was expected that the standard PFM would have breakthrough and show a significant amount of error in methanol flux measurements during the tests. 1,4-dioxane and methylene chloride flux were expected to be accurately measured by the standard PFMs in these tests since breakthrough for these contaminants should not occur at the low durations. Since this set of PFMs were tested for short durations, Darcy flux was not measured since it would have a high error, thus GAC without impregnated tracers was used.

The next series of tests on this PFM modification focused on the capture of 1,4-dioxane. A contaminant solution of 200 ppm 1,4-dioxane and 50 ppm methanol and methylene chloride was used. The high concentration was used for 1,4-dioxane in order to achieve contaminant breakthrough in the standard PFMs for these tests. GAC with tracers on it was used in order to measure Darcy flux which would help calculate a correction factor for the modified portion of the PFMs. Three PFMs were tested here with three, six, and thirteen day deployments. It was expected that there would be error in the 1,4-dioxane flux measurements for all three of these tests in the standard PFM portion due to contaminant breakthrough in the PFM. Methanol was expected to have a significant amount of error in the standard PFM flux measurement. Breakthrough of methylene chloride should not occur at these deployment durations with a low concentration of 50 ppm. The expectation was that the modified portion of the PFM would not have contaminant breakthrough during this set of box tests, although it was expected that breakthrough of Methanol may occur.

f. Results

Results from the box aquifer tests are shown in Figure 4-6, Figure 4-7, Figure 4-8, and Figure 4-9. The Darcy flux measurements from the three long duration tests are displayed in Figure 4-6. The actual applied Darcy flux is plotted against the PFM measured Darcy flux, with a 1:1 line plotted for reference. In order for the PFM measurements to be considered accurate the plotted points should fall near the 1:1 line. The Darcy flux measured by both the standard and modified portions of the PFMs are displayed, as well as the modified PFM after a correction factor had been determined and applied. The corrected convergence factor used was 0.25, since this was the average difference in the Darcy flux measurements between the standard and modified portions of the PFM. The Darcy flux measurement from the modified PFM was then divided by the corrected convergence factor.

Figure 4-7, Figure 4-8, and Figure 4-9 show the PFM contaminant flux measurements, with the actual applied contaminant flux plotted against the PFM measured contaminant flux. Figure 4-7 (A) shows the methanol flux measured from the standard portion of the PFM, and 4-7 (B) shows the methanol flux measured from the modified portion of the PFM after the corrected convergence factor of 0.25 had been applied. Breakthrough of methanol occurred in both the standard and modified portions of the PFM, which is interpreted from Figure 4-7 since the slope of the actual to measured flux is well below one. This data indicates that the modification made to the PFM would still not be adequate for an accurate measurement of the methanol flux.

Figure 4-8 (A) shows the 1,4-dioxane flux measured from the standard potion of the PFM and 4-8 (B) shows the 1,4-dioxane flux measured from the modified portion. This data is promising for the selected modification. The data points plotted at a lower actual flux were from the tests done with a solution concentration of 50 ppm 1,4-dioxane. The three data points plotted at the higher actual flux values are from the 3, 6, and 13 day box aquifer tests, when a concentration of 200 ppm 1,4-dioxane was used in the contaminant solution. From Figure 4-8 (A) a portion of the standard PFM did not accurately measure 1,4-dioxane flux due to contaminant overload and breakthrough on the GAC at the higher flux. Based on the column test data breakthrough should have occurred at this point, as was seen in the data. Figure 4-8 (B) shows that the modified PFM was able to better measure the 1,4-dioxane mass flux, as the slope for this data is much closer to one in the actual vs measured flux plot than the slope for the standard PFM data. Figure 4-9 (A) shows the methylene chloride flux measured from the standard portion of the PFM and Figure 4-9 (B) shows the methylene chloride flux measured from the modified portion. Looking at Figure 4-9 (A) the standard PFM measured the methylene chloride flux very well, as was expected. Figure 4-9 (B) shows that the measurement of methylene chloride flux with the modified PFM good as well, with a slope of approximately 1.

A relationship for quantifying the contaminant mass flux for low partitioning contaminants does exist, and is shown below as Equation 4-1 (Hatfield et al., 2004).

$$J_C = \frac{q_D m_C}{\alpha \pi r^2 b A_{RC} \theta R_{DC}} \qquad (4\text{-}1)$$

In Equation 4-1 J_C is the contaminant mass flux, q_D is Darcy flux, m_C is the mass of contaminant collected on the PFM, α is the convergence factor, r is the radius of the PFM, b is the length of the PFM, A_{RC} is the fraction of the GAC containing the contaminant, θ is the volumetric water content, and R_{DC} is the retardation factor of the contaminant. Equation 4-1 is different from the simplified flux equation typically used in determining PFM measured flux, which is shown below as Equation 4-2.

$$J_C = \frac{1.67 m_C}{\alpha \pi \mathrm{r} b t} \qquad (4\text{-}2)$$

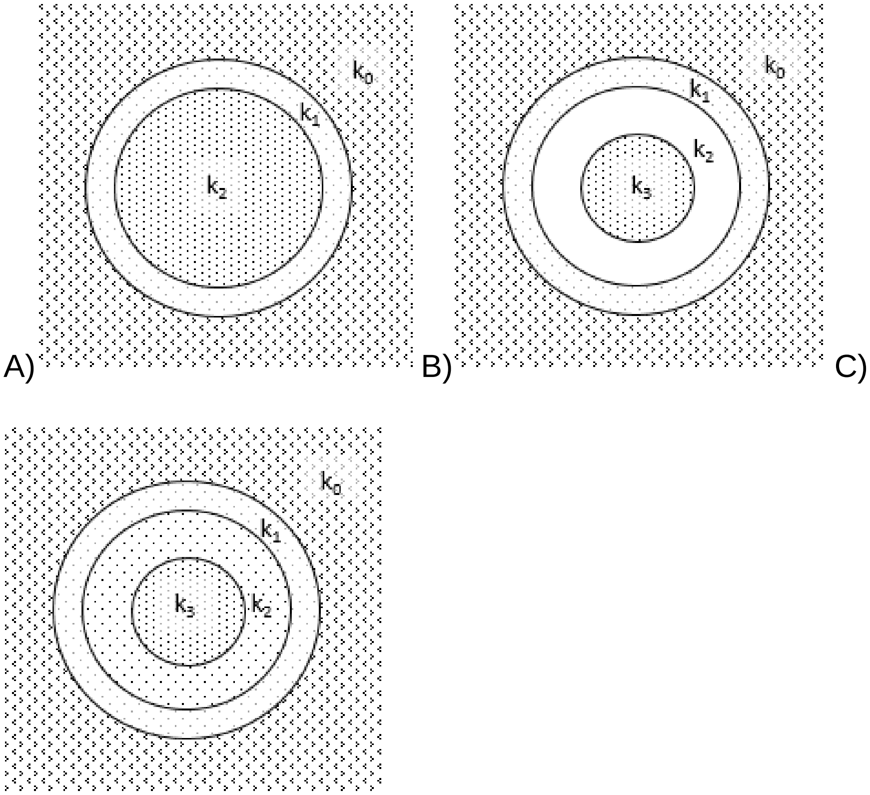
The flux results obtained using Equation 4-1 were compared to the flux calculated from Equation 4-2, which is typically used. Based on the retardation factors calculated from the 1-D column test and the mass collected and Darcy flux data from the PFM box aquifer tests the contaminant flux was calculated with Equation 3-1 for methanol and 1,4-dioxane. Equation 4-1 was only applied for the tests where Darcy flux was measured with tracer data. An A_{RC} value was calculated from Equation 4-3.

$$q_D = \frac{1.67 A_{RC} r \theta R_{DC}}{t} \qquad (4\text{-}3)$$

Figure 4-10 compares the methanol flux for the standard PFM calculated with Equation 4-1 to the methanol flux calculated with Equation 4-2 for the 3, 6, and 13 day box aquifer tests. Figure 4-10 shows that both Equation 4-1 and Equation 4-2 gave almost the same flux measurement for methanol. Figure 4-11 displays the application of both Equation 4-1 and Equation 4-2 to the 1,4-dioxane data. Figure 4-11 shows that Equation 4-1 gave a 1,4-dioxane flux measurement with slightly more error than Equation 4-2, but the values were similar. Since Equation 4-1 did not allow for flux to be calculated more accurately and it is less simple than Equation 4-2, it would not be beneficial to use it over the standard equation, which here is Equation 4-2.

g. Conclusions

An error analysis was completed comparing the error in flux measurements with standard PFMs and modified PFMs. Table -7 summarizes the average error in each contaminant flux measurement for both the standard and modified portions of the PFMs. Table B-6, showing the percent error for each individual PFM box aquifer test, can be found in Appendix B. A previously stated error in standard PFM measurements is about 30% (Annable et al., 2005,Goltz et al., 2007). For methanol flux, an error much greater than 30% was observed in both the standard and modified PFMs. In all box aquifer tests there was breakthrough of the low-partitioning compound methanol. While the error in the standard PFM was 80% for methanol flux, it was 66% in the modified PFM. Although the error in the modified PFM is lower than the error in the standard PFM, both PFMs have error that is significant, so neither PFM technique would be recommended for obtaining methanol flux. The amount of error in the 1,4-dioxane flux measurements was low enough for both methods to be considered suitable techniques. The average standard PFM error was 25% and the average modified PFM an error was 17%. The shorter duration tests did not have any 1,4-dioxane breakthrough in the standard PFM, so only the error in the long duration tests with breakthrough should be compared to determine the effectiveness of the modified PFM. Table 4-8 shows the error in 1,4-dioxane flux measurements for each PFM box aquifer test and indicates the tests in which breakthrough occurred. When averaging the error in the tests with breakthrough, the standard PFM error was 41% and the modified PFM error was only 21%. This demonstrated that the modified PFM performed better than the standard PFM in measuring the 1,4-dioxane flux when breakthrough occurred. The amount of error in the methylene chloride flux measurements was reasonable, with the standard PFM averaging an error of 16% and the modified PFM an error of 34%. Breakthrough of methylene chloride did not occur in any of the tests. While the error for this contaminant is on the high side for the modified PFM, it still gives a reasonable flux approximation.



5. Figure 4-1. Top view diagrams for PFMs modified with a high hydraulic conductivity zone. A) Standard PFM, B) 1” PFM in a 2” well screen, C) 1” PFM surrounded by gravel.

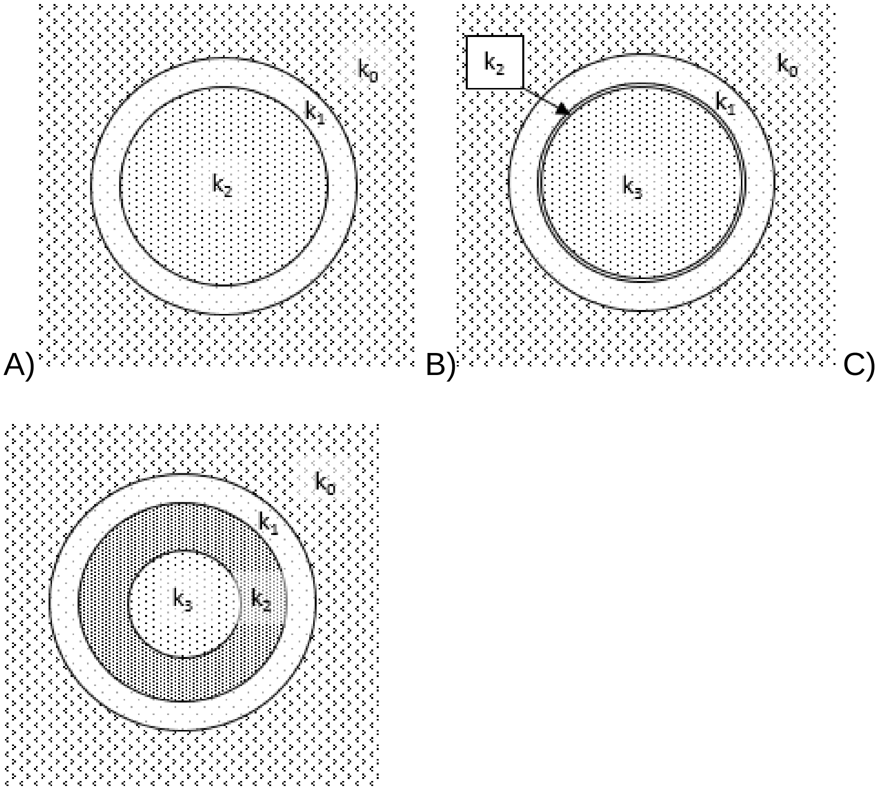


Figure 4-2. Top view diagrams for PFMs modified with a low hydraulic conductivity zone. A) Standard PFM, B) 2” PFM with modified fabric, C) 1” PFM surrounded by 100 – 140 mesh sand.

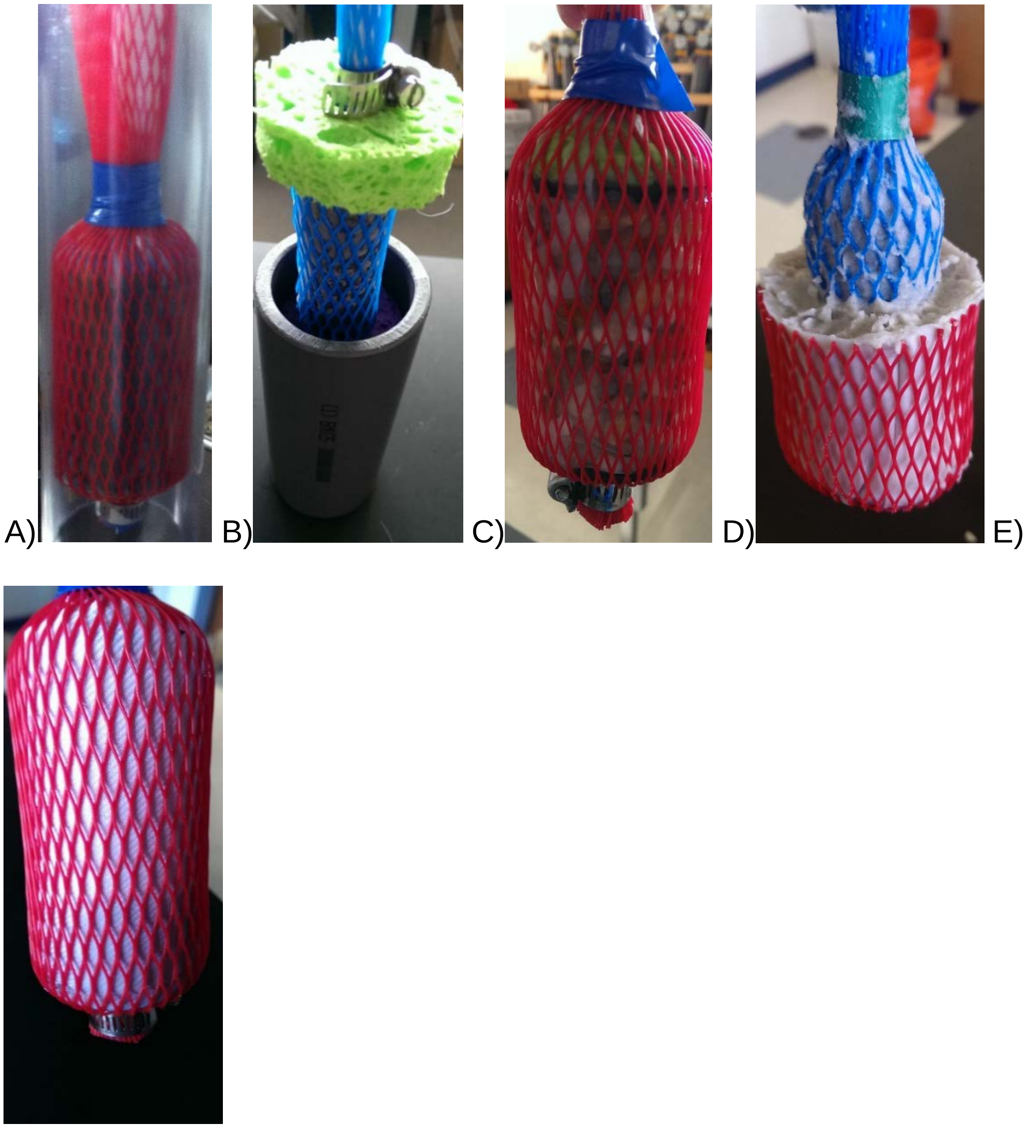


Figure 4-3. Images of PFMs tested in initial screening of modifications. A) Standard PFM, B) 1” PFM in a 2” well screen, C) 1” PFM surrounded by gravel, D) 1” PFM surrounded by 100 – 140 mesh sand, E) 2” PFM with different fabric (polyester in this photo).

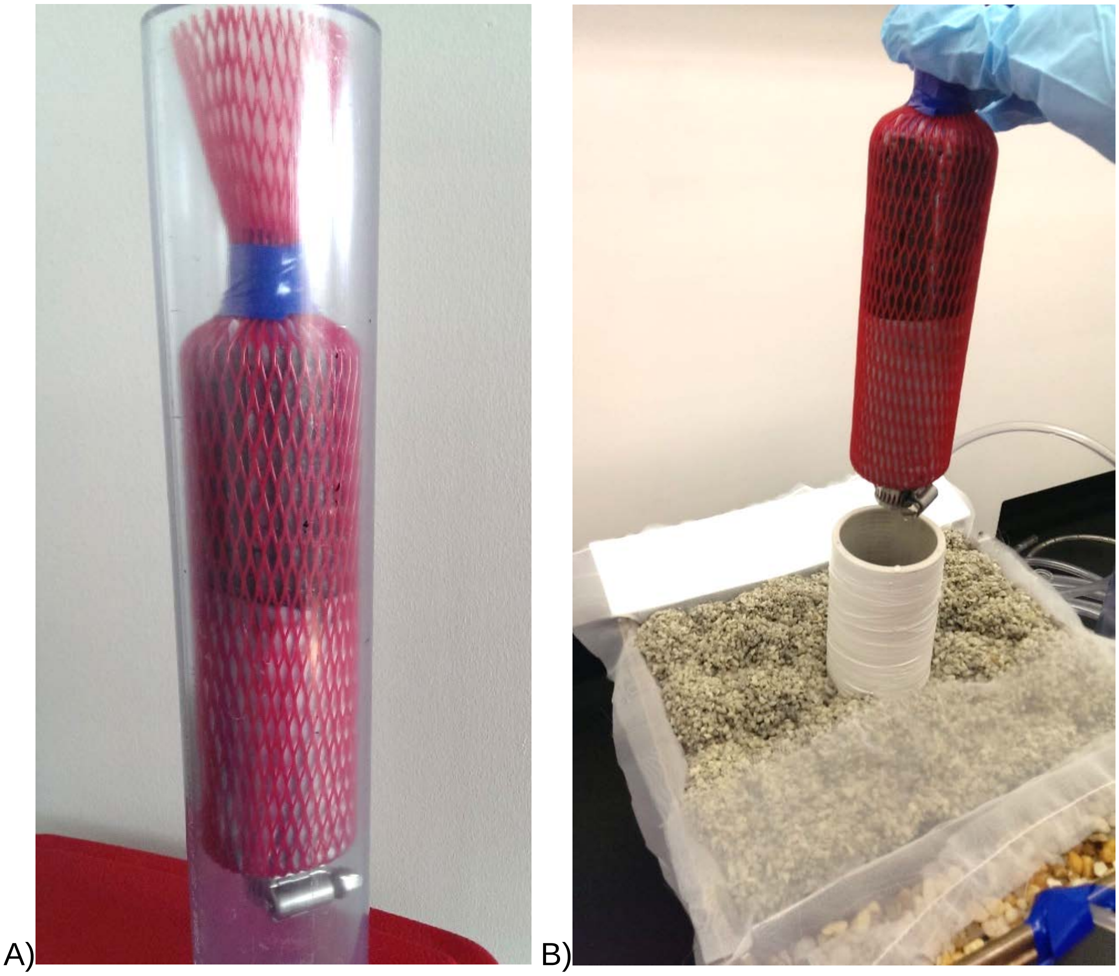


Figure 4-4. Images of the PFM design that was extensively tested. Alternating layers were used. The top layer is the standard PFM portion and the bottom layer is the modified PFM portion. A) Modified design in clear PVC tube ready to deploy, B) Modified PFM being deployed in the box aquifer.

Figure 4-5. Box aquifer setup for extensive testing on the modified PFM design. Photo courtesy of Meghan Thiemann.

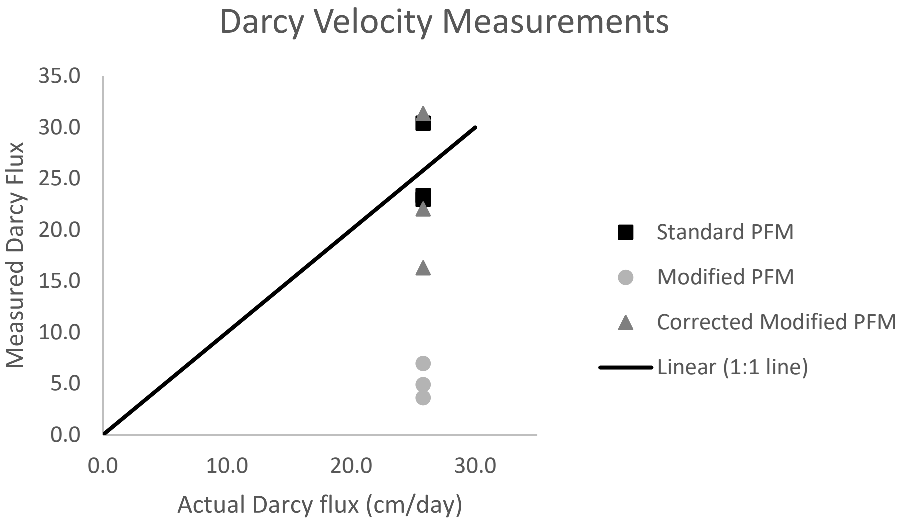


Figure 4-6. Darcy flux measurements from the extensive box aquifer tests on the two layer design. The measurements from the standard PFM are shown by the grey diamonds. The measurements from the modified PFM with 97%/3% cotton/spandex before a correction factor was applied are shown by the light grey circles. The Darcy flux measured after the values from the modified PFM were corrected are shown by the black squares.

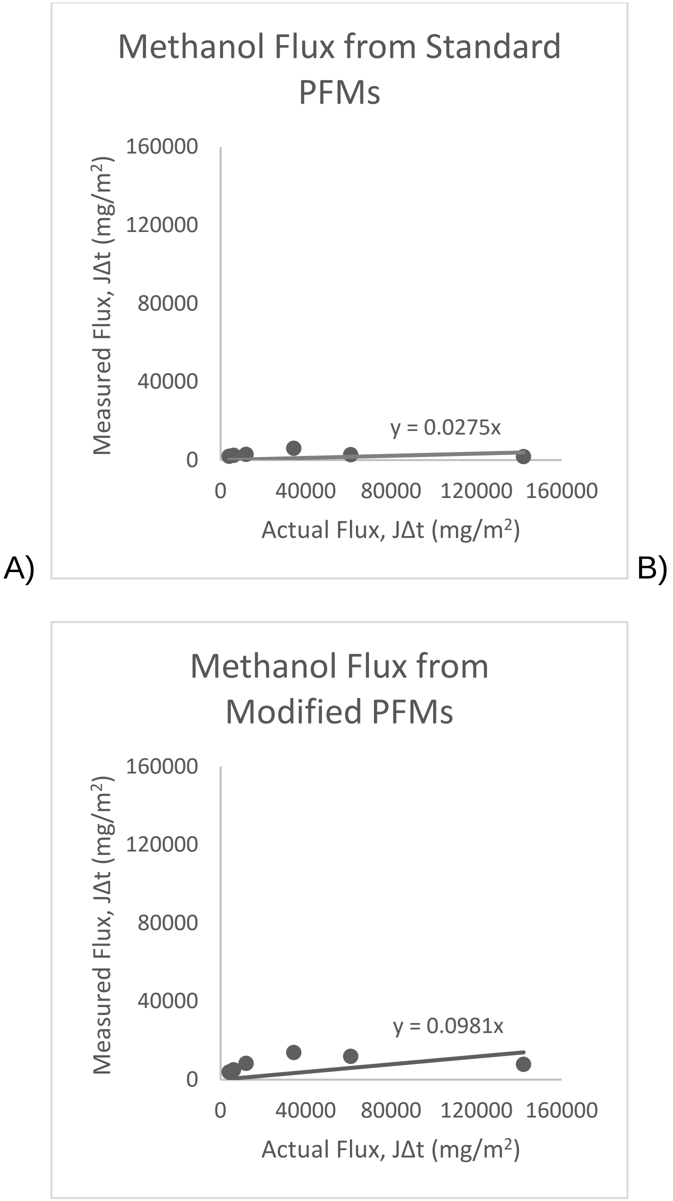


Figure 4-7. Methanol flux measurements from the PFM versus the actual flux values. A) Standard PFM flux measurements, B) Two layer modified PFM with 97%/3% cotton/spandex flux measurements after the correction factor is applied.

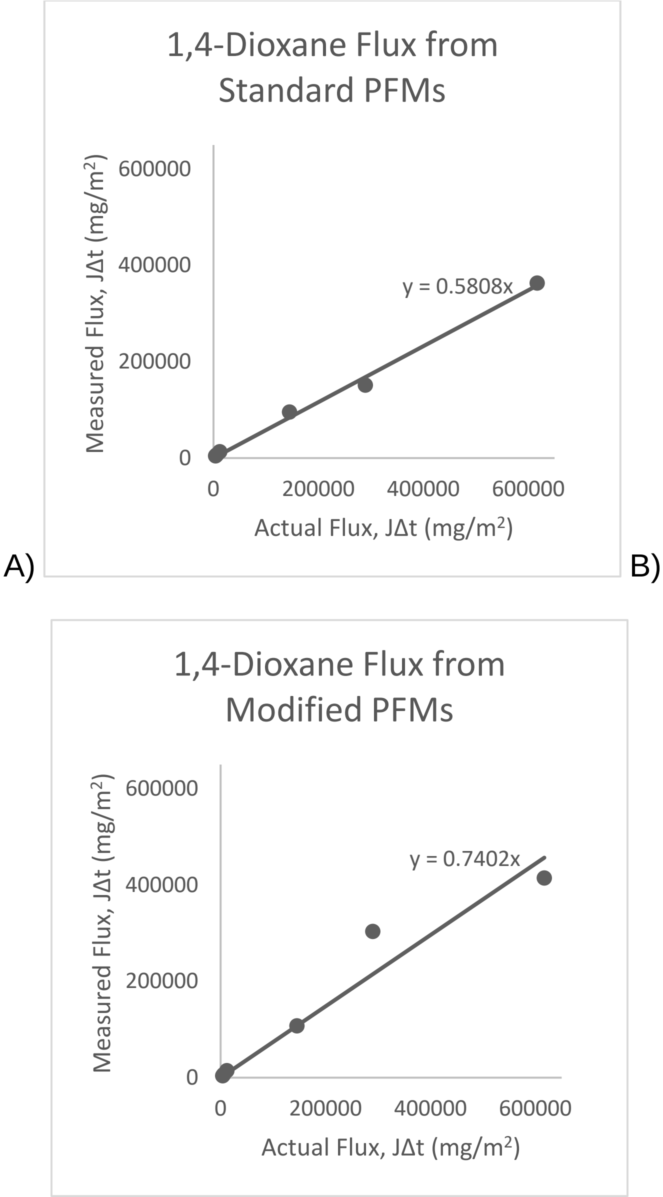


Figure 4-8. 1,4-dioxane flux measurements from the PFM versus the actual flux values. A) Standard PFM flux measurements, B) Two layer modified PFM with 97%/3% cotton/spandex flux measurements after the correction factor is applied.

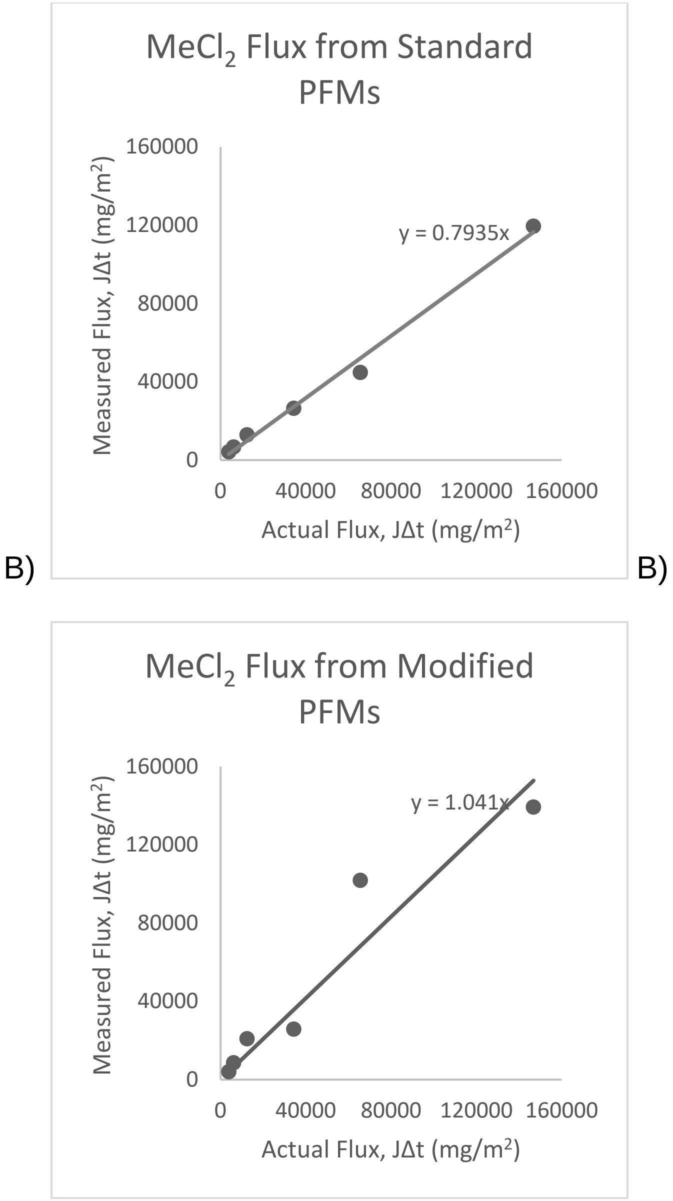


Figure 4-9. Methylene chloride flux measurements from the PFM versus the actual flux values. A) Standard PFM flux measurements, B) Two layer modified PFM with 97%/3% cotton/spandex flux measurements after the correction factor is applied.

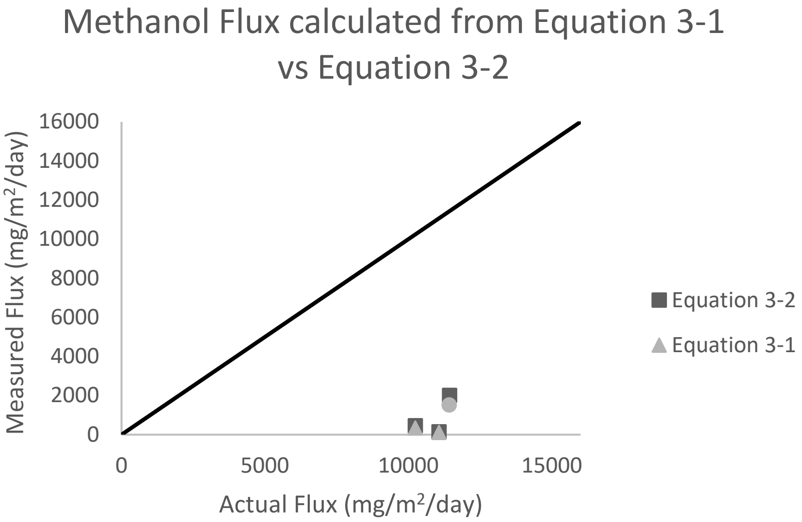


Figure 4-10. Methanol flux calculated from Equation 3-1 compared to the flux calculated from Equation 3-2 for the data from the standard PFMs in the box aquifer tests.

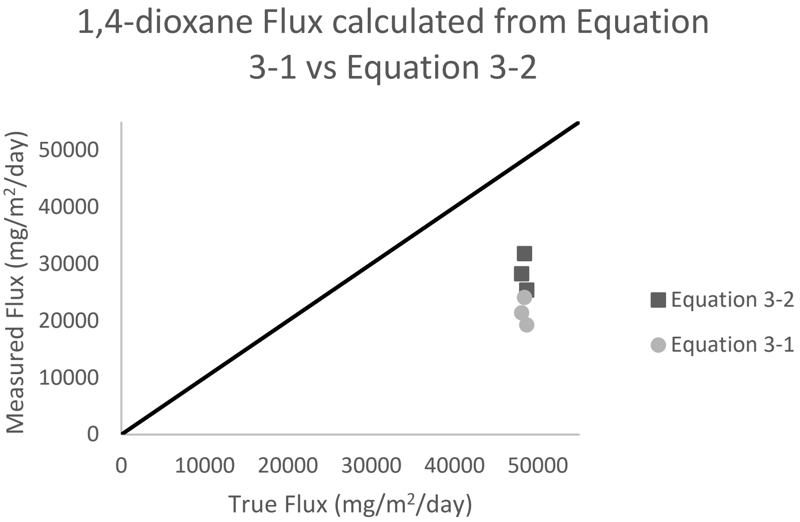


Figure 4-11. 1,4-dioxane flux calculated from Equation 3-1 compared to the flux calculated from Equation 3-2 for the data from the standard PFMs in the box aquifer tests.

Table 4-1. Actual and measured Darcy velocities for box aquifer tests.

Type of PFM	Actual Darcy flux (cm/day)	Measured Darcy flux (cm/day)	Difference in q (Actual/Measured)
Standard PFM	27.6	24.2	1.1
1" PFM with ½" empty annular gap	27.6	7.1	3.9
1" PFM with gravel	27.8	21.9	1.3
1" PFM with sand	27.6	2.3	12.0
2" PFM with 97% Cotton fabric	27.6	7.8	3.5
2" PFM with Polyester fabric	27.8	2.0	14.1
2" PFM with Duckcloth	27.8	0.7	37.7

Table 4-2. Actual and measured 1,4-dioxane flux for box aquifer tests.

Type of PFM	Actual Flux ($mg/m^2/day$)	Measured Flux ($mg/m^2/day$)	Flux Difference (Actual/Measured)
Standard PFM	2792	2023	1.4
1" PFM	2672	518	5.2
1" PFM with gravel	2701	1642	1.6
1" PFM with sand	2665	101	26.3
2" PFM with 97% Cotton fabric	2686	529	5.1
2" PFM with Polyester fabric	490	115	4.2
2" PFM with Duckcloth	489	36	13.7

Table 4-3. Percent difference in the actual applied Darcy flux and 1,4-dioxane flux and the PFM measured values.

Type of PFM	Percent difference in Darcy flux (%)	Percent Difference in 1,4-dioxane flux (%)
Standard PFM	13	32
1" PFM	118	135
1" PFM with gravel	24	49
1" PFM with sand	169	185
2" PFM with 97% Cotton fabric	112	134
2" PFM with Polyester fabric	174	124
2" PFM with Duckcloth	190	173

Table 4-4. Actual and measured Darcy velocities for box aquifer tests at low Darcy flux.

Type of PFM	Actual Darcy flux (cm/day)	Measured Darcy flux (cm/day)	Difference in q (Actual/Measured)
2" PFM with 97% Cotton fabric	5.0	5.4	0.9
1" PFM with sand	5.0	2.3	2.1

Table 4-5. Actual and measured 1,4-dioxane fluxes for box aquifer tests at low Darcy flux.

Type of PFM	Actual Flux (mg/m^2/day)	Measured Flux (mg/m^2/day)	Flux Difference (Actual/Measured)
2" PFM with 97% Cotton fabric	486	414	1.2
1" PFM with sand	477	71	6.7

Table 4-6. Percent difference in the actual applied Darcy flux and 1,4-dioxane flux and the PFM measured values for the tests with low Darcy flux.

Type of PFM	Percent difference in Darcy flow (%)	Percent Difference in 1,4-dioxane flux (%)
2" PFM with 97% Cotton fabric	7	16
1" PFM with sand	72	148

Table 4-7. Percent errors in PFM flux measurements for the standard PFMs and modified PFMs for each contaminant.

Methanol (% error)		Methylene Chloride (% error)		1,4-dioxane (% error)	
Standard PFM	Modified PFM	Standard PFM	Modified PFM	Standard PFM	Modified PFM
79.1	66.2	16.3	34.1	25.4	17.1

Table 4-8. Comparison of percent error in standard and modified PFM 1,4-dioxane flux measurements with breakthrough and without breakthrough.

Breakthrough?	Standard PFM Percent Error	Modified PFM Percent Error
No	16	9
No	8	9
No	5	21

Yes	34	26
Yes	48	5
Yes	41	33

5. Evaluation of a Diffusion Based PFM

Another proposed method for capturing low partitioning contaminants by use of a PFM is to incorporate a diffusion domain into the flux meter. Passive diffusion bag (PDB) samplers that allowed for both accurate and inexpensive methods for measuring VOC concentrations in groundwater have been extensively tested (Ma et al., 2013,Vroblesky and Campbell, 2001). The sampler consists of low-density polyethylene (LDPE) tubes filled with deionized water and sealed at each end. Polyethylene is low-cost and has a simple chemical structure, making it ideal for passive samplers (Lohmann, 2012). Contaminants partition across the LDPE into the DI water, following the local concentration gradient. Over time the concentration in the water in the PDB would be equal to the concentration in the surrounding groundwater. This idea could possibly be incorporated into a PFM to capture contaminants that are not well retained by the GAC. One method of incorporating the PBD sampler would be to keep the diffusion domain filled with water, and place it inside a PFM. This would allow simultaneous measurement of the Darcy flux and contaminant concentration. The Darcy flux would be measured through use of eluting tracers as in the standard PFM, and the contaminant concentration would be measured by the PDB sampler inside the PFM. It would take a longer time for the PDB sampler to reach equilibrium with the surrounding water, so the deployment time of the flux meter would be long enough to accurately measure the water flux from the tracers. An alternative approach is to fill the PDB sampler with GAC. This would allow for continuous capture of the contaminants and would not depend on reaching an equilibrium state. The presence of GAC would require a much longer duration to reach maximum capacity because only the contaminants that partitioned across the LDPE would be captured.

a. Diffusion Batch Experiments

i. Preliminary Batch Experiments

Static batch tests were completed to test the application of the PDB to low partitioning contaminants (Vroblesky and Campbell, 2001). The contaminants used in these tests include 1,4-dioxane, methylene chloride, 1,1-DCE, and 1,2-DCE. 1,1-DCE and 1,2-DCE are not considered low-partitioning contaminants, but they were used in these tests for comparison since they were predicted to diffuse across the LDPE (Vroblesky and Campbell, 2001). Unlike the other tests, methanol is not used here because alcohols do not partition through polyethylene (Baner and Piringer, 1991,Divine and McCray, 2004). Two types of media inside the diffusion domain were tested and compared, deionized water and GAC. In the first batch test dry GAC was used, and in the other tests wet GAC was used.

First, a simple batch test was conducted. This consisted of placing sample vials inside a jar filled with a contaminant solution for one week. Twenty milliliter vials were used as the sample chambers. A one liter jar was used to hold both a sample vial with dry GAC and a sample vial with water. Two 250 mL jars were used, one for a sample vial with water and one for a sample vial with dry GAC. The 1 L jar with both types of samples would be compared to the jars with an individual sample to see the effect of multiple samples in one jar on the time to equilibrium. Once a 20 mL sample vial was filled with the sample material, a square piece of polyethylene plastic was placed over the opening. The plastic screw cap was then secured over the polyethylene to close the container. An opening was made in the septa that was the size of the plastic cap opening with an area of 1.54 cm^2. This allowed the polyethylene to be exposed. The sample vials were placed inside their respective containers, then the contaminant solution was added and the lid then secured. A sample of the initial contaminant solution was collected. After six days, the jars were opened and the final jar solution was sampled. Water samples were collected from the diffusion vials. The GAC in the other vials was transferred to 40 mL vials and an extraction solution, IBA, was added. These 40 mL vials were put on the rotator for about 24 hours (Annable et al., 2005), and the extraction solution was transferred to GC vials and analyzed by the GC-FID. This same test was performed with 20 mL vials with an aluminum crimp cap instead of the 20 mL vials with a screw cap, and these jars only sat for two days before sampling. The opening on the aluminum caps was 0.64 cm^2, which is smaller than the previous caps used, however the aluminum caps were more secure.

Based on the results of this initial test it did not appear that there was a significant difference in the jar that contained both a water and GAC diffusion vial and the jars that contained only a single diffusion vial. Table 5-1 shows results of the diffusion vials with water in them by displaying the percentage that each contaminant reached equilibrium between the water in the diffusion vial and the water in the jar that contains the diffusion vial. While 1,1-DCE, 1,2-DCE, and methylene chloride partitioned well through the LDPE barrier, 1,4-dioxane did not, only reaching 0.2% of equilibrium. At 100% equilibrium the contaminant concentration in the water in the diffusion vial would equal the contaminant concentration in the water in the jar. 1,4-dioxane is s hydrophilic polar molecule, so this may be the reason that it did not partition well across the LDPE membrane. Studies on diffusion samplers indicate that hydrophilic polar molecules will diffuse slowly through the plastic or they will not diffuse through at all (Ehlke et al., 2004). In 2013, Ma et al. used Equation 5-1 to fit their data collected from contaminant diffusion experiments similar to the ones conducted in this study, where $C_s(t)$ is the contaminant concentration in the diffusion sample, $C_{s,e}$ is the contaminant concentration in the diffusion sample at equilibrium, D_m is the diffusion coefficient for the contaminant in the LDPE, A is the exposed area of LDPE, t is the time from the test start until sampling, V_s is the volume of water in the diffusion vial, and L_m is the LDPE thickness.

$$C_s(t) = C_{s,e}\left(1 - \exp\left(\frac{-D_m A t}{V_s L_m}\right)\right) \qquad (5\text{-}1)$$

From the data collected for the diffusion vials with water in the initial diffusion batch test Equation 5-1 was used to predict the amount of time it would take for the contaminants to reach equilibrium. This could not be done for the diffusion vials with GAC because these samples would not reach equilibrium, since the GAC would continuously sorb the contaminant once it partitioned through the LDPE barrier. First, the diffusion coefficient for each contaminant was calculated using a contaminant concentration and time from the experiment. After calculating the diffusion coefficient Equation 5-1 was used to plot the predicted concentration in the diffusion vial at a specific time and estimate when the sample would reach equilibrium. This plot is shown in Figure 5-1.

The diffusion vials with GAC were expected to capture a higher amount of contaminant than the diffusion vials with only water, however the reverse occurred, with the water samples containing a higher mass of each contaminant than the GAC samples.

Dry GAC had been used, but was sitting at the bottom of the vial. The phase directly on the other side of the LDPE in the jars containing the diffusion vials with GAC was air, so this could possibly be a reason for less mass partitioning into the GAC diffusion samples.

Based on the results of the initial diffusion tests, a longer test was designed. This batch test was conducted in order to determine the time required for each contaminant in the system to reach equilibrium. Although 1,4-dioxane did not appear to partition through the LDPE it was still used in this test to see if any more would partition through over a longer time interval. In this batch test the 20 mL vials with the aluminum caps were used. The septa was completely removed from the caps and replaced by Teflon that had been cut to fit just inside the cap, with a hole punched the size of the opening on the aluminum cap that was 0.64 cm^2. The Teflon and aluminum cap was used instead of the plastic cap and the normal septa, which consisted of a Teflon side and a rubber side, to prevent mass loss from contaminants partitioning into the plastic. 250 mL jars were used and each jar contained a single vial. Two setups were run in parallel, one set containing water sample vials, and the other set containing GAC sample vials. The GAC sample vials were filled with GAC and water this time, having as little air as possible to prevent any losses from volatilization of the chlorinated contaminants and the possibility of air on the other side of the LDPE potentially inhibiting partitioning. Each setup consisted of eight 250 mL jars. One jar was used as a control without a sample vial. The other jars would be sampled at 1, 2, 4, 7, 10, and 14 days. The control was sampled on day 14 of the batch tests. An image of these jars with the sample vials inside is displayed in Figure 5-2. After sampling the first few sets, it appeared that the water samples were reaching equilibrium at a slower rate than had been anticipated, thus more jars with both water and GAC diffusion samples were prepared. These new sets were sampled at 3 weeks and 4 weeks. To determine the effect of packing a media around the diffusion vial, a set of jars with glass beads was tested. These were setup like the other systems with glass beads placed around the diffusion vials. The contaminant solution was then poured in to fill the pores between the glass beads. The set of jars with glass beads were sampled at 7 days and the results were compared to a jar sampled at 7 days not containing the glass beads.

The results of this longer diffusion test are shown in Figure 5-3, Figure 5-4, Figure 5-5, Figure 5-6, and Figure 5-7. When comparing Figure 5-3 to the predicted results from the initial test in Figure 5-1 it can be seen that equilibrium took longer to reach than had been predicted. When plotted as a log-log plot the results are linear, as shown in Figure 5-4. The 1,4-dioxane data is not shown in the plots because it did not partition through the LDPE as was seen in the first test.

Figure 5-5, Figure 5-6, and Figure 5-7 compare the contaminant mass collected in the GAC diffusion vials to the contaminant mass collected in the water diffusion vials, with Figure 5-5 for 1,1-DCE, Figure 5-6 for methylene chloride, and Figure 5-7 for 1,2-DCE. These plots reflect the expected results with water samples reaching equilibrium in contrast to the GAC diffusion vials which continue to accumulate mass and do not reach equilibrium. They also indicate that the water filled diffusion samplers accumulate mass at a faster rate initially.

The jars with the glass beads captured less mass than the jars without the glass beads as expected. The contaminants in the water diffusion vials in the jar with glass beads had reached about half the mass required for equilibrium compared to the jar without the glass beads present. If a diffusion sampler were placed inside a PFM, this indicates that it will take longer for contaminant capture when the diffusion domain is surrounded by an inert media rather than having direct contact with the contaminated water.

ii. Diffusion Plastic Bag Batch Experiments

An additional batch test was completed in an effort to achieve faster equilibrium times than in previous tests. A major factor effecting equilibration time is the surface area of the LDPE (Vroblesky and Campbell, 2001). The same contaminants were used, but rather than using 20 mL vials with the LDPE over the opening, a LDPE bag was employed. These bags were 2 mm thick LDPE and constructed using a food sealer. The LDPE contact area was be much greater for the diffusion bags than for the 20 mL diffusion vial. While the average surface area for the LDPE over the 20 mL vial opening was 0.64 cm^2, the average surface area for the LDPE bags was 46 cm^2, giving the LDPE about 66 times more surface area for the LDPE. 1,4-dioxane was still used as a contaminant in this test. Some of the LDPE bags were filled with deionized water, and others were filled with wet GAC. Procedures were similar to the batch experiments described above. Three jars were tested for diffusion bags filled with water and were sampled at 1, 2, and 3 days. It was expected that after one day all chlorinated contaminants would reach equilibrium between the water in the diffusion bag and the surrounding jar solution. All three jars had the same contaminant concentrations. Four jars were set up for the diffusion bags filled with GAC. Durations were 1, 3, 5, and 9 days.

Table 5-2 shows the results for the diffusion bags with water. As expected, the samples of deionized water in the diffusion bags came to equilibrium with the surrounding jar's solution after a period of one day, with the exception of 1,4-dioxane.

While 1,4-dioxane continued to exhibit low partitioning through the LDPE, it did reach 3% of equilibrium with the diffusion bag, much greater than was seen in the diffusion vials. Figure 5-8, Figure 5-9, Figure 5-10, and Figure 5-11 display the results for the diffusion plastic bags with GAC. The amount of contaminant adsorbed by the GAC in these tests was much greater than the amount that came to equilibrium with the diffusion bags filled with water, even after only 1 day. In the jar sampled on day 9 almost all the initial 1,1-DCE and 1,2-DCE mass was captured by the GAC in the diffusion bag.

iii. Box Aquifer Tests, PFMs with a Diffusion Domain

The diffusion bags described above in Section 4.2.2 were tested in the box aquifer as was done for the standard PFMs in Section 2.2 and the modified low permeability PFMs described in Chapter 3. Both the diffusion bags filled with GAC and diffusion bags filled with water were tested. A two layer PFM was made. The diffusion bag with GAC was placed in the bottom layer of the PFM, with course sand packed around it, and the diffusion bag with water was in the top layer. The crinoline socks material used in the standard PFM was used to hold the course sand and diffusion bag. There were 5 PFMs with diffusion domains tested, with the shortest deployment duration being 2 days and the longest 13 days. The diffusion bags with water all came to equilibrium with the contaminant solution passed through the box, which was 40 ppm $MeCl_2$ and 1,2-DCE and 25 ppm trichloroethylene (TCE). The amount of mass collected was the same regardless of deployment duration, so there could be no flux correlation with the diffusion bags with water. The results of the diffusion bags containing GAC are shown in Figure 5-12 and Figure 5-13. Figure 5-12 displays the contaminant mass collected for each PFM deployed, and it shows a linear increase in mass collected over time. It can be inferred from the linear results that the flux could be easily determined based on the mass collected by the GAC in the diffusion domain. The amount of mass collected by each diffusion domain was then compared to the actual flux that was passed through the PFM with the diffusion domain. This data is displayed in Figure 5-13. Again, the results are linear. The plot of the mass collected versus contaminant flux can be used as a calibration curve. If a PFM with the GAC diffusion domain were deployed at a contaminated site, then the contaminated mass collected by the GAC could be used to directly determine the contaminant flux via the calibration curve.

iv. Conclusions

The evaluations conducted in this study indicate that the incorporation of a LDPE diffusion domain in a PFM is a possibility. This proposed method would not measure flux of contaminants that do not partition through LDPE, such as hydrophilic polar compounds like 1,4-dioxane and alcohols like methanol (Baner and Piringer, 1991,Divine and McCray, 2004,Ehlke et al., 2004). Chlorinated compounds such as methylene chloride, 1,1-DCE, 1,2-DCE, and TCE do partition well through LDPE. The batch tests conducted indicate that a diffusion domain filled with GAC would be favorable over a diffusion domain with water because it would continuously accumulate contaminant mass rather than reaching an equilibrium state. The area of LDPE exposed is a major determinant in the rate of diffusion of the contaminant through the diffusion domain. Since the diffusion vials required a significant amount of time until equilibrium was reached, the diffusion bags are recommended. Diffusion coefficients for each contaminant through the LDPE were estimated from both the diffusion vial and diffusion bag batch tests. The diffusion coefficients are displayed in Table 5-3. These coefficients may not be necessary for flux determination, however, since a calibration curve could be generated from lab tests as was discussed in Section 4.4. Box aquifer tests conducted on the diffusion bags with GAC indicate that it would be suitable for contaminant flux measurements. A possible PFM design is to alternate layers with the diffusion domain as was done for the PFM with modified permeability. One layer would contain the diffusion bag with GAC surrounded by a course sand, and the other layer a standard PFM, allowing the PFM design to simultaneously measure contaminant flux and Darcy flux.

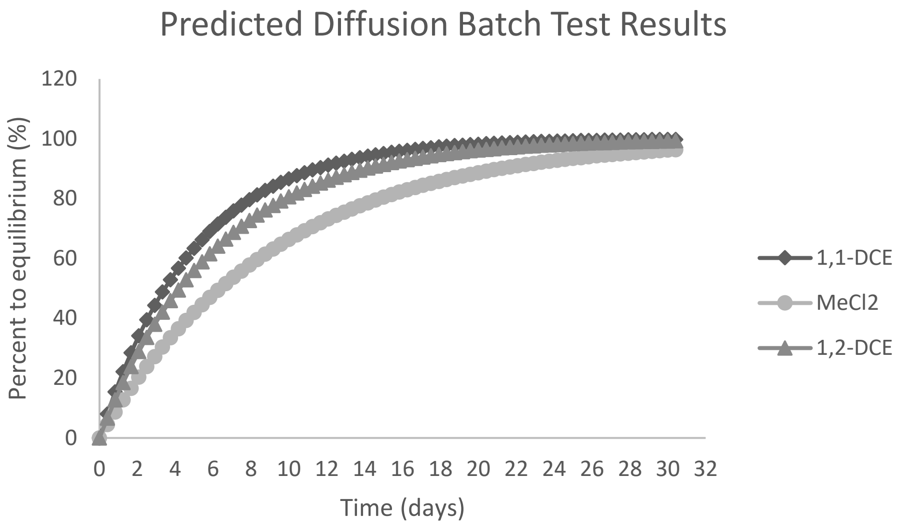


Figure 5-1. Plot of the predicted time until the contaminants reach equilibrium in the static diffusion batch test with the diffusion vials.

Figure 5-2. Image of the static diffusion batch test setup.

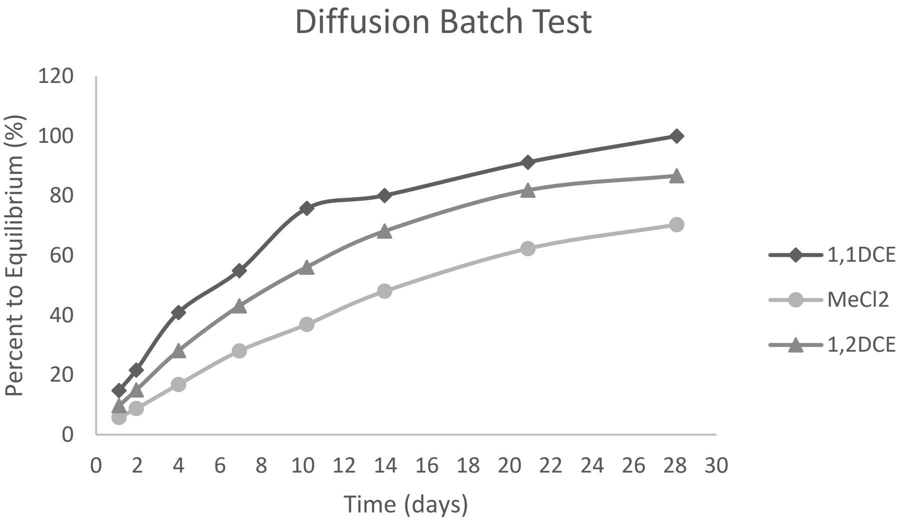


Figure 5-3. Results from the long static diffusion batch test.

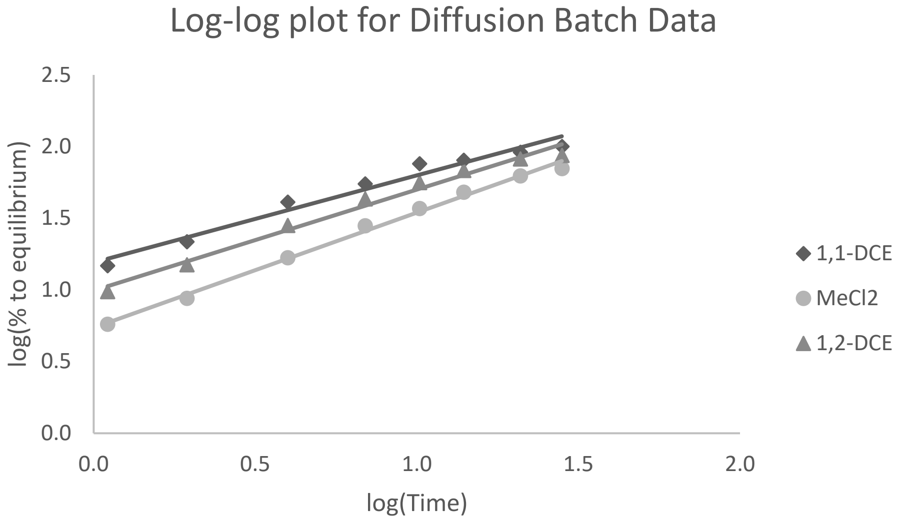


Figure 5-4. A plot of the results from the static diffusion batch test on a log-log plot.

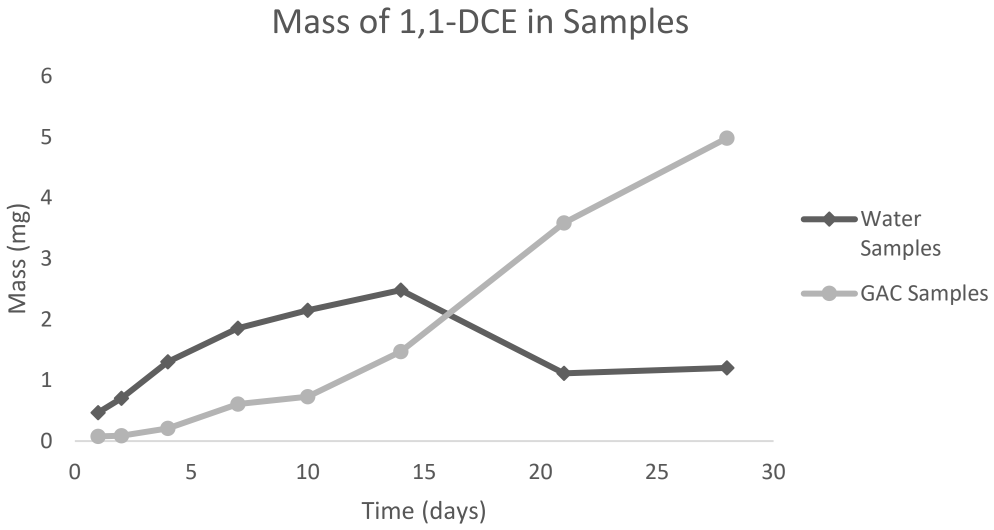


Figure 5-5. A plot of the mass of 1,1-dichloroetylene captured by each diffusion vial for the static diffusion batch test, showing the mass collected by the vials with GAC versus the mass collected in the vials with water.

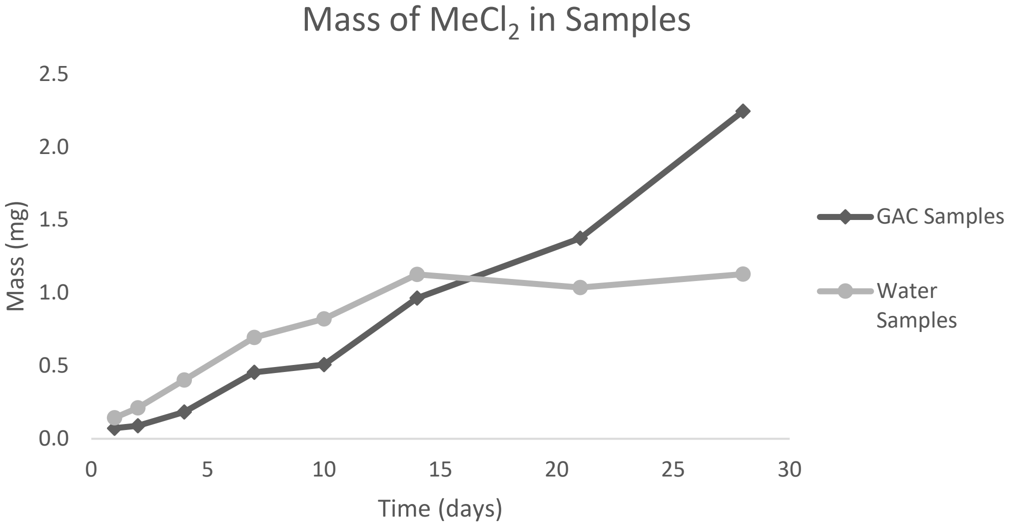


Figure 5-6. A plot of the mass of methylene chloride captured by each diffusion vial for the static diffusion batch test, showing the mass collected by the vials with GAC versus the mass collected in the vials with water.

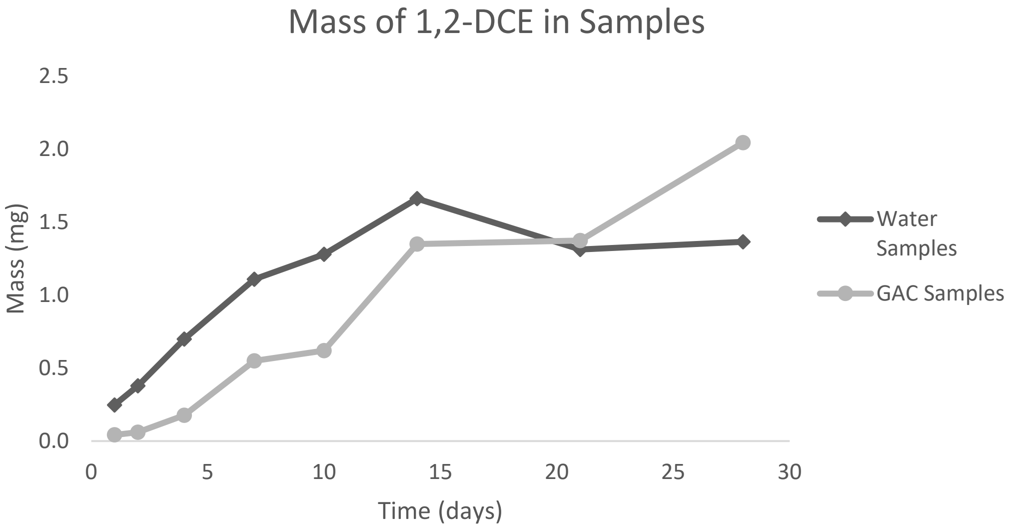


Figure 5-7. A plot of the mass of 1,2-dichloroetylene captured by each diffusion vial for the static diffusion batch test, showing the mass collected by the vials with GAC versus the mass collected in the vials with water.

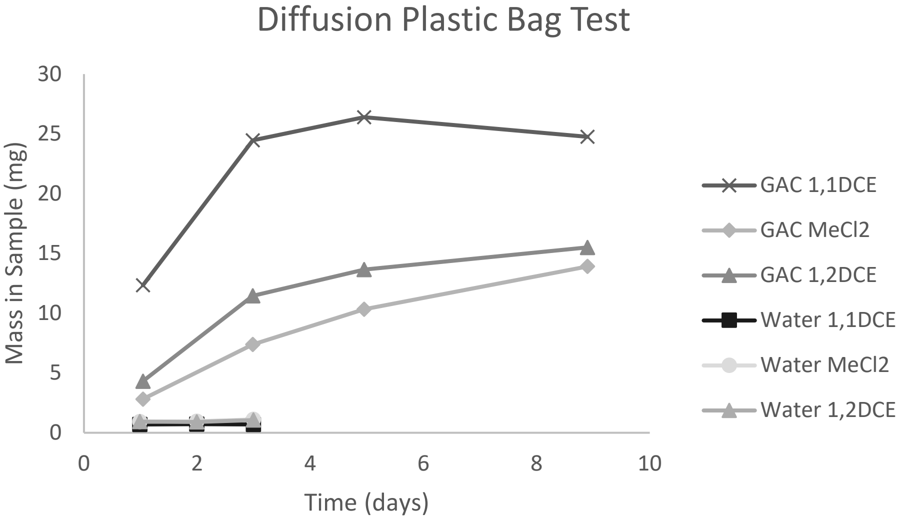


Figure 5-8. A plot of the mass of each contaminant collected in the diffusion plastic bags with GAC and the diffusion plastic bags with water.

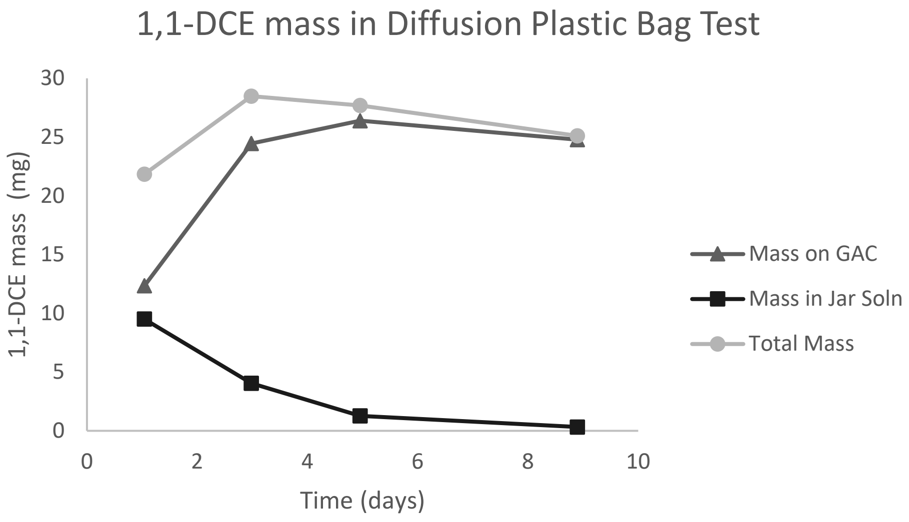


Figure 5-9. A plot of the mass of 1,1-dichloroethylene collected in the diffusion plastic bags filled with GAC compared to the mass in the solution in the jar surrounding the diffusion plastic bag.

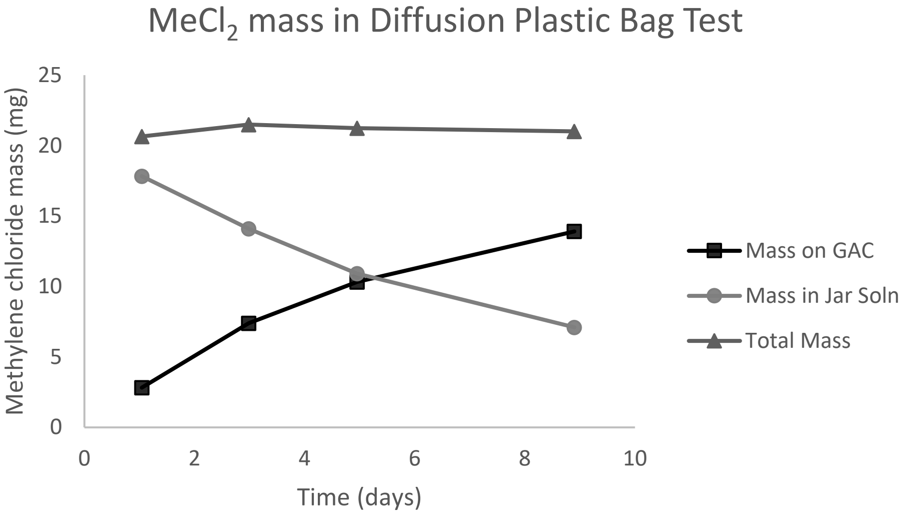


Figure 5-10. A plot of the mass of methylene chloride collected in the diffusion plastic bags filled with GAC compared to the mass in the solution in the jar surrounding the diffusion plastic bag.

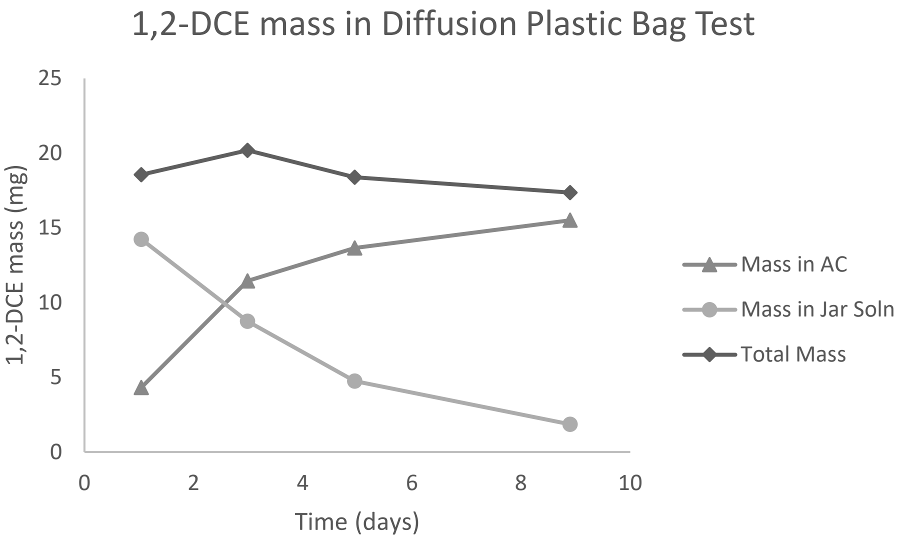


Figure 5-11. A plot of the mass of 1,2-dichloroethylene collected in the diffusion plastic bags filled with GAC compared to the mass in the solution in the jar surrounding the diffusion plastic bag.

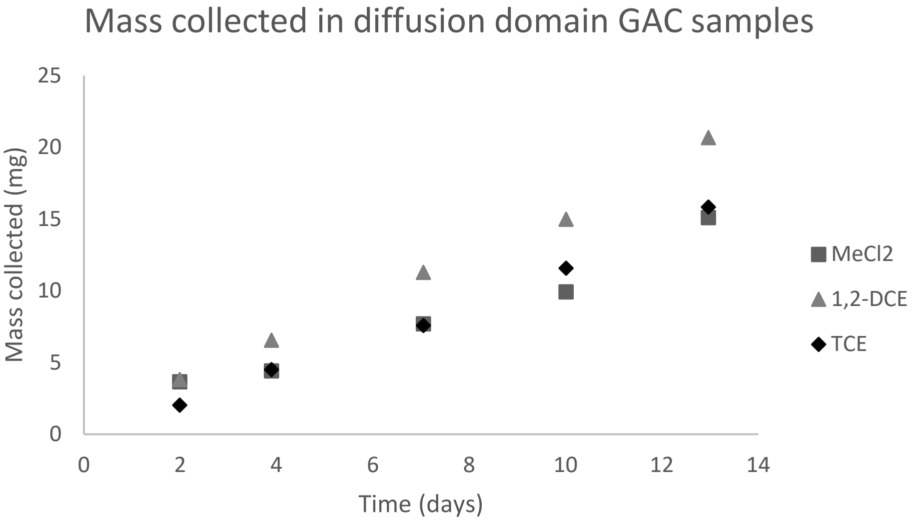


Figure 5-12. A plot of the mass of methylene chloride, 1,2-dichloroethylene, and trichloroethylene collected in the GAC diffusion domains over time.

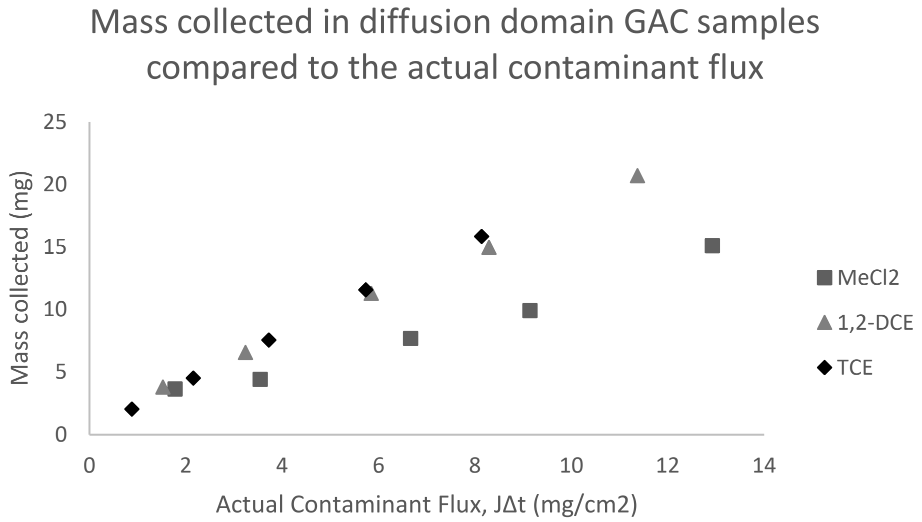


Figure 5-13. A plot of the mass of methylene chloride, 1,2-dichloroethylene, and trichloroethylene collected in the GAC diffusion domains compared to the actual flux through the diffusion domain.

Table 5-1. Percent to equilibrium for the diffusion vial water samples in the initial diffusion batch test.

Time	1,1-dichloroethylene	Methylene chloride	1,2-dichloroethylene	1,4Dioxane
6 days	89	53	74	0.2
6 days	82	50	70	0.2
2 days	30	15	23	0.1

Table 5-2. Percent to equilibrium for each contaminant in the diffusion plastic bag test.

Time	1,1-dichloroethylene	Methylene chloride	1,2-dichloroethylene	1,4Dioxane
1 day	100	96	100	1.1
2 days	101	100	100	2.8
3 days	102	100	101	3.3

Table 5-3. Molecular diffusion coefficients (D_m) from diffusion batch experiments.

Sampler	Media	D_m for 1,1-DCE (cm2/s)	D_m for MeCl2 (cm2/s)	D_m for 1,2-DCE (cm2/s)	D_m for 1,4-dioxane (cm2/s)
Vials	Water	9.0×10^{-7}	3.6×10^{-7}	6.2×10^{-7}	1.6×10^{-9}
Bags	Water	2.9×10^{-7}	1.7×10^{-7}	1.9×10^{-7}	6.7×10^{-10}
Vials	GAC	4.5×10^{-8}	1.7×10^{-8}	2.2×10^{-8}	3.6×10^{-10}
Bags	GAC	3.6×10^{-6}	8.3×10^{-7}	1.9×10^{-6}	2.6×10^{-9}

6. Field 1,4-Dioxane Measurements, Conclusions and Implication for Future Research

The PFM modifications evaluated in this study show potential solutions to obtaining low-partitioning contaminant flux while simultaneously measuring Darcy flux. Based on the results of this study, the PFM with modified permeability may provide accurate flux measurements for 1,4-dioxane. This modification involved the addition of a 97%/3% cotton/spandex fabric over a standard PFM to reduce the permeability and divert water flow. It was unsuccessful in measurement of methanol flux. Methanol is an extreme case, however, since it exhibits partitioning much lower than most contaminants. In this study, only three box aquifer tests were conducted on the modified PFM when 1,4-dioxane breakthrough occurred. To verify the use of the modified design more box aquifer tests with 1,4-dioxane breakthrough occurring in a standard PFM should be performed. If possible, a test that has complete breakthrough for 1,4-dioxane should be performed. It would also be useful to test for the maximum deployment duration of the modified PFM. Further calibration is necessary for the modified PFM. One test of the new design was conducted at a low Darcy flux of 5 cm/day. In this box aquifer test the modified PFM provided measurements similar to the standard PFM, indicating that the change was not significant. This most likely occurred at the lower Darcy flux because diffusion was a major flow component, unlike tests performed at a high flux where most of the flow through the PFM was advective. This design should be further tested at low Darcy velocities to determine its effectiveness.

The use of a diffusion domain with LDPE in a PFM was evaluated in this study. The results as well as previous studies on LDPE diffusion bags indicate that 1,4-dioxane and methanol will not partition well through LDPE. The diffusion bags were still evaluated to determine their applicability in a PFM. GAC was used as the media inside diffusion bags and compared to diffusion bags with water, which have been extensively tested. While the diffusion bags filled with water reach an equilibrium state with the contaminants in the surrounding solution, the diffusion bags with GAC do not. The GAC will allow the diffusion bag to continuously collect contaminant mass. Methylene chloride, 1,1-DCE, 1,2-DCE, and TCE partition well through the diffusion bags. Methylene chloride is a low-partitioning compound compared to other chlorinated solvents. At sites with high methylene chloride concentrations this design could be useful. Box aquifer tests conducted on the diffusion bags with GAC provide data for the diffusion bag in a dynamic system. The results from these tests indicate that the diffusion domain would be able to measure contaminant flux based on the amount of contaminant mass collected and a calibration curve from lab experiments. A design that incorporates the GAC diffusion bag in a PFM should be developed. Originally it was thought that the diffusion bag could be surrounded by more GAC that is impregnated with tracers to allow for contaminant flux and Darcy flow measurement. This may require too long of a deployment for a significant amount of mass to be collected in the diffusion bag, however. An inert media such as course sand could prove useful in surrounding the diffusion bag in a PFM, as this was used in the box aquifer tests. The PFM could be configured to have alternate layers, with one layer being a standard PFM to measure Darcy flux and the other layer the diffusion bag containing GAC and surrounded by course sand to determine contaminant flux.

Field tests should be conducted for the designs selected in this study, the modified permeability PFM and the diffusion domain. To efficiently test the designs in the field, it is recommended to develop a PFM with 3 layers that include a standard PFM, the modified permeability PFM, and the diffusion domain. Accurate flux measurements in the field tests would indicate successful PFM designs.

During the active period of this research project, there were two field sites identified where PFM deployments were conducted in well screens that had observed evidence of 1,4-dioxane presence. Enviroflux Inc. was contracted to conduct PFM deployments for chlorinated solvents and the University of Florida research group agreed to extend the basic chlorinated solvent compounds to include characterization of 1,4-dioxame mass flux at these two sites. 1,4-Dioxame flux profiles are provided from the two industrial sites considered in this project Site 1 and Site 2 (Figures 6-1 and 6-2). In these tests the standard PFM design using granular activated carbon were employed.

PFMs were deployed at Site 1 in August 2014 for a period of two weeks. Figure 6-1 shows the vertical distribution of 1,4-dioxane mass flux and volumetric water or Darcy flux with 1,4-dixoane flux corresponding to increases in Darcy flux. The resulting flux-averaged 1,4-dixoane concentration for this well was 460 μg/L. Mass fluxes of 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 6-1).

PFMs were deployed at Site 2 in September 2014 for 15 days. 1,4-Dixoane was detected in two wells at the site with average mass fluxes of 76 and 3 mg/m^2/day. The figure 6-2 results are similar to the ones described for Site 1 and the resulting flux-averaged concentrations for these wells were 68 and 600 μg/L, respectively. Mass fluxes of 1,1-DCE, cis-DCE, 1,2-DCA, TCE, and 1,1,1-TCA were also simultaneously detected by PFMs in these wells. However, in the PFM-1 well, 1,4-dioxane was much higher than the other contaminants, suggesting that a DNAPL source may be located upstream of the wells tested and that the chlorinated ethenes may eventually migrate reaching higher concentrations at these wells to these wells. It is generally observed that 1,4-dioxane is more mobile than chlorinated solvent constituents and thus may be depleted from the source zone more rapidly. Data on 1,4-dioxane concentrations in groundwater in the wells were not currently publicly available for comparison.

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. For dilute plumes with concentrations below 30 ug/L detection limits may be an issue thus longer deployment times are recommended. Continued interest in 1,4-dioxane mass flux has been expressed and will be encouraged to help move such measurements into site management plans.

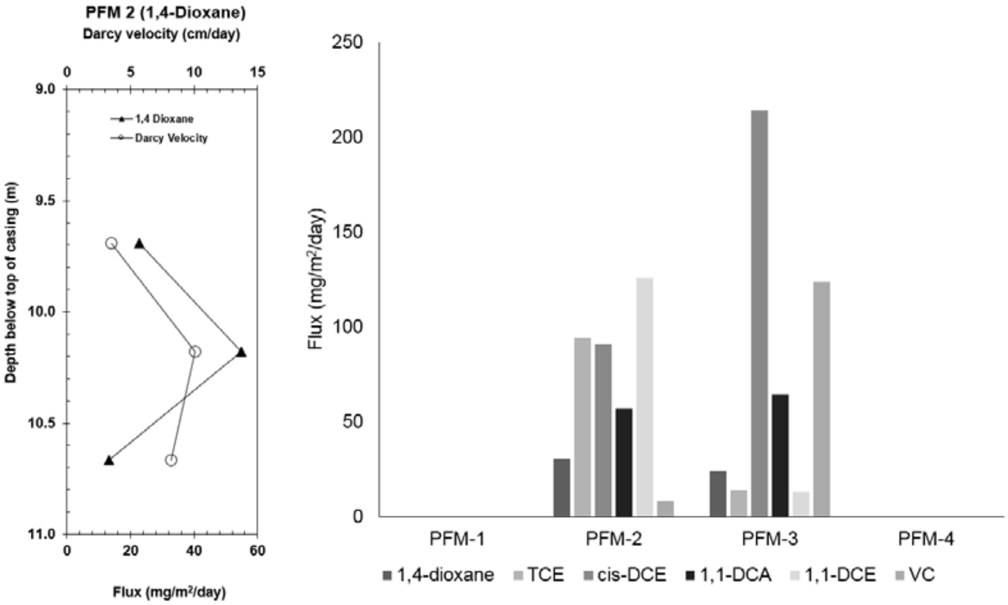


Figure 6-1. Mass flux measurements at Site 1 (confidential site). (A) Mass flux profile for PFM-2 and (B) Average mass flux of contaminations for each well at Site 1.

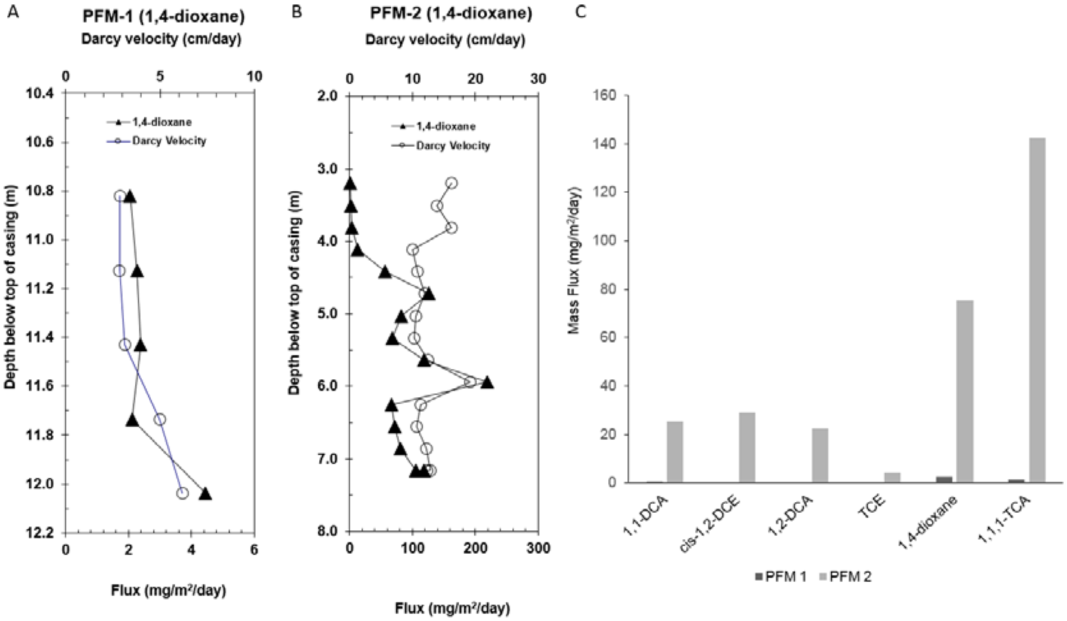


Figure 6-2. Mass flux measurements at Site 2 (confidential site). (A) Mass flux profile for PFM-1, (B) Mass flux profile for PFM-2, and (C) Average mass flux of contaminations for each well measured at Site 2.

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APPENDIX A
METHODS

Extraction Methods

An extraction test was performed with multiple solutions to determine the extraction efficiencies for 1,4-dioxane from GAC. Extraction solutions tested include acetone, isobutanol (IBA), an acetone-hexane mixture, 1-hexanol, and 1-octanol. Similar methods to this test have been used in previous studies (Annable et al., 2005,Lee et al., 2007,Stucker et al., 2011). First a known amount of GAC was placed in a 40 mL vial. Next 30 mL of the contaminant solution with a 1,4-dioxane concentration of 1,030 ppm was added to each vial. The vials were put on the rotator for approximately 24 hours. A sample of the equilibrium solution was taken and analyzed by the GC-FID. The contaminant solution was removed from the vial carefully not removing any of the GAC. The extraction solution was then added to the vials. After rotating, samples of the extraction solutions were analyzed on the GC-FID. The extraction efficiencies were calculated based on the difference in mass extracted and mass adsorbed and are shown in Figure A-1. Extraction solutions selected varied based on which tracers and contaminants were used for each specific experiment.

Another extraction test was conducted for all contaminants used throughout the study, which include methanol, 1,4-dioxane, methylene chloride, 1,1-DCE, and 1,2-DCE. This test was performed for a double extraction of IBA followed by heptane. Methanol extraction efficiency was only completed for the IBA extraction. In the double extraction 20 mL of IBA was used to extract contaminants from the GAC first. After samples of the IBA were taken, the IBA was removed from the sample and 20 mL of heptane was added. The reason for the double extraction was that a low percentage of the chlorinated contaminants are extracted from the GAC with IBA. This extraction efficiency test was done similarly to the test described above. The efficiency for

Methanol extracted by the IBA was 70%. The extraction efficiencies for the remaining contaminants by the double extraction method are displayed below in Figure A-2.

Hydraulic Conductivity Tests Sands

Hydraulic conductivities were determined for three different sands, one used to pack the 3D boxes and two sieved sands, 80 – 100 mesh and 100 – 140 mesh size. There were three different boxes used during the study, each packed with the same type of sand, which was a commercial patio leveling sand produced by Sunniland. Hydraulic conductivity tests were done for the sand used to pack each box since the sand was obtained at different times. The sand was washed before using to rinse away small floating particles. Two different methods were used to measure the hydraulic conductivity of the sand, a standard falling head column test and a radial flow test. In this study there were three different box aquifer setups used. Only the falling head test in the clear PVC pipe was used to test the hydraulic conductivity of the sand used for Box 1 and Box 3 as well as the 80 – 100 and 100 – 140 mesh sand. Both methods were used to test the sand of Box 2 to compare results.

Vertical Flow Falling Head Test

The first test was a falling head test employing a clear PVC pipe for the column. Fabric would be secured to the bottom of the column with rubber bands. The sand would then be packed into the column. To prevent layering of the sand, a metal rod was used to stir the sand each time more was added. The hydraulic conductivity was then determined using a falling head approach. This test was done twice, each time with a different sand height to ensure that the hydraulic conductivity of just the sand, and not the sand and the fabric, were measured. The hydraulic conductivity of the sand was back calculated from the two hydraulic conductivities measured.

One flux meter modification considered in this study was packing a high mesh (finer) sand around a one inch flux meter, so hydraulic conductivities of both 80 – 100 and 100 – 140 mesh sand were tested by falling head tests in the clear PVC pipe using the same method as above. The hydraulic conductivities of these sands were needed to determine if they would be suitable for packing around a one inch PFM to create a very low permeability region around the PFM. Since the hydraulic conductivity of both the fabric and the sand was desired, only one column length for each type of sand was used. The 80 – 100 and 100 – 140 mesh sand would only be used with the 97% cotton fabric since the crinoline socks material on a standard PFM will not hold this sand. It was determined that the 80 – 100 mesh sand had a hydraulic conductivity that was about half that of the sand used to pack the box and the 100 – 140 mesh sand had a hydraulic conductivity that was about one quarter of the hydraulic to hold the sand in place.

Radial Flow Test

The hydraulic conductivity of the sand used as the box aquifer media was also tested using a radial flow method. In this test, the sand was packed around a two inch well screen. The same fabric used in the vertical flow falling head test was used to cover the slots in the well screen as well as to hold the packed sand around the well screen. Rubber washers were used at the top and bottom of the well screen inside the fabric to keep the cylindrical shape of the sand packed around the well screen as well as to make the sand thickness uniform. The bottom of the well screen was capped. The top of the well screen was connected to a clear PVC pipe. Both constant head and falling head tests were used with this setup. The hydraulic conductivity determined using this method was similar to the hydraulic conductivity found in the first method. The hydraulic conductivity calculations were slightly different for this test, using radial flow equations rather than 1D flow equations. Table A-1 displays the hydraulic conductivity results for each sand and method used.

Fabrics

Another flux meter modification was to change the material surrounding and containing the GAC. In a standard PFM, crinoline socks material is used that has a hydraulic conductivity approaching infinity, with water able to rapidly flow into the GAC. Fabrics with much lower hydraulic conductivities were tested. These fabrics would produce lower water flow through the PFM, allowing deployment of the flux meter for a longer duration. This approach is discussed in more detail in Chapter 3. Fabric materials tested include 100% cotton, 100% polyester, 60%/40% cotton/polyester, 70%/2%/28% cotton/spandex/polyester, 97%/3% cotton/spandex, and duck cloth, which is a thick and tightly woven 100% cotton material. The falling head method was used to test the hydraulic conductivities of theses fabrics. One layer of the fabric was placed on the end of a clear PVC pipe, secured with rubber bands. The PVC pipe was filled with water while the bottom end with the fabric was blocked. The time required for the head to drop over a fixed distance was recorded and used to estimate the hydraulic conductivity. Table A-2 contains the hydraulic conductivities of each fabric.

GAC and Gravel

The hydraulic conductivity of the GAC was also measured with a falling head test. Since a standard PFM uses the crinoline socks, which have a negligible hydraulic conductivity, the hydraulic conductivity of a standard PFM should be equal to that of the GAC. A falling head test was completed as previously described. The hydraulic conductivity of the GAC was determined to be 316 m/day, which is equal to the hydraulic conductivity of a standard PFM. The hydraulic conductivity of a coarse gravel was also determined this way. The gravel is involved in a PFM modification that was discussed in Chapter 3. It was determined to have a hydraulic conductivity of almost 900 m/day.

Flow Field Determinations

Hydraulic conductivity tests were needed because the hydraulic conductivity is an important parameter used to determine the flow field in the 3D box aquifers as well as the application of certain materials to a modified PFM. The flow field around the PFM was needed to accurately interpret the PFM measurements, since the flow tends to either diverge or converge towards the PFM depending on the hydraulic conductivity of the surrounding aquifer (Klammler et al., 2007a). In order to accurately interpret the fluxes measured by the PFM as the actual groundwater fluxes, the amount of water converging or diverging must be considered. Analytical expressions to derive flow fields were developed by Klammler et al. in 2007. The flow convergence factor, α, was calculated for each box aquifer and flux meter combination. When the flow convergence factor is greater than one, the flow around the PFM is convergent and when it is less than one, the flow field is divergent. For the standard flux meter the flow field was calculated from Equation A-1 shown below.

$$\propto = \frac{4}{\left(1+\frac{k_0}{k_1}\right)\left(1+\frac{k_1}{k_2}\right)+\left(1-\frac{k_0}{k_1}\right)\left(1-\frac{k_1}{k_2}\right)\left(\frac{r_2}{r_1}\right)^2} \qquad \text{(A-1)}$$

In Equation A-1 k_0 is the hydraulic conductivity of the box aquifer sand, k_1 is the hydraulic conductivity of the well screen, k_2 is the hydraulic conductivity of the PFM, r_1 is the radius to the outside of the well screen, and r_2 is the radius of the PFM (Klammler et al., 2007a). To calculate the flow field of the modified PFMs Equation A-2 was used.

$$\propto = \frac{8}{\left(1+\frac{k_0}{k_1}\right)\left(1+\frac{k_1}{k_2}\right)\left(1+\frac{k_2}{k_3}\right)+\left(1-\frac{k_0}{k_1}\right)\left(1-\frac{k_1}{k_2}\right)\left(1+\frac{k_2}{k_3}\right)\left(\frac{r_2}{r_1}\right)^2+\left(1+\frac{k_0}{k_1}\right)\left(1-\frac{k_1}{k_2}\right)\left(1-\frac{k_2}{k_3}\right)\left(\frac{r_3}{r_1}\right)^2} \qquad \text{(A-2)}$$

In Equation A-2 k_0 is the hydraulic conductivity of the box aquifer sand, k_1 is the hydraulic conductivity of the well screen, k_2 is the hydraulic conductivity of the modification material layer, k3 is the hydraulic conductivity of the PFM GAC layer, r_1 is the radius to the outside of the well screen, r_2 is the radius to the outside of the modified media, and r_3 is the radius of the PFM GAC layer (Klammler et al., 2007a). In Klammler's analysis of flow fields for PFMs in a well, Equation A-2 was used when a filter pack was installed around the well screen, with the different hydraulic conductivity zones being the aquifer, filter pack, well screen, and then PFM in order of outer ring to inner ring. In this study Equation A-2 was applied to the modified PFMs, with the hydraulic conductivity zones being the box aquifer media, the well screen, the modification material, and then the PFM.

For all boxes and PFM combinations the flow field was divergent due to the fact that the well screen hydraulic conductivity is less than the sand in the box aquifer and no filter pack or gravel was used around the well screen. The flow convergence factor for each box with a standard PFM was calculated to be between 0.7 and 0.8. For the modified PFMs most of the convergence factors were between 0.6 and 0.8, with the exception being a one inch PFM surrounded by gravel, having a much lower convergence factor of 0.47. A convergence factor was not calculated for the PFM design with a one inch PFM inside a two inch well screen. A convergence factor could not be calculated for this scenario because the hydraulic conductivity of the empty annulus would be near infinite. These values were applied to the PFM measurements in the box aquifer tests. In calculating the convergence factor the hydraulic conductivity of the effect of the well screen was assumed to be 2.0 m/day, which had been previously calculated by Klammler et al. in 2007 and Annable et al. in 2005. Table A-3 displays the flow convergence factors for each type of PFM.

Based on these theoretical calculations, the flow diverges for all PFM designs used in this study. In the theoretical flow field calculations, the highest impact to the flow convergence factor would come from changing the hydraulic conductivity of the media surrounding the well screen or changing the hydraulic conductivity of the well screen itself, however these factors were held constant for each set of box aquifer tests. Changing these factors has a much greater impact on the convergence factor than changing the modified media hydraulic conductivity based on the results of Equation A-2. Flow fields were analyzed to determine the difference in flow divergence from PFM modifications. Based on the flow convergence factor calculations, the flow field will not be significantly changed by the PFM modifications made in this study. These calculations would suggest that theoretically, modifying the PFM would not make a significant difference in the amount of flow passing through the PFM. This prediction was tested in a set of box tests on the modifications in Section 3.2.3. The flow convergence factors calculated were applied to the PFM measured contaminant and water flux results, and then a second convergence factor was calculated based on the remaining difference between the actual contaminant and water fluxes and the measured contaminant and water fluxes.

Packing Method for a standard PFM

The crinoline socks material was cut a few inches more than the length of the entire PFM and was secured to the center tube via electrical tape and a metal clamp. The center tube with the materials attached was placed in a packing tube and the crinoline socks were secured over the end of the packing tube, which was a piece of two inch schedule 80 PVC pipe. A rubber washer was placed at the bottom of the PFM to help it keep the cylindrical shape once it is packed with GAC, which was done next. A rubber washer and a sponge were placed on top of the packed GAC. The end of the crinoline socks was taped to the center tube to close the PFM. Next the red plastic mesh was secured to the bottom of the PFM and it was transferred to a clear schedule 40 PVC pipe and ready to deploy.

Packing Method for the two layer 97%/3% cotton/spandex PFM

The PFM was assembled following the same procedures for making a standard PFM and then adding the 97%/3% cotton/spandex fabric. The crinoline socks material was cut the length of a few inches more than the entire PFM and the 97% cotton fabric cut the length of a few centimeters more than half the length of the PFM. Both pieces of fabric were secured to the center tube via electrical tape and a metal clamp. The center tube with the materials attached was placed in the packing tube and the crinoline socks were secured over the end of the packing tube. A rubber washer was placed at the bottom of the PFM. The GAC was packed to just below where the 97% cotton fabric ended. Two rubber washers were placed on top of the packed GAC, which would prevent water flow between the two layers. At this point there would still be a small part of the 97% cotton fabric showing above the washers. The remainder of the PFM was packed with GAC and a washer and a sponge were placed on top. The end of the crinoline socks was taped to the center tube to close the PFM. Next the red plastic mesh was secured over the PFM and it was transferred to a clear PVC pipe and ready to deploy.

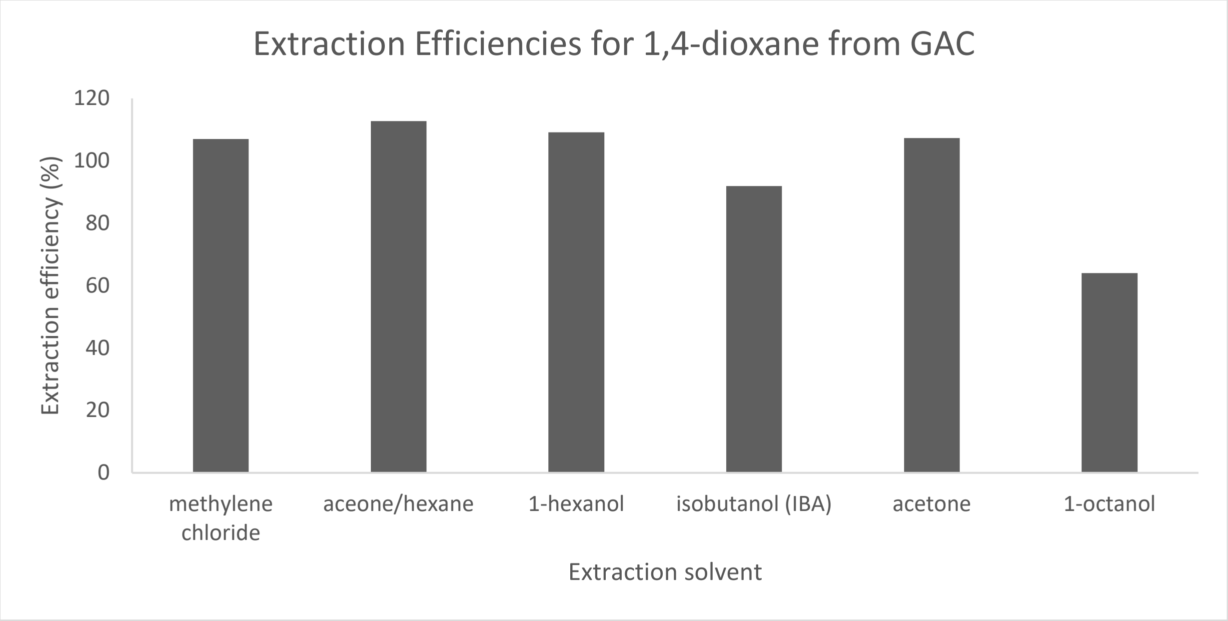

Figure A-1. Extraction efficiencies for 1,4-dioxane extracted from GAC with different extraction solvents.

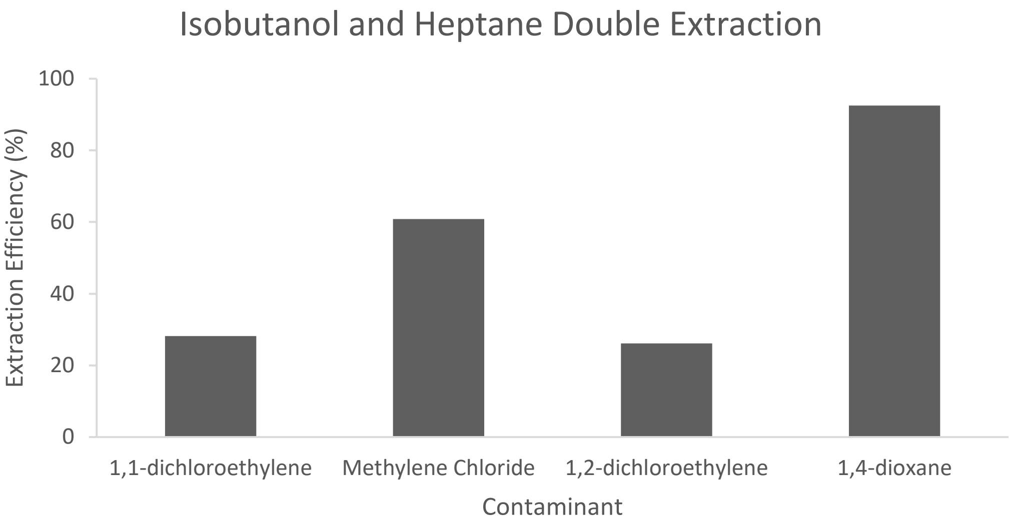

Figure A-2. Extraction efficiencies for different contaminants from GAC using an isobutanol and heptane double extraction method.

Table A-1. Hydraulic conductivity values for sands tested

Sand tested, Method	Hydraulic Conductivity (m/day)
Sand for Box 1, Falling Head	24.9
80-100 Mesh Sand with 97% cotton fabric, Falling Head	10.9

100-140 Mesh Sand with 97% cotton fabric, Falling Head	5.2
Box 2 Sand, Radial Flow (constant head)	18.8
Box 2 Sand, Falling Head	17.3
Box 3 Sand, Falling Head	21.4

Table A-2. Hydraulic conductivity values for fabrics tested

Fabric tested, Method	Hydraulic Conductivity (m/day)
97%/3% Cotton/Spandex, 1 layer Falling Head	2.9
97%/3% Cotton/Spandex, 2 layers Falling Head	2.0
97%/3% Cotton/Spandex, 6 layers Falling Head	2.9
97%/3% Cotton/Spandex, Well Screen Method	2.8
100% Polyester, Falling Head	6.7
70%/2%/28%Cotton/Polyester/Spandex, Falling Head	3.3
60%/40% Cotton/Polyester, Falling Head	1.5
100% Cotton, Falling Head	3.0
Duckcloth 100% Cotton Fabric, Falling Head	0.8

Table A-3. Convergence factors for different PFM and box combinations

PFM Type	Box	Convergence Factor
Standard PFM	1	0.73
Standard PFM	2	0.75
Standard PFM	3	0.79
1" PFM with gravel	2	0.47
1" PFM with sand	2	0.65
2" PFM with 97% cotton fabric	2	0.72
2" PFM with 97% cotton fabric	3	0.72
2" PFM with polyester fabric	2	0.77
2" PFM with Duckcloth	2	0.64

APPENDIX B
TABLES

Table B-1. Applied and PFM measured Darcy flux and 1,4-dioxane flux for standard PFM box aquifer tests from section 2.2.2.

Test	Actual Darcy flux (cm/day)	Actual 1,4-dioxane Flux (mg/m2/day)	Measured Darcy flux (cm/day)	Measured 1,4-dioxane Flux (mg/m2/day)
1	24.5	440.6	26.5	550
2	32.4	583.2	38.0	694
3	7.9	142.6	9.7	287
4	64.8	1166.4	77.5	1508
5	41.8	751.7	44.4	770
6	4.2	75.2	8.7	165

Table B-2. Darcy flux data for 97%/3% cotton/spandex PFM design in the extensive box aquifer tests.

Actual Darcy flux (cm/day)	Standard PFM measured Darcy flux (cm/day)	Modified PFM Measured Darcy flux (cm/day)	Modified PFM Darcy flux with correction factor (cm/day)
25.8	30.8	7.2	35.8
25.8	23.7	5.0	25.2
25.8	23.3	3.7	18.6

Table B-3. Methanol flux measurements for 97%/3% cotton/spandex PFM design in the extensive box aquifer tests.

Duration	Actual Flux (mg/m2/day)	Standard PFM Flux (mg/m2/day)	Modified PFM Flux (mg/m2/day)	Modified PFM Flux with correction (mg/m2/day)
8 hours	12007	5045	956	4777
12 hours	11981	4423	1095	5476
24 hours	12034	2793	1237	6186
3 days	11428	2005	928	4638
6 days	10241	459	401	2006
13 days	11066	145	124	618

Table B-4. 1,4-dioxane flux measurements for 97%/3% cotton/spandex PFM design in the extensive box aquifer tests.

Duration	Actual Flux (mg/m2/day)	Standard PFM Flux (mg/m2/day)	Modified PFM Flux (mg/m2/day)	Modified PFM Flux with correction (mg/m2/day)
8 hours	11954	13892	2603	13013
12 hours	11954	10994	2618	13089
24 hours	11981	12573	2894	14472
3 days	48347	31833	7165	35824
6 days	48625	25420	10201	51005
13 days	48028	28289	6453	32265

Table B-5. Methylene chloride flux measurements for 97%/3% cotton/spandex PFM design in the extensive box aquifer tests.

Duration	Actual Flux (mg/m2/day)	Standard PFM Flux (mg/m2/day)	Modified PFM Flux (mg/m2/day)	Modified PFM Flux with correction (mg/m2/day)
8 hours	11454	12671	2436	12179
12 hours	11928	13066	3441	17205
24 hours	12481	13026	4202	21009
3 days	11427	8816	1718	8592
6 days	10989	7503	3418	17092
13 days	11427	9305	2169	10846

Table B-6. Percent error in both standard and modified PFM measurements for each box aquifer test.

	Methanol % error		Methylene Chloride % error		1,4-dioxane % error	
Time	Standard PFM	Modified PFM	Standard PFM	Modified PFM	Standard PFM	Modified PFM
8 hours	58	60	11	6	16	9
12 hours	63	54	10	44	8	9
24 hours	77	49	4	68	5	21
3 days	82	59	23	25	34	26
6 days	96	80	32	56	48	5
13 days	99	94	19	5	41	33