FINAL REPORT

A High Resolution Passive Flux Meter Approach Based on Colorimetric Responses

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The standard Passive Flux Meter (PFM) is a well-established device used for measuring groundwater and contaminant mass flux in screened wells. The PFM is a permeable device that contains granular activated carbon impregnated with alcohol tracers which is deployed in a flow field for a designated period of time and requires laboratory analysis to quantify Darcy flux. To expedite test results, a modified PFM based on the visual analysis of colorimetric responses, herein referred to as a colorimetric Passive Flux Meter (cPFM), was developed. Various dyes and sorbents were evaluated for their ability to determine colorimetric response to water flow.

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Abstract

The standard Passive Flux Meter (PFM) is a well-established device used for measuring groundwater and contaminant mass flux in screened wells. The PFM is a permeable device that contains granular activated carbon impregnated with alcohol tracers which is deployed in a flow field for a designated period of time and requires laboratory analysis to quantify Darcy flux. To expedite test results, a modified PFM based on the visual analysis of colorimetric responses, herein referred to as a colorimetric Passive Flux Meter (cPFM), was developed. Various dyes and sorbents were evaluated for their ability to determine colorimetric response to water flow. Rhodamine, fluorescent yellow, fluorescent orange, and turmeric dyes were the final dyes selected while 100% wool and a 35% wool-blend with 65% rayon were the final sorbent materials selected for use in the cPFM. Ultraviolet light image analysis was used to calculate average color intensity, which was then used to quantify Darcy flux. The error range evaluated for Darcy flux using the cPFM were as low as 26% for laboratory tests and 34% for field tests with the optimal dye and sorbent combinations, which is comparable to the error range reported for Darcy flux using the standard PFM of 15%.

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1. INTRODUCTION AND OBJECTIVES

Groundwater Hydrology and Contaminant Transport Background

Groundwater is a quintessential resource that is critical to the sustenance of human life. More than half of the United States population (51.7%) relies on groundwater for their drinking water, with 95% of the world's available freshwater being groundwater (Fetter, 1999; Goltz et al., 2007). The contamination of groundwater can come from numerous sources, jeopardizing both water quality and quantity. These contaminants can infiltrate groundwater from actions on the land surface, such as industrial waste spills; from the vadose zone, such as septic tank leakages; or from systems penetrating below the aquiclude, such as fracking. The ability of an aquifer to receive, store, or transmit water or contaminants is dependent on multiple aquifer characteristics (USEPA, 1993). Fluctuations in permeability, hydraulic gradient, porosity, and flow area can cause large-scale differences in the resulting Darcy flux and contaminant mass flux across different subsurface environments.

Flux measurements can be used to help prioritize the cleanup of a contaminated site. For example, if a majority of the contaminant mass is located within low permeability regions, the contaminant leaving the source zone will be relatively low. On the other hand, a relatively small source zone in a high permeability region can result in a large contaminant mass flux leaving the area (Goltz et al., 2007). Therefore, the attenuation of contaminants in the subsurface is a difficult and expensive process to achieve clean up goals. As such, high resolution in situ flux measurements can produce critical data necessary to optimize the design and evaluate the performance of proposed contaminant source and groundwater remediation systems (Rao et al, 2002; Annable et al., 2005). Continued measurements of the Darcy flux and contaminant mass flux can then generate the extents and severity of the source one, dissolved plume, and the efficiency of the remediation efforts.

Historically, emphasis was placed on quantifying the magnitudes of water and contaminant flows with minimal attention put on the directionality. The standard approach to determining flow direction in the subsurface uses a water table contour map, and a certain minimum number of observation wells in the area of interest (Klammler et al., 2007). While other methods in the preceding decade have arisen for determining directionality, this report will focus on the advances of the colorimetric passive flux meter, a modified version of the current passive flux meter design.

Standard Passive Flux Meter

The passive flux meter (PFM) is a well-developed method for simultaneously measuring the magnitudes of groundwater and contaminant fluxes in the porous subsurface (Annable et al., 2005; Basu et al., 2006; Hatfield et al., 2004). The PFM consists of a sorptive permeable medium inserted into a monitoring well to intercept contaminated groundwater. The design includes granular activated carbon with alcohol tracers preloaded. While deployed in the saturated zone, groundwater flows drive the release of "resident tracers". The design of the PFM assumes that advective flux dominates over diffusive flux, and therefore, the diffusion component can be ignored (Hatfield et al., 2004). These PFM's can be interspersed spatially to capture the plume area as well as vertically segmented layers of the exposed sorbent allow for depth variations of both water and contaminant mass flux from a single PFM (Annable et al., 2005). The PFM deployment duration is traditionally approximately two weeks but can vary depending on the expected groundwater flow to attempt to yield MR values in an acceptable range. For a two-week duration in a 2-inch diameter well the detection limit for the standard PFM is approximately 0.7 cm/day to ensure advective dominated flows inside the PFM (Hatfield et al., 2004).

Once extracted, the PFM is returned to the laboratory where discrete samples of the granular activated carbon are removed from each layer and placed in vials determining the mass of sample. In addition, initial C_0 sample are preserved. Vials are then filled with a predefined volume of either Methylene Chloride (MeCl) or Isobutanol (IBA) as an extraction solvent. The field samples are rotated for 24 hours to equilibrate the sample and solvent. Samples are then allowed to settle for 24 hours. After settling, a subsample is taken from each sample and analyzed for the alcohol tracers and contaminants with a Gas Chromatograph with a FID (flame ionization detector).

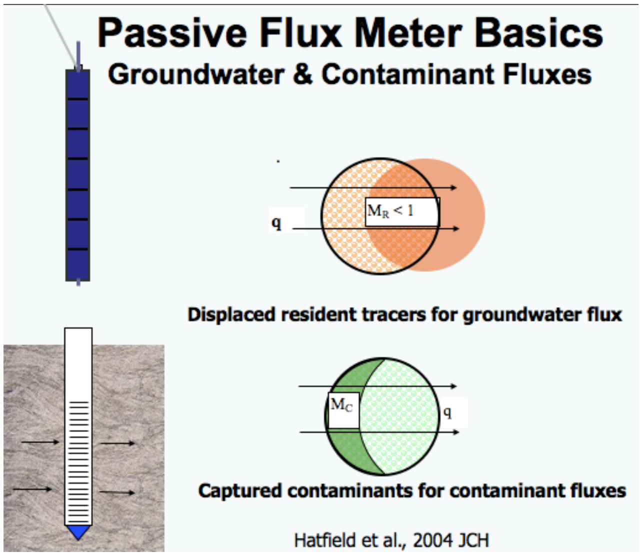
The mass fraction of resident tracers lost is used to determine the groundwater flux while the mass of contaminant sorbed is used to determine the contaminant flux, detailed in Figure 1-1. These variables as well as the PFM deployment time, the cumulative water passed through the PFM, the radius of the PFM, the water content, the well convergence factor, and the retardation factor of the tracer are used to quantify time-averaged groundwater and contaminant fluxes at discrete locations (Annable et al., 2005). This analytical method is based on the assumptions that the tracers partitioning is reversible, linear, and instantaneous (Hatfield et al., 2004). The above described approach is a well-established method for measuring groundwater flux. Although the PFM yields high quality data though, it requires extensive laboratory analysis, is time consuming, and expensive. Therefore, an alternative method was proposed.

Colorimetric Passive Flux Meter

The primary goal of environmental remediation is site closure by achieving the required risk reduction for regulatory compliance or liability reduction at the least cost (Rao et al., 2002). An alternative method of site assessment to the standard PFM was proposed to attenuate the high cost and extensive laboratory analysis while retaining high resolution data. The proposed method, the colorimetric passive flux meter (cPFM), delivers high resolution in-situ groundwater flux data through measuring colorimetric responses. This method is based on the same inversely proportional relationship between the mass of tracer remaining on the sorbent and cumulative groundwater flow intercepted as the standard PFM, shown in Figure 1-2. In the case of the cPFM though the sorbent is a fabric material and the tracer is a fluorescent or natural dye. Figure 1-3 shows an example of a cPFM disk after exposure to groundwater flow and the comparison to the initial condition. From evaluation of the color intensity, the magnitude and direction of groundwater flow can be determined.

Numerous visible dyes and sorbents were tested and narrowed down based on their ability to adsorb and desorb properly (Dombrowski, 2016). The sorbent material candidates were narrowed down to 100% wool and a wool-rayon blend through a series of testing. Preliminary investigations have been conducted for using cotton as a sorbent material in the future as well (see Appendix B). The tracer candidates were narrowed down to only fluorescent dyes: rhodamine, fluorescent yellow, fluorescent orange, and turmeric.

The objective of this project was to test the efficacy of the cPFM in producing high resolution groundwater flux data while lowering the cost. This was first done through laboratory testing followed by multiple field deployments. Specific dye and sorbent combinations were tested to narrow in on optimal combinations for varying subsurface characteristics and flow regimes. External influences on colorimetric response, such as contaminant concentrations and pH, were additionally assessed (see Appendix D). While the main body of this work focuses on the measurement of groundwater flux colorimetrically, Section 3, is devoted to efforts to measure contaminant mass flux colorimetrically.


Passive Flux Meter Basics

Groundwater & Contaminant Fluxes

Displaced resident tracers for groundwater flux

Captured contaminants for contaminant fluxes

Hatfield et al., 2004 JCH

Figure 1-1. Depiction of PFM theory

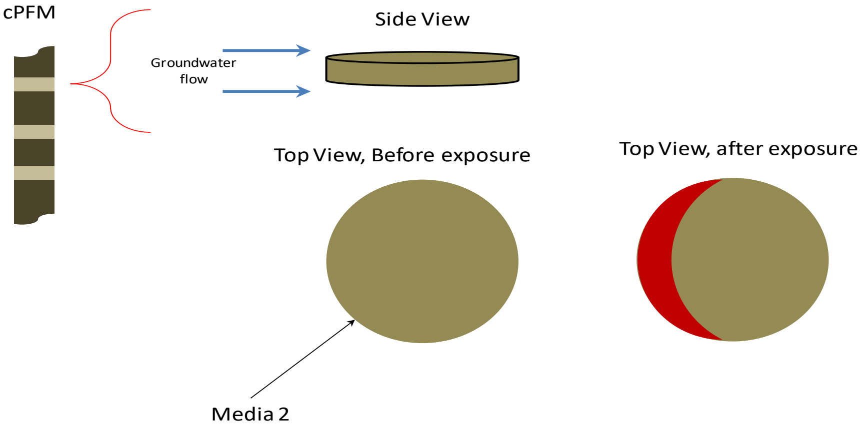


Figure 1-2. Depiction of cPFM theory

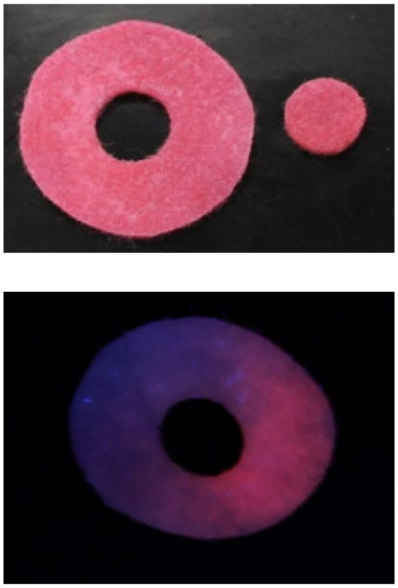


Figure 1-3. Dyed rhodamine disk before and after exposure to flow. Photo courtesy of Kaitlin Dombrowski.

2. LABORATORY TESTING METHODOLOGY

Laboratory Testing Apparatus Construction

Two laboratory boxes were constructed to simulate a 3-D aquifer system. Box 1 is stainless steel with dimensions of 40 cm x 30 cm x 13 cm. Box 2 is plastic with dimensions of 46 cm x 30 cm x 20 cm. For both boxes, 5 cm from each end of the flow direction, a mesh divider was installed. Each end separated by a mesh divider was filled homogenously with gravel to facilitate even distribution of the inflow and even collection of the outflow. At the midpoint of the flow length, well screens were installed, oriented orthogonal to the flow direction. Box 1 consisted of one well screen while box 2 consisted of two well screens equidistantly located in the center. The well screens were glued to a rectangular plexiglass plate to inhibit water flowing upward through the bottom of the well as well as to structurally keep the wells in place. Sand was then packed around the well screens to hold it in place while the box was filled using a single homogeneous wet packed sand layer (Sunniland patio sand) for the center and the ends separated off by the mesh divider filled using gravel. The pre-rinsed wet packed sand and gravel were slowly filled with water incrementally to avoid trapping air. The sand and gravel were compacted using an electric vibrator to remove air voids.

Box 1 has a 20 L mariotte bottle attached to the inlet side of the box while Box 2 has both a 20 L and 25 L mariotte bottles attached to the inlet side of the box at a set reservoir height to maintain a constant head within the 3-D aquifer box. This allowed constant flow into the box and maintained an equal hydraulic head between the reservoir and box. Box 1 has a rotary piston pump (FMI Fluid Metering Inc. Lab Pump RRP pump) while Box 2 has a peristaltic pump (Cole-Parmer Masterflex Model 7016-20) connected to the outflow to sustain a designated flow through each of the boxes. Tubing was then fed from the pump to an outlet to dispense of the outflow. Figure 2-1 and 2-2 are images of Box 1 and Box 2, respectively.

cPFM Construction Attributes

Dying Process

The cPFM is based on of the same fundamental theory, and therefore, the same underlying assumptions as the standard PFM. As such, the dyes chosen must abide by the same assumptions as the alcohol tracers. These entail the dye partitioning being reversible, ideally linear, and instantaneous. Additionally, as the dye tracers elute into the subsurface environment, they must have minimal impact on the environment. An extensive selection process was conducted to determine the best sorbent materials and dye candidates for 3-D box aquifer experiments (Dombrowski, 2016). The sorbent materials selected are a 100% wool fabric and a wool-rayon blend (35% wool, 65% rayon). The dye tracers selected are Rhodamine (CAS# 37299-86-6), C.I. Yellow-Green (CAS# 518-47-8), and Fluorescent Orange (Bright Dyes Item # 106006) as well as Turmeric. Turmeric is a natural spice whose yellow hue comes from a group of compounds known as curcuminoids, namely curcumin (Ravindran et al., 2007).

Fabric disks for a 2-inch well (5.08 cm) were sized to a diameter of 4.57 cm. The dye solution for the fluorescent dyes was then prepared by mixing 0.5 g of liquid dye concentrate with 50 mL of water in separate containers for each fabric disk. For turmeric dye, 0.5 tablespoons of turmeric powder were mixed with 1 L of water and boiled for 30 minutes, being stirred periodically. This mixture was then set out to cool for 1 hour before being filtered to remove any residual particulate matter.

Before inserting sample disks into the dye solution, they were fully saturated with tap water to remove all of the air voids. Individual disks were sealed into distinct containers of dye solution and then placed on a mechanical shaker at 120 RPM (revolutions per minute) for one hour. Figure 2-3 shows samples in their respective dye solutions before going on the mechanical shaker. After the designated duration, the fabric disk was uniformly dyed and removed from the shaker. Each sample was then removed from its respective container and dried. The free dye water remaining on each dyed disk was removed by putting each disk in the center of a clean, dry, folded paper towel on top of a sheet of translucent film and gently rolled out with a PVC tubing over the paper towel. This process was done three times per sample with a new paper towel to remove all of the excess dye water. The center reference disk with an inner diameter of 5/8-inch was then removed and stored in a sealed bag.

cPFM Design

The cPFM is a layered system with vertically segmented samples within each device. This allows for measurements to be taken at any desired depths and level of resolution. The construction of the cPFM begins with a 1/2-inch center tubing sheathed in a permeable fabric sock attached at the base with a 1/2-29/32-inch hose clamp. The inner components of the cPFM are then layered, incrementally being gently compressed to remove any air voids allowing preferential flow paths.

Each dye and sorbent combination has a duplicate sample separated with a rigid plexiglass washer above and below it. The washers were sized with a 1 7/8-inch outer diameter and a 5/8-inch inner diameter so as to fit the well screen (2-inch) and the center tube (1/2-inch). These rigid washers facilitate uniform horizontal flow by inhibiting vertical flow between the fabric disks while providing structure to the cPFM, as the fabric, rubber washers, and sponges are flexible.

Next, a sponge spaced between two rubber washers was layered between each dye sorbent combination to block the transport of dye vertically by absorption. This prevents the potential for sample contamination from the dye of another sample. Thus, from bottom up, the layering of the cPFM is as follows: rubber washer, sponge, rubber washer, plexiglass washer, sample disk, plexiglass washer, duplicate sample disk, plexiglass washer. This layering was then repeated for each dye and sorbent combination and then topped off with a final layering of a sponge between two rubber washers.

Once all of the inner components of the cPFM were installed and compressed, the permeable sock was pulled up over the top and taped flush against the top rubber washer. A red mesh lining was then attached at the base layered between the taping and hose clamp and then sealed snugly along the length of the cPFM and taped overtop of the permeable sock at the top of the device. The red mesh facilitated the incoming groundwater flow to travel along the veins of the mesh. This helped ensure that water reached each colorimetric layer regardless of their location in regards to the well screen openings. At this point, the cPFM was ready to be installed in a 2-inch diameter well. Figure 2-4 shows a built cPFM before deployment.

Box Aquifer Tests

2-D Aquifer Box

To properly measure Darcy Flux using the cPFM, the elution behavior of each dye and sorbent fabric had to be determined. This was done by running 2-D box tests consisting of a 2-inch wide dyed fabric strip held between two rectangular glass panels held upright to allow horizontal flow. A reservoir was set up to maintain a constant head within the box and a pump was installed to pump water at a constant rate. Once the pump was turned on, images were taken under UV-light continually at increasing interval lengths throughout the duration of the test from a camera mounted on a tripod. The images were then analyzed in Image J, a Java-based image processing program, to determine the image intensity. The program measured the average image intensity with the mean gray value feature (elaborated on in Computational Analysis section). This information was then used to estimate the retardation factor of each of the dyes for wool-blend through a 3-segment piecewise approach (Dombrowski, 2016). Figure 2-5 shows the 2-D elution curve for rhodamine on wool-blend with the piecewise method. The retardation factor was then determined from the 3-segment piecewise approach using Equation 2-1 (see Hatfield et al., 2004 for further details).

$$R = \frac{1}{\sum\left(\frac{MR_1 - MR_2}{R_1} + \frac{MR_2 - MR_3}{R_2} + \frac{MR_3 - MR_4}{R_3}\right)} \tag{2-1}$$

For 100% wool the 2-D elution test did not produce viable results, and as such a linear proportionality was made between the retardation factor, alpha value, and the average of the MR values from all of the previous 3-D box tests, shown in Equation 2-2,

$$R_{WB}\frac{\sum_{i-1}^{n}(1 - MR_i)}{\propto_{WB}} = R_W\frac{\sum_{i-1}^{n}(1 - MR_i)}{\propto_W} \tag{2-2}$$

where R_{WB} and R_W are the retardation factors for wool-blend and 100% wool, $\propto_{WB}$ and $\propto_W$ are the convergence factors for wool-blend and 100% wool, and MR_i is the MR value from each 3-D box aquifer test (see Section 5 for further details on each variable). This produced linearly proportional retardation factors for 100% wool based off of the measured 2-D elution 3-segment piecewise results of wool-blend and experimental data collected from 3-D box aquifer tests of wool-blend and 100% wool. These values are summarized in Table 2-1.

3-D Aquifer Box

3-D aquifer box experiments were then conducted for varied deployment durations each containing all dye combinations on a single sorbent material per screened well. cPFMs were inserted and extracted slowly so as to not disrupt the flow field and cause excessive dye loss from installation or extraction. After a predefined period of time, the cPFM was extracted and analyzed. The results of the 3-D box experiments are summarized in Section 5.

Moisture Content Analysis

When photographing sample and reference disks it is imperative that both be at similar moisture contents. A wetter sample will dilute the color of the disk, and therefore, lessen the image value. As a result, improperly equalizing moisture conditions can cause errors in the image value analysis conducted in ImageJ. This error propagates to the mass remaining on the sorbent used for the Darcy velocity calculations.

Numerous experiments were conducted to determine the effects of moisture content on the image value of the sample. These include the duration of reference disk storage, type of reference disk storage, amount of water added to the reference disk, and comparison of wet versus dry samples and reference disks. These tests were conducted on all of the fluorescent dyes (rhodamine, fluorescent yellow, and fluorescent orange) and turmeric as well as for both sorbent materials (100% wool and wool-rayon blend).

Sample disks were uniformly dyed as per the standard dying methods described here and partitioned into four reference disks per sample disk. One set of reference samples was stored in individual airtight bags while another set were stored in individual airtight bags inside a sealed container with water wet sponges on a bed of water, shown in Figure 2-6. At duration increments of 2, 4, 6, and 10 days, a different reference sample was removed to be photographed and its image value measured as per the standard analysis method described here.

Computational Analysis

Once the cPFM was extracted from the well, the device was disassembled to retrieve the sample disks and the references were removed from the moisture controlled box. Reference disks then had the appropriate number of drops of water added to them to equalize the moisture content between the sample and reference. Corresponding sample and reference disks were then photographed under UV-light. The camera used was a Canon EOS 60D digital camera with a EFS 18-135 mm. image stabilizer lens. All external light sources were removed as well as the distance to the image and zoom were kept constant across all tests so as to maintain the surrounding environmental conditions for repeatability of testing.

Images were analyzed using Image J, a Java-based image processing program that measures the average image intensity with the mean gray value feature. The mean gray value is the average gray value within the selected area of the image. This value is the sum of all of the gray values of all pixels in the selection divided by the total number of pixels. For Red Green Blue (RGB) images, the mean image value was calculated by converting each pixel to grayscale (Rasband, 2012). This was done using Equation 2-3.

$$Gray = \frac{(Red + Green + Blue)}{3} \tag{2-3}$$

The image value and area was determined for the sample disk as well as the hollowed out inner diameter. From this the overall sample image value and area was obtained. This was additionally done for the reference disk. The ratio of the image value of the overall sample disk to the reference gave the residual resident tracer mass on the sorptive matrix after exposure (MR). Equation 2-4 shows how the MR was calculated.

$$MR = \frac{(Sample\ Image\ Value)}{(Reference\ Image\ Value)} \tag{2-4}$$

The sample image value was obtained by taking the difference between the area-weighted overall sample and the hollowed out inner diameter. This value was then divided by the difference in the two areas. The sample image value was then used with the reference image value in Equation 2-3 to determine the MR. The MR was then used to in the Darcy flux calculation, discussed in Section 5.

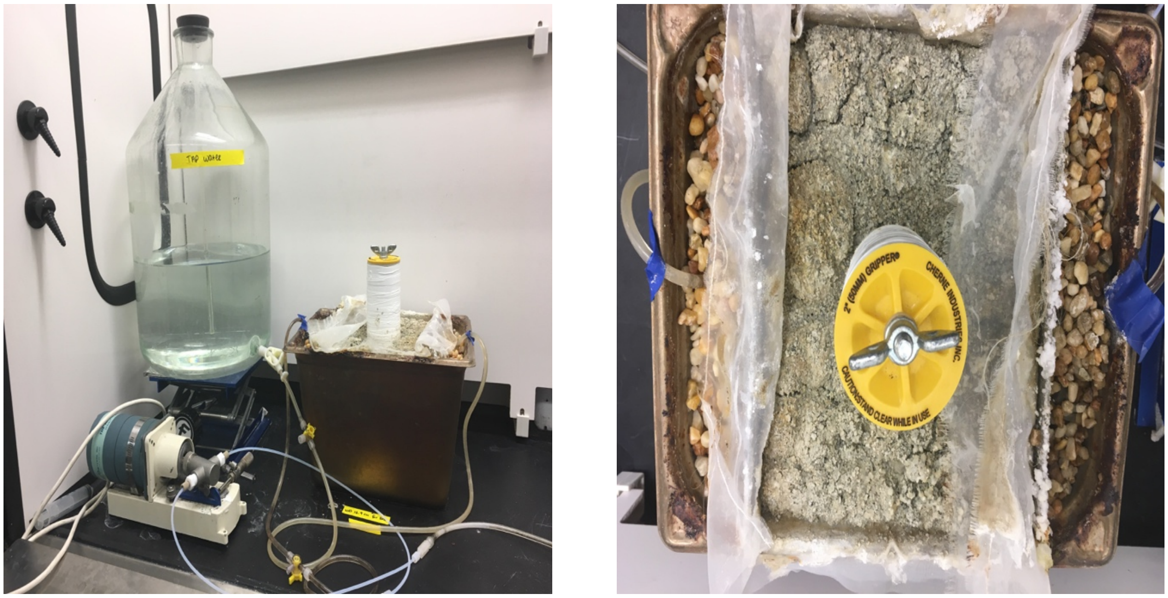


Figure 2-1. 3-D aquifer box 1.

Figure 2-2. 3-D aquifer box 2.

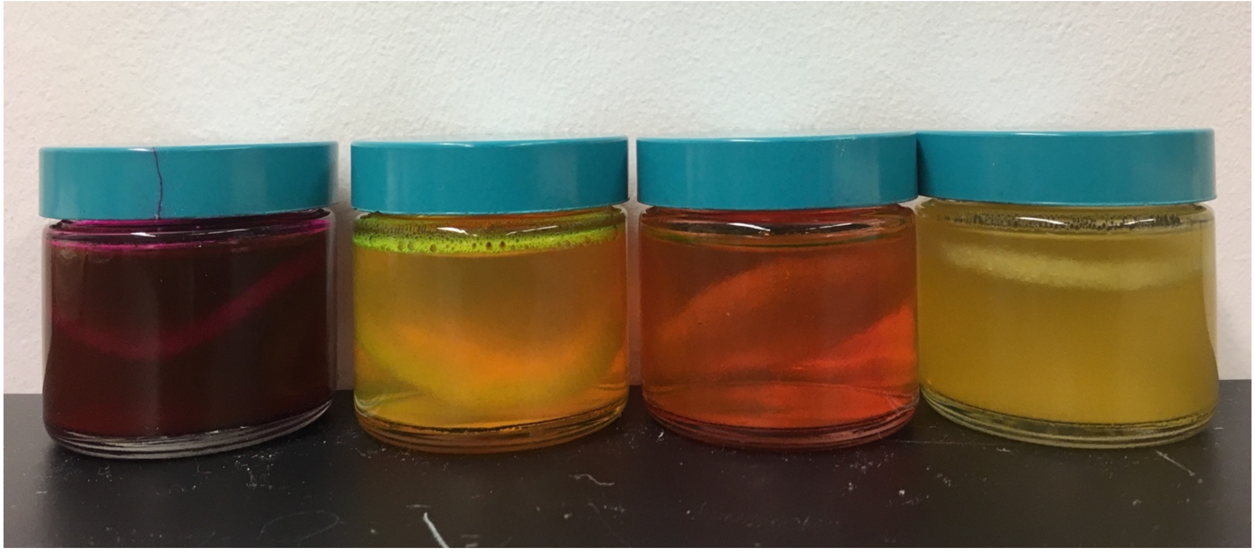


Figure 2-3. Samples in their respective dye solution from left to right: rhodamine, yellow, orange, turmeric.

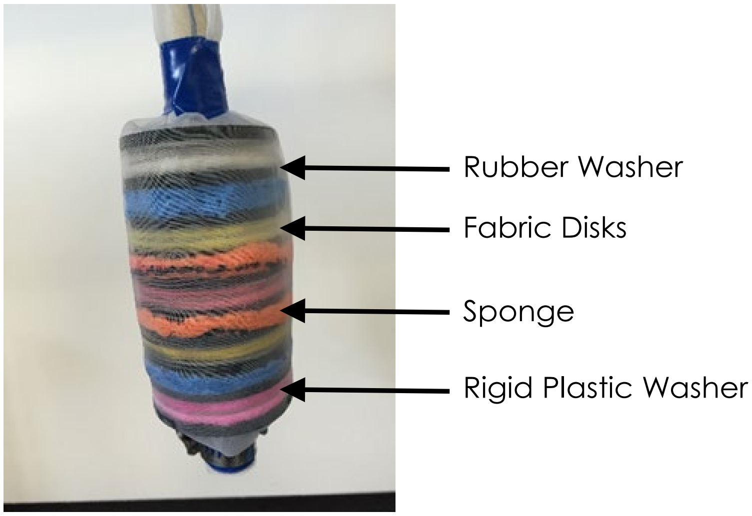


Figure 2-4. cPFM design.

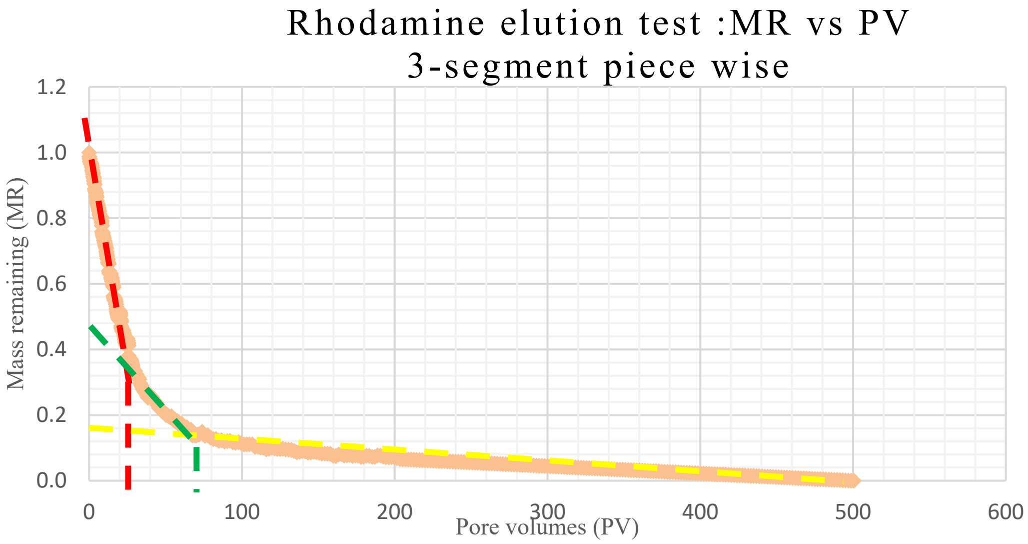


Figure 2-5. 3-segment piecewise approach for determining the retardation factor: rhodamine on wool-blend

Figure 2-6. Moisture box for reference sample storage.

Table 2-1. Retardation values for each dye and sorbent material combination

	Retardation Value			
Sorbent Material	Rhodamine	Orange	Yellow	Turmeric
Wool-Blend	54	58	86	220
100% Wool	77	300	116	729

3. MEASURING CONTAMINANT FLUX METHODOLOGY

Preliminary Design

A colorimetric method for measuring contaminant mass flux was proposed. The method utilizes Gastec Trichloroethylene (TCE) Detector Tubes (Zefon International, Inc) for various measurement ranges (0.125 – 8.8, 1 – 70, and 20 – 1300 ppm). These tubes allow a designated gas concentration to be measured based off of colorimetric response, as seen in Figure 3-1. A hole was made in the Teflon top of a 40 mL vial cap to snugly fit the end of the Gastec tube. The tips of a fresh detector tube were then broken off so as to allow the transfer of the gaseous phase of the compound of interest, in this case TCE.

The first design consisted of placing a stainless steel bowl filled with sand onto of a Thermolyne Type 2200 Hot Plate. The hot plate was preheated to be approximately 200° F at the midpoint of sand layer. Vials were filled with 10 g of a stock solution or a 10 times diluted solution of TCE sorbed granular activated carbon. The Gastec tube ends were then broken off and the base end (indicated by the arrow on the tube) was inserted into the hole in the Teflon cap. Vials were then immediately buried in the preheated sand pack to insulate the heating of the vial all around and allow for gaseous transport from the activated carbon into the Gastec. Figure 3-2 illustrates this setup. This design ultimately did not generate accurate results, reading minimal to no TCE concentration for all samples tested.

Revised Design

A revised design also using the Gastec detector tubes was developed. The design consisted of filling a 40 mL vial with 20 mL of Ethanol and then approximately 10 g of TCE sorbed granular activated carbon. This mixture was put on a sonicator (FS14H Fisher Scientific) to accelerate the TCE extraction rate from the GAC to the Ethanol prior to analysis. The ends of the Gastec tube were then broken off and the base end was fastened in the pump inlet of a piston-type hand pump that draws a fixed volume of gas (Rae Systems LP-1200). A tubing connected to a hollow needle was fastened to the bottom of the Gastec. The needle was then inserted through the Teflon cap of the vial terminating in the air (head space) of the vial. Another hollow needle was then inserted through the cap and into the Ethanol solution to act as an air vent. Figure 3-3 shows an image of this design. The pump was then slowly pulled to create a suction force for the gaseous TCE to travel through the Gastec tubing. After the sample volume of 100 mL of gas had passed through, the TCE concentration could be read from the colorimetric stain length directly along the printed scale of the Gastec tubing, as seen in Figure 3-4. This approach was applied to samples from Charleston Air Force Base in South Carolina, discussed in the following Section.

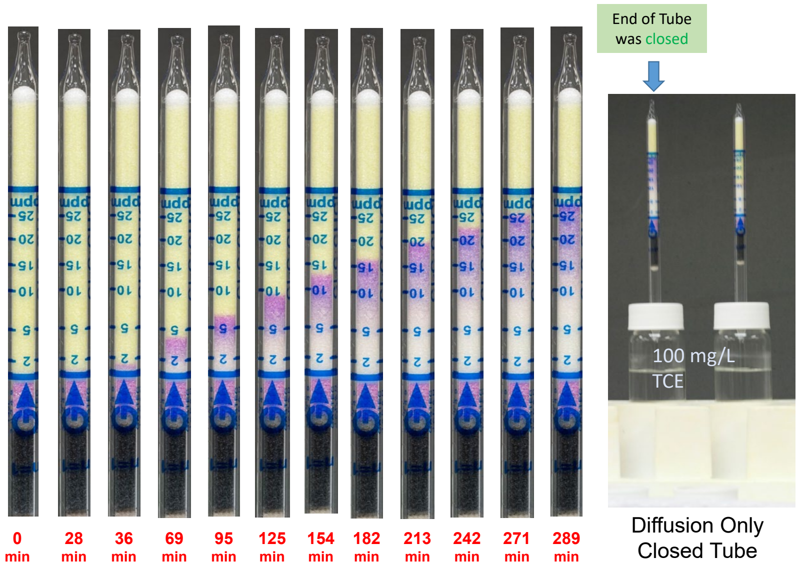


Figure 3-1. Gastec detector tubes for measuring contaminant concentrations.

Figure 3-2. Preliminary colorimetric contaminant test.

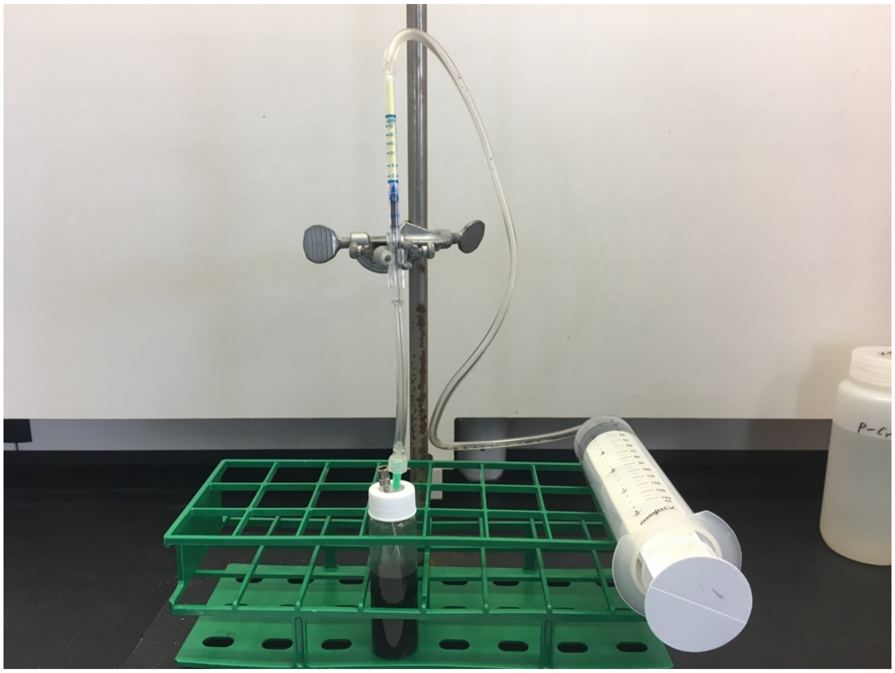


Figure 3-3. Revised colorimetric contaminant test.

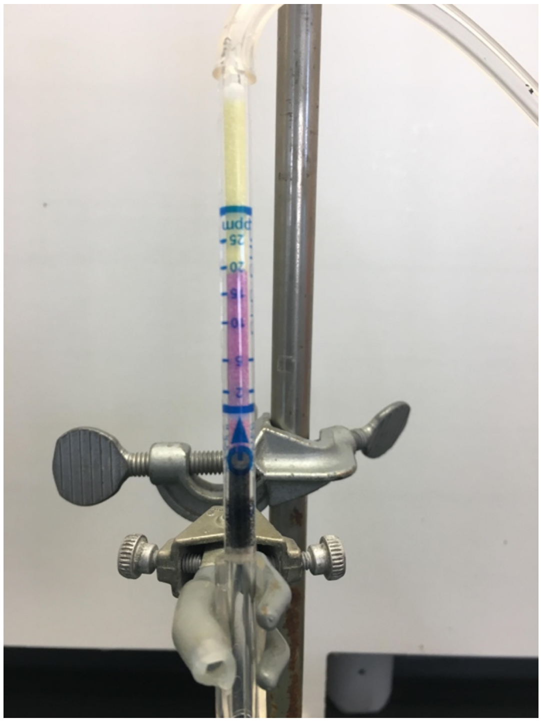


Figure 3-4. Revised colorimetric contaminant Gastec reading.

4. FIELD DEPLOYMENTS

Charleston Air Force Base, South Carolina

Site History & Characterization

Zone 4 of the Charleston Air Force Base is in close proximity to the flight line. Historically Trichloroethene (TCE) was used for the cleaning of aircraft parts. This has resulted in two distinct TCE plumes in zone 4. Plume 1 was derived from an oil/water separator at Building 543 while plume 2 derived from a solvent spill in 1978 at Building 532. TCE concentrations at Plume 1 historically exceeded 100,000 micrograms per liter (µg/L), extending 600 feet. TCE concentrations at plume 2 exceeded 10,000 (µg/L), extending 600 feet as well.

Since the time of contamination, numerous treatment procedures have been conducted on site. These include: molasses and bicarbonate buffers were injected into plume 1 in 2003; molasses, whey and bicarbonate buffers were injected into plume 1 and 2 in 2004; emulsified vegetable oil (EVO) injected in plume 1 in 2008; and EVO injected into plumes 1 and 2 in 2010. Both MW 25 and 89-02 are 2-inch wells.

Laboratory and Field Deployment Design

cPFMs sections were installed into two of the standard PFMs being deployed. The monitoring wells (MW) selected for implementing the cPFM were MW 25 and MW 89-02, both of which are located in Plume 1.

For each PFM there were two distinct colorimetric sections each using a different sorbent. The colorimetric section loaded in the bottom of the PFM used wool-blend while the section loaded in the top of the PFM used 100% wool. Each sorbent section had samples of rhodamine, yellow, and orange dyes. Additionally, each PFM had one blank disk made of wool-blend to use as a background and indicator of potential colorimetric responses by environmental soil color and other environmental factors.

Once sample disks were prepared as per the approach described in this report, the reference disks were stored in a Ziploc bag and sealed in a moisture regulated container to keep the reference disks relatively moist. The PFMs were deployed in the aforementioned screened wells for 23 days before being retrieved. After being returned from the field site, the samples were analyzed as per the above described method. Images of the cPFM are shown in Figure 4-1 and results are summarized in Section 5.

Black Hall University of Florida, Florida

Site History & Characterization

Approximately 40 years ago, a landfill had been present in the area of Black Hall on the University of Florida campus. In more recent years, three 2-inch monitoring wells were installed into the Upper Floridan aquifer, approximately 55 feet deep, to evaluate any effects of the landfill on groundwater.

Laboratory and Field Deployment Design

Multiple colorimetric PFM deployments were conducted in these monitoring wells to compare the measurement of Darcy flux from the standard and colorimetric PFM. The first deployment consisted of one PFM with two colorimetric layers and GAC-based layers above and below both for reference. Each layer contained samples of rhodamine, yellow, and orange dyes, as well as turmeric for both 100% wool and wool-blend. The PFM was deployed for 20 days before being retrieved and analyzed as per the above described method.

The second deployment followed the same structure as the first (two colorimetric layers with three GAC-based layers positioned above and below the colorimetric). The top of the two layers followed the same layering as the first deployment entailing all combinations of both sorbents and four dyes. The bottom layer was made of entirely rhodamine samples: four 100% wool and four wool-blend samples, shown in Figure 4-2. The PFM was deployed for 12 days before being retrieved and analyzed as per the above described method. The results of both deployments at the Black Hall well are summarized in Section 5.

Joint Base Lewis–McChord near Tacoma, Washington

Site History & Characterization

The University of Florida research group has been involved with field studies at Joint Base Lewis–McChord since around 2013. The group is currently evaluating the long-term conditions at the site following thermal remediation at the East Gate Disposal Yard (EDGY). This lead to the publication on pre- and post-remedial mass flux and mass discharge measurements (Brooks et al., 2008). We used the recent deployment of PFMs to include measurements using the colorietric approach to compare with the standard PFM results.

Zone 4 of the Charleston Air Force Base

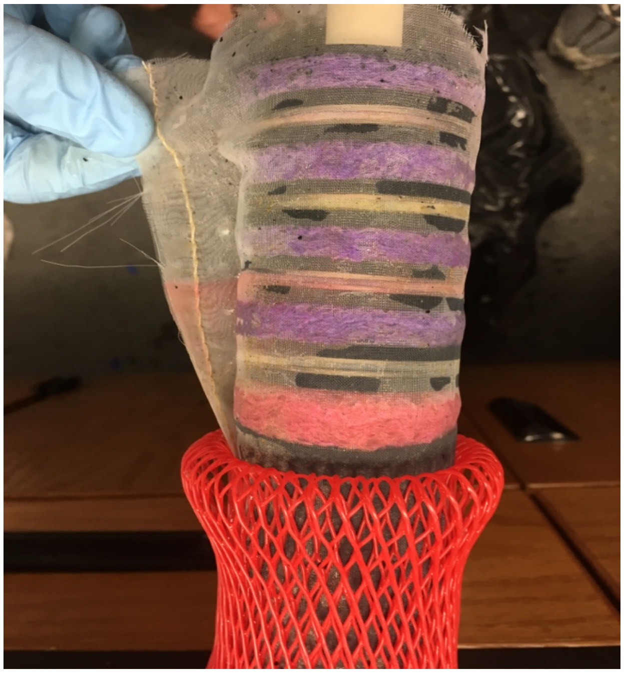


Figure 4-1. Charleston cPFM showing flow direction by dye travel.

Figure 4-2. Black Hall cPFM entire rhodamine layer.

5. RESULTS AND FUTURE WORK

Both laboratory and field experiments were conducted to assess the efficacy of a colorimetric approach to measuring groundwater flux within the PFM. These results were summarized through 3-D box aquifer laboratory experiments and deployment of the cPFM in monitoring wells at contaminated sites. Critiques of the cPFM method were incrementally made through determining the influence different variables had on colorimetric response, such as moisture content and sample storage. A summary of laboratory and field test results and their corresponding margins of error is included for comparison between the standard PFM and cPFM as well as a cost comparison analysis. Initial tests were conducted to measure contaminant mass flux colorimetrically as well.

Laboratory Testing

Laboratory testing of the cPFM entailed experiments in two separate 3-D box aquifer testing apparatuses with different simulated aquifer geometries and varied flow rates. Tests spanned from 1 to 7 days, 16 to 130 pore volumes, and Darcy fluxes ranging from 25 to 69 cm/day. These systems were used to evaluate the Darcy flux calculations and simulate the subsurface environment and conditions the cPFM would be deployed in. A designated deployment duration was set prior to installation and the outflow rate was measured daily and averaged over the deployment period. This value was then converted to a flux using the box cross-sectional area. This was defined as the actual flux and was used as a reference to assess the accuracy of the cPFM as well as a check on the consistency of the set flow rate during the test duration. The Darcy flux was then calculated based on the colorimetric changes due to 3-D box aquifer deployments using Equation 5-1 (Hatfield et al., 2004)

$$q_D = 1.67\frac{R * \theta * r * (1 - MR)}{t * \propto} \tag{5-1}$$

where R is the retardation factor of the resident dye on the fabric media, (summarized in Table 2-1), θ is the water content of the fabric, r is the radius of the cPFM device, MR is the relative mass of dye remaining in the fabric obtained from the UV light image analysis of each sample and reference disk in ImageJ, t is the test deployment duration, the geometric coefficient of 1.67 (see Hatfield et al., 2004 for details), and $\propto$ is the flow convergence factor (summarized in Tables 5-1 and 5-2). The $\propto$ value was determined using the measured hydraulic conductivity of the cPFM sorptive media, the well screen, and the surrounding aquifer, as well as the radius of the well and the cPFM. The $\propto$ value for a fully screened well excluding a filter pack was calculated using Equation 5-2 (Klammler et al., 2006)

$$\propto = \frac{4}{\left(1+\frac{1}{K_s}\right)\left(1+\frac{K_s}{K_D}\right)+\left(1-\frac{1}{K_s}\right)\left(1-\frac{K_s}{K_D}\right)\left(\frac{1}{R_s}\right)^2} \tag{5-2}$$

where K_s represents the ratio of the hydraulic conductivity of the well screen to the hydraulic conductivity of the surrounding aquifer. K_D represents the ratio between the hydraulic conductivity of the sorptive media, in this case being the fabric, and the hydraulic conductivity of the surrounding aquifer. R_s represents the ratio between the outer radius of the well screen and the radius of the cPFM. The flow convergence factor is applied for the horizontal, flow, direction. Tables 5-1 and 5-2 summarize the values comprised in the calculation of alpha for wool-blend and 100% wool, respectively.

The results of the 3-D aquifer box cPFM tests are summarized in Figures 5-1 through 5-8 for each dye and sorbent material combination. In all of the figures, the plots are of the measured volume of water determined from the cPFM as a function of the actual volume of water measured and averaged daily during the test duration. The gray dashed line in all of the figures denotes a 1-1 line indicating a direct correlation between the cPFM measurement and the actual measurement. As can be seen in the figures, certain dye and sorbent material combinations produce significantly better results than others. Fluorescent orange and yellow yielded the best fit to the 1-1 line for wool-blend with percent errors of 26% and 28%, respectively. Rhodamine had an average error of 46% while turmeric had an error of 55%. Fluorescent yellow and rhodamine yielded the best results for 100% wool with percent errors of 28% and 35%, respectively. Fluorescent orange had an average error of 63% while turmeric had an error of 162%. Table 5-3 summarizes the percent error for each dye and sorbent material combination.

A curve fitting exercise was conducted to each of the dye and sorbent material combinations to determine a correction factor to best fit cPFM and applied volumes (i.e., fit the 1-1 line). A sensitivity analysis was conducted on the Darcy flux equation (Equation 5-1) to determine which parameters had the largest influence on the output. It was determined that the results were most sensitive to changes in R and $\propto$, and thus, the correction factor was applied to the ratio of these values in Equation 5-1. The average percent error for each dye and sorbent combination was then compared for the initial $R/\propto$ values and the modified values. Table 5-5 summarizes the initial $R/\propto$ values, the correction factor, C_F, and the adjusted $R/\propto$ values, and their corresponding percent errors. It is notable that C_F is greater than 1 for all combinations except for turmeric on 100% wool. This indicates that nearly all of the cPFM combinations tend to underestimate groundwater flux on average. It can be seen in the table that for many of the combinations the curve fitting did little or nothing to improve the results, and in some cases, increased the average percent error. The two exceptions to this being rhodamine on wool-blend and turmeric on 100% wool, both of which saw diminished average error after applying the adjusted $R/\propto$ values. Rhodamine on wool-blend decreased its error by 25% while turmeric on

100% wool decreased its error by 125%. The plot of the adjusted $R/\propto$ values applied to rhodamine on wool-blend is shown in Figure 5-9 and can be compared to the original plot in Figure 5-1. It can be seen that the correction factor linearly shifted the plot upwards to result in a strong fit to the 1-1 line. The nature of many of the plots not improving, and even worsening, with the adjusted values could be a matter of the inherit degree of uncertainty still in the data as well as outliers skewing the results.

Field Testing

Field testing of the cPFM has been conducted at the Charleston Air Force Base, South Carolina and a University of Florida campus well located at Black Hall. The alpha values that were applied in the laboratory studies were used to evaluate the data from both field sites, assuming the hydraulic conductivities of the surrounding aquifer and well screen at the site to be similar to those of the laboratory setting. The $\propto$ values were 0.78 for wool-blend, 0.81 for 100% wool, and 0.80 for standard activated carbon based PFMs. If additional information is available and calculated alpha values are significantly different at other field sites these values can be adjusted to provide higher quality estimates of Darcy flux.

For all field tests the PFMs have been constructed with alternating GAC-based and colorimetric-based layers with the GAC-based standard PFM results averaged from above and below the colorimetric layer, acting as the reference for comparison to the cPFM results. Tests were conducted for varying durations to assess the accuracy of the cPFM at a range of MR values. Test durations ranged from 12 to 23 days with standard PFM Darcy flux measurements ranging from 5 to 10 cm/day with future deployments intending to expand upon the Darcy flux range. The field test results followed trends similar to those for laboratory test results. The dye and sorbent material combinations with the lowest percent error were fluorescent orange on wool-blend and rhodamine on 100% wool with errors of 22% and 25%, respectively. Fluorescent yellow and rhodamine on wool-blend both yielded promising results with percent errors of 33% and 36%, respectively, followed by fluorescent yellow on 100% wool with an error of 43%. Fluorescent orange on 100% wool had an error of 166% indicating that the dye and sorbent combination did not perform as desired. Additionally, turmeric produced percent errors in the multiple hundreds for both sorbent materials, eliminating it from future field testing. For reference, the margin of error on the standard PFM for measuring local fluxes averaged over the screen interval at two field sites was within 15% of the imposed groundwater flow (Annable et al., 2005). The results of the cPFM field tests can be seen in Figures 5-10 through 5-17 and their percent errors summarized in Table 5-4. It is notable that the PFM error was averaged over multiple PFMs while the cPFM error was from single point measurements.

Charleston Air Force Base, South Carolina: Findings

Darcy velocities were obtained for five GAC-based segments within each PFM as well as for two cPFM segments. The Darcy velocities from the standard PFM design were averaged for sections above and below those of the colorimetric samples to use as a reference of comparison at similar depths for the two approaches. The comparison of Darcy velocities between the standard PFM and colorimetric approaches for each dye and sorbent selection is summarized in Tables 5-6 and 5-7 for monitoring wells 25 and 89-02, respectively.

The results for MW 25 produced the best Darcy velocities for rhodamine on both 100% wool and wool-blend, with Darcy values within 2 cm/day of the standard PFM result. Orange on wool-blend produced the next best results, being within 3 cm/day of the standard PFM result. Yellow on both sorbent materials overestimated the Darcy velocity by approximately a factor of 2 while orange on 100% wool overestimated the Darcy value by a factor of 4.

For MW 89-02, Orange on 100% wool and yellow on wool-blend show the best results, both producing Darcy velocities within 1 cm/day of the standard PFM result. The results of rhodamine and orange on wool-blend were within 3 cm/day and yellow on 100% wool was within 4 cm/day of the standard PFM result. Rhodamine on 100% wool underestimated the Darcy velocity by approximately a factor of 5 in this case.

Black Hall University of Florida, Florida: Findings

Two separate field deployments were conducted at the same well at the University of Florida Black Hall site. For both tests the PFM consisted of two colorimetric segments with three GAC-based segments positioned above and below each of the colorimetric layers. The Darcy velocities from the standard PFM design were averaged for sections above and below those of the colorimetric samples to use as a reference of comparison at like-depths for the two approaches. The results of the first deployment are summarized in Table 5-8 while the results of the second deployment are summarized in Tables 5-9 and 5-10.

The first deployment yielded the best results for wool-blend on all three of the fluorescent dyes with Darcy velocities within 1 cm/day of the standard PFM. For 100% wool, rhodamine and yellow were both within 2 cm/day of the standard PFM result. Turmeric consistently yielded results overestimating the Darcy velocity by a factor of at least 4.

The second deployment was split into two layers: one layer segmented by each dye, as per previous deployments, and another layer of all rhodamine samples. This second layer consisted of four rhodamine samples on wool-blend and four on 100% wool, all separated by one rigid disk between each. For the layer including all dye and sorbent combinations, wool-blend on orange yielded the best results, being within less than 1 cm/day off. Rhodamine and yellow were both within 3 cm/day of the standard PFM result. For 100% wool, rhodamine and yellow yielded the best results, both being within 1 cm/day of the standard PFM result. Turmeric consistently yielded results overestimating the Darcy flux by a factor of at least 3. For the rhodamine layer with four samples per sorbent material, the averaged result for 100% wool was within 2 cm/day of the standard PFM result while that of wool-blend was within 3 cm/day.

Detection Range

The PFM's five alcohol tracers allow for a broad detectable range of measuring mass flux. For a two-week duration in a 2-inch diameter well the detection limit for the standard PFM is approximately 0.7 cm/day to ensure advective dominated flows inside the PFM (Hatfield et al., 2004). The upper limit of detection is nearly indefinite by the ability to add longer carbon-chained tracers (although this can present its own complications). Just as each alcohol tracer has its own detection spectrum in the PFM, each dye and sorbent combination has a distinct detection spectrum in the cPFM. Table 5-11 summaries the detectable ranges for each dye and sorbent combination for the cPFM. These values are based off of a 14-day deployment in a 2-inch diameter well for MR values ranging from 0.2 to 0.9. The lowest detectable groundwater flux from a dye and sorbent combination is for rhodamine on wool-blend with a value of 1.8 cm/day while the highest detectable groundwater flux is from turmeric on 100% wool with a value of 185 cm/day. It is notable that turmeric has thus far not produced consistently accurate results and that other dye and sorbent combinations might need used for acquiring accurate measurements of higher fluxes. The detection range could be expanded upon by adjusting the deployment duration and/or the cPFM diameter. At the moment though in testing the cPFM concurrently with the PFM these variables are remaining constant. Investigation into new sorbent materials could extend the detectable range of the cPFM.

Moisture Content

Equalizing the moisture content between the sample and reference disks is crucial to producing accurate cPFM results. Discrepancies in moisture content can lead to errors in the

ImageJ analysis of the mean image value for both sample and reference disks, propagating errors into the MR values and Darcy flux. Experiments were conducted to assess the optimal amount of water to add to reference samples to equalize moisture content to sample disks, difference in reference storage techniques, and how color intensity of reference disks changes over storage duration. These variables were assessed with samples after 2, 4, 6, and 10 days of reference disk storage. The reference samples were stored in two different ways: one set was stored in individual airtight bags while another set was stored in individual airtight bags inside a sealed container with water wet sponges on a bed of water (Figure 2-6). The results of these tests are summarized in Figures 5-18 through 5-21 for rhodamine, yellow, orange, and turmeric, respectively.

The average standard deviation in image values across each dye and sorbent material combination and storage duration was 3.83 for reference samples stored in only an individual airtight bag and was 3.53 for reference samples additionally stored inside the moisture box. This indicates that the influence of moisture content on the image value is only minimally influenced by the storage type of the reference samples and the duration they are stored within durations spanning 2 to 10 days, with a slightly lower standard deviation resulting from reference samples stored in the moisture box. As a result, all samples were stored this way moving forward.

Contaminant Flux Testing

The colorimetric Gastec-based design of measuring contaminant flux was applied to the GAC samples from MW 89-02 from the Charleston Air Force Base field site and compared to the standard PFM approach results. At low concentrations (approximately 5 mg/m^2/day and below) the colorimetric approach yielded similar results to that of the standard PFM. The top sample in MW 89-02, located at 31 ft., had a significantly higher flux (approximately 17 mg/m^2/day) while the colorimetric approach did not exceed approximately 5 mg/m^2/day. This is likely due to the concentration being outside of the scale range for the Gastec tubes used (No. 132LL) with a measurable range of 0.125 – 8.8 ppm and a scale range of 0.25 – 4.0 ppm. In the future, a Gastec tube with a higher scale range could be used when the concentration exceeds that of the tubing being used; the 132L model has a measurable range of 1 – 70 ppm and a scale range of 2 – 25 ppm. Figure 5-22 summarizes the results comparing the standard PFM and colorimetric PFM approaches to measure DCE flux. Further testing will be conducted to create a calibration curve to determine the correlation and consistency of this approach. Additionally, further tests will be conducted to determine if and where losses could be occurring within the colorimetric approach resulting in diminished measurements of contaminant flux at higher flux values.

Cost Comparison Analysis

One of the objectives of this project was to demonstrate how cPFMs could be used to collect high resolution data while reducing the high cost. A breakdown of the material, labor, analysis, and shipping costs for both the standard PFM and cPFM was completed and is summarized in Table 5-12. The cost breakdown was based on a single 2-foot design. The overall cost for the standard PFM came out to be \$176 while that of the cPFM came out to be \$113, resulting in a 36% cost reduction. It can be seen from Table 5-12 that the material and labor costs were fairly comparable between the two methods with the cPFM costing slightly more in both categories. The largest differences accrued in the analysis comparison and the shipping costs. The shipping costs are significantly lower for the cPFM because only the colorimetric disks need to be shipped back for analysis compared to the entire device for the standard PFM. Additionally, in the future the intention is to be able to conduct the sampling analysis on-site for the cPFM, resulting in even lower costs and faster results. It is notable that the percent of cost reduction could fluctuate in a scaled up cost assessment for a full field deployment but that regardless the cPFM is expected to significantly lower the cost.

Interpretations and Future Work

Moving forward, further laboratory testing could be done to improve the accuracy of the cPFM and refine the method for the cFPM. Additionally, field tests should become an increasingly larger component of this project for assessing how accurately colorimetric response can measure groundwater flux in differing hydrogeological properties, flow rates, and contaminants present. Further areas of potential future work or limitations of the application of the cPFM include but are not limited to effects of varying soil types and colors, strong ionic levels such as salt water, presence of free phase of NAPL (non-aqueous phase liquid), and microbial activity or oxidation of metal or inorganics (iron sulfides, sulfate, soluble uranium, etc.).

An alternative cPFM design is to be investigated using small diameter, direct push probes. By creating a cPFM designed for a diameter of 0.75 inches compared to 2 inches the deployment duration reduces by a factor of approximately 3. This can be done with small diameter probes, minimizing material costs, in shallow groundwater sites. The reduction in deployment duration makes the possibility of deploying and retrieving direct push PFMs in a single trip, further reducing costs, as well as expanding the detection range of the cPFM. This method, as well as the tradeoff in accuracy with PFM diameter reduction would need to be investigated.

Another avenue of the project moving forward is making testing apparatuses that are accessible and feasible on site in the field for rapid results. For the case of measuring Darcy flux, this entails the construction of a sealed box to inhibit light from entering with a UV light, sample platform, and camera lens fitting. For the case of measuring contaminant flux, this consists of securing the pump and Gastec tubes in a controlled environment as well as a rotator or sonicator to accelerate the TCE extraction rate from the GAC to the Ethanol prior to analysis. These systems would allow for on-site access to results and save on return shipping costs and lengthy analysis work of the standard PFM.

The majority of this body of work was focused on measuring groundwater flux. Extensive work should still be done to develop and test a viable method for measuring contaminant mass fluxes colorimetrically. This component of the project should be built upon and applied to other potential contaminants, firstly including chlorinated solvents and eventually other contaminants of interest.

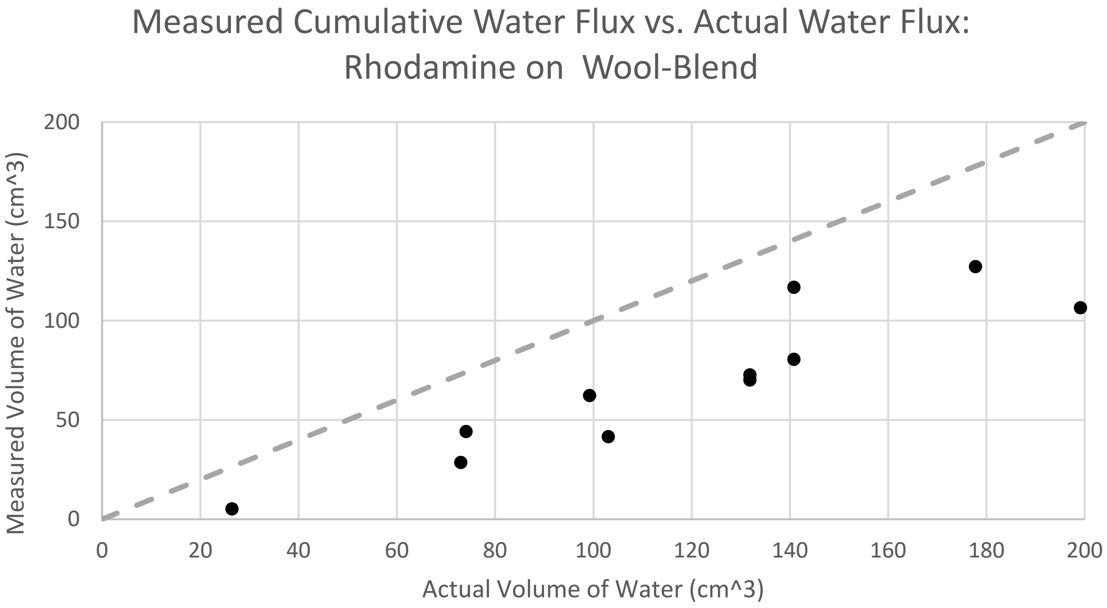


Figure 5-1. Measured Darcy flux versus actual Darcy flux: rhodamine dye on wool-blend sorbent fabric

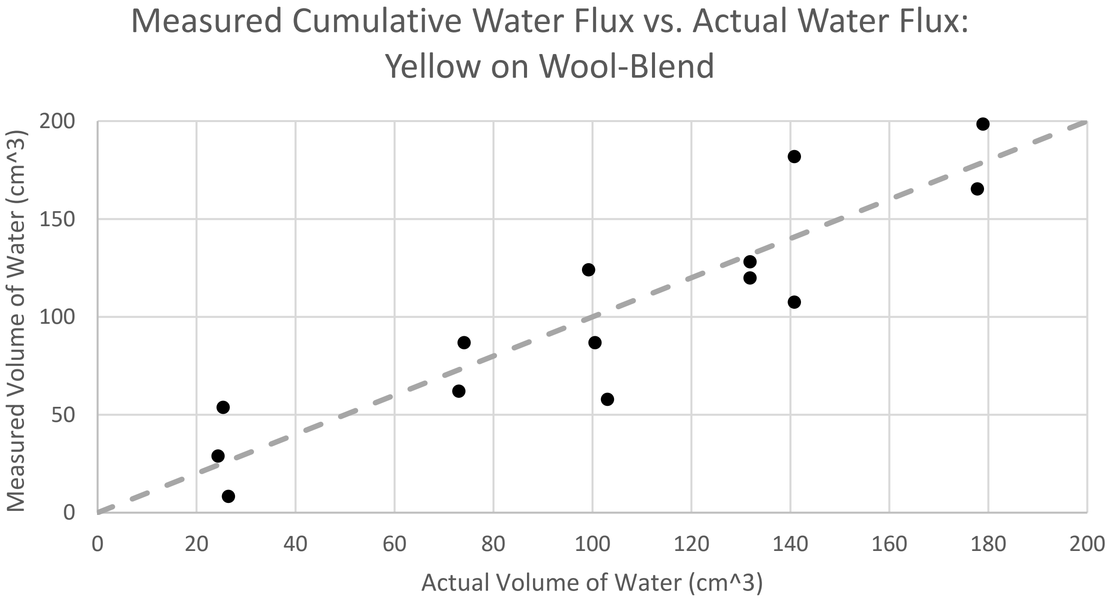


Figure 5-2. Measured Darcy flux versus actual Darcy flux: yellow dye on wool-blend sorbent fabric

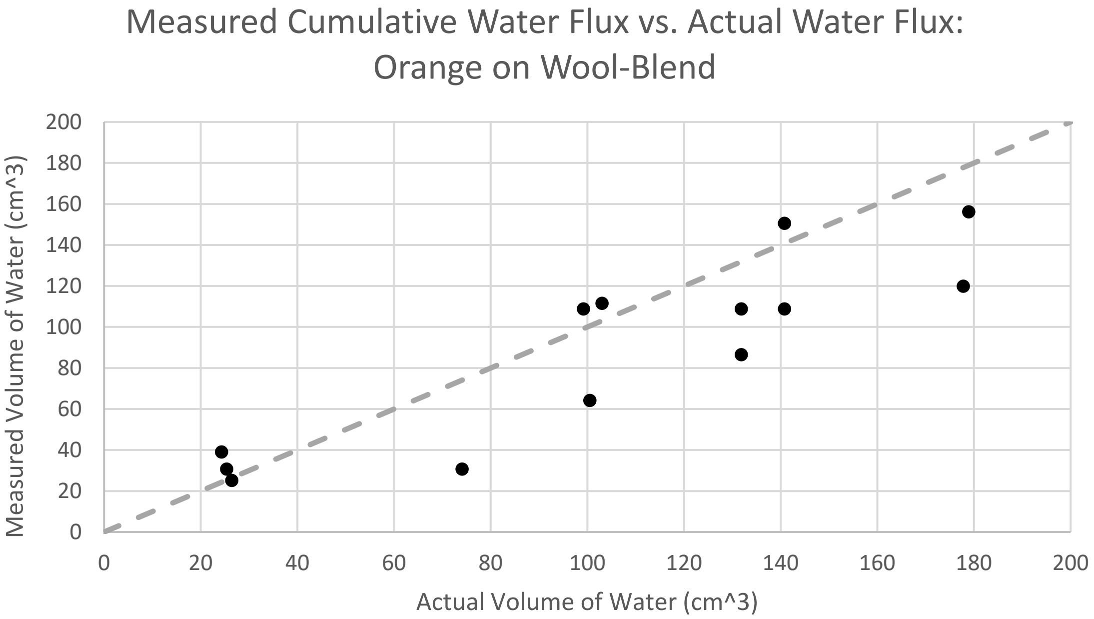


Figure 5-3. Measured Darcy flux versus actual Darcy flux: orange dye on wool-blend sorbent fabric

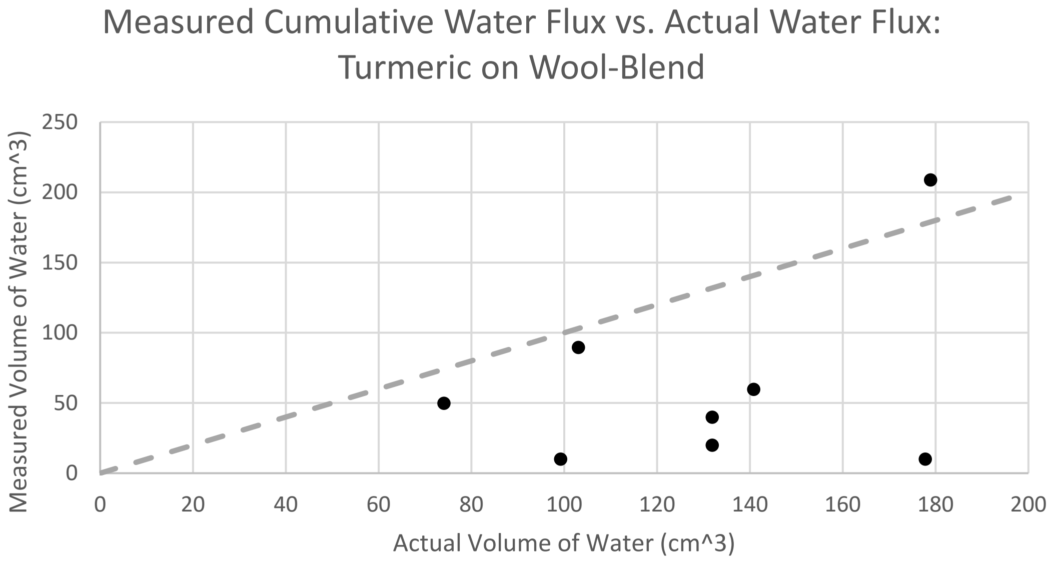


Figure 5-4. Measured Darcy flux versus actual Darcy flux: turmeric dye on wool-blend sorbent fabric

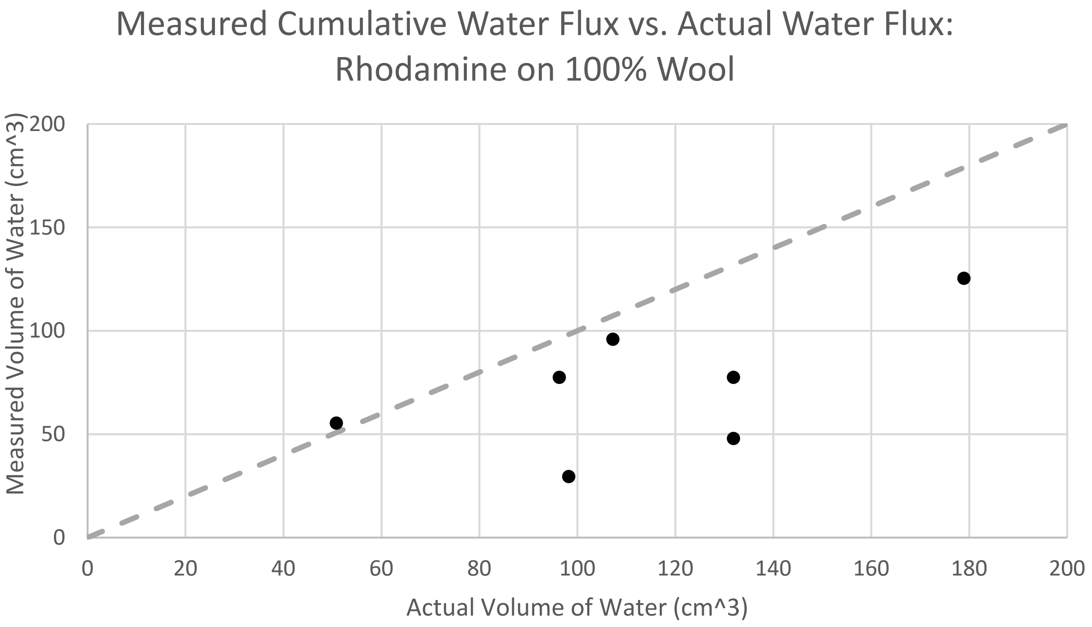


Figure 5-5. Measured Darcy flux versus actual Darcy flux: rhodamine dye on 100% wool sorbent fabric

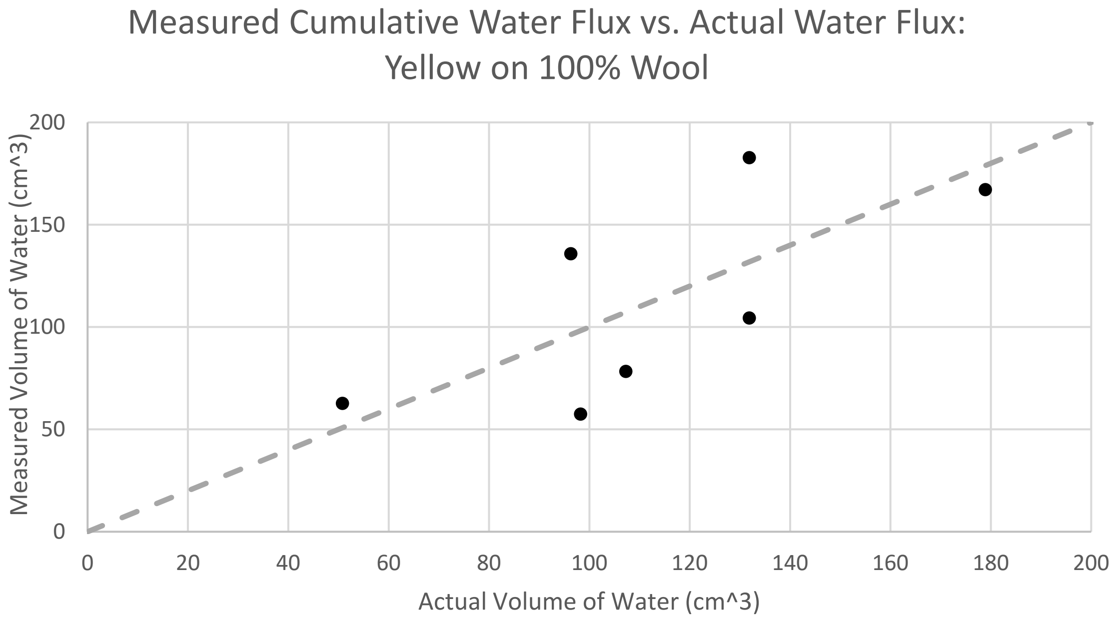


Figure 5-6. Measured Darcy flux versus actual Darcy flux: yellow dye on 100% wool sorbent fabric

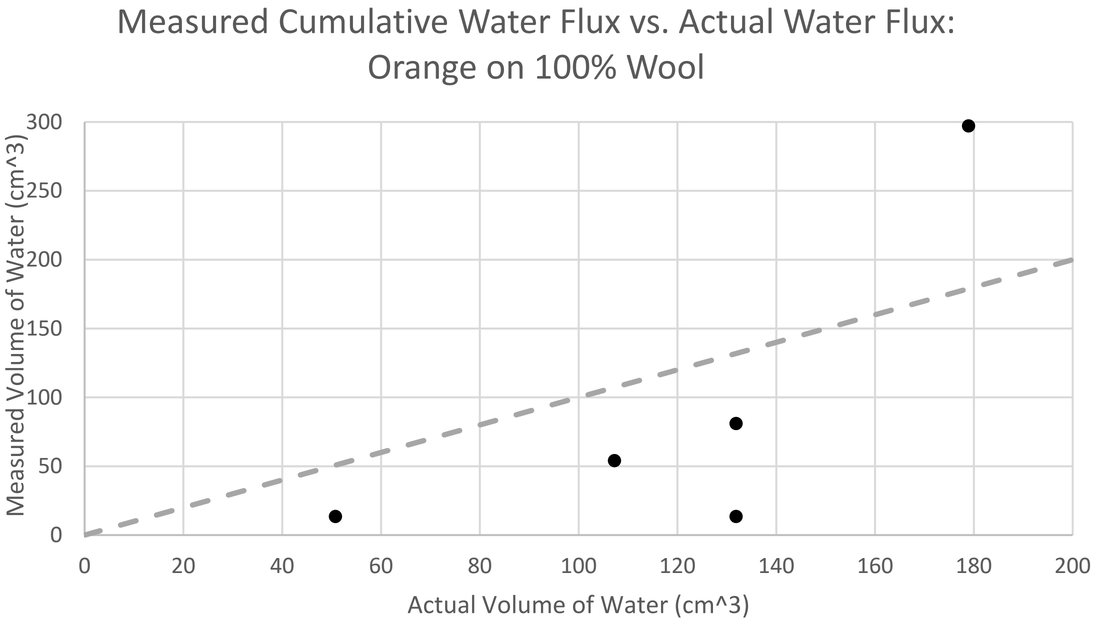


Figure 5-7. Measured Darcy flux versus actual Darcy flux: orange dye on 100% wool sorbent fabric

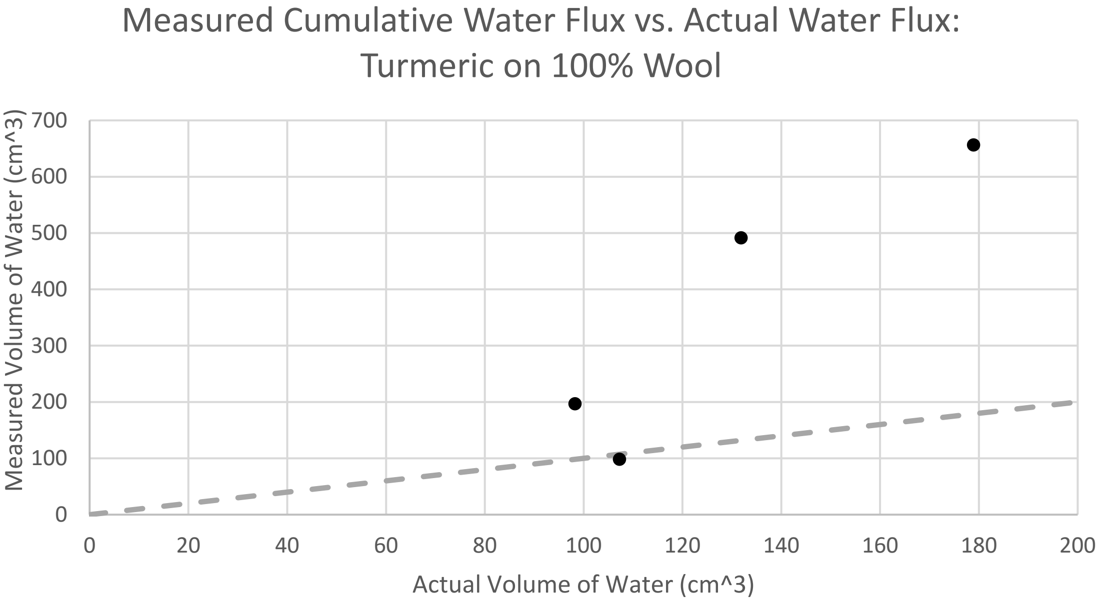


Figure 5-8. Measured Darcy flux versus actual Darcy flux: turmeric dye on 100% wool sorbent fabric

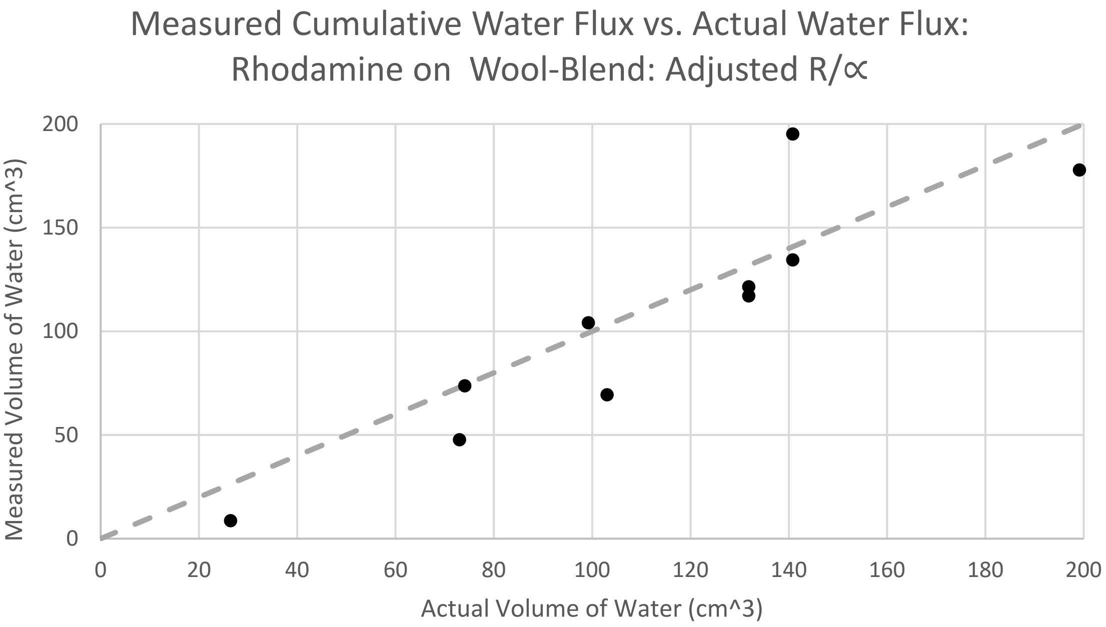


Figure 5-9. Adjusted R/∝ coefficient applied to rhodamine on wool-blend sorbent fabric laboratory data

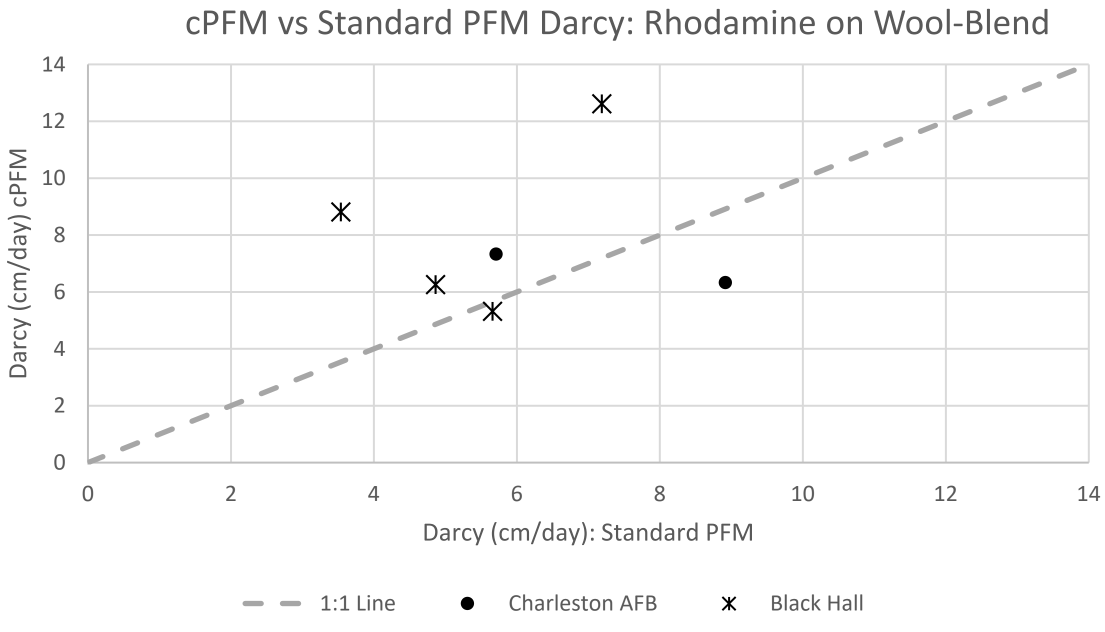


Figure 5-10. cPFM Darcy flux versus standard PFM Darcy flux: field site data: rhodamine on wool-blend sorbent fabric

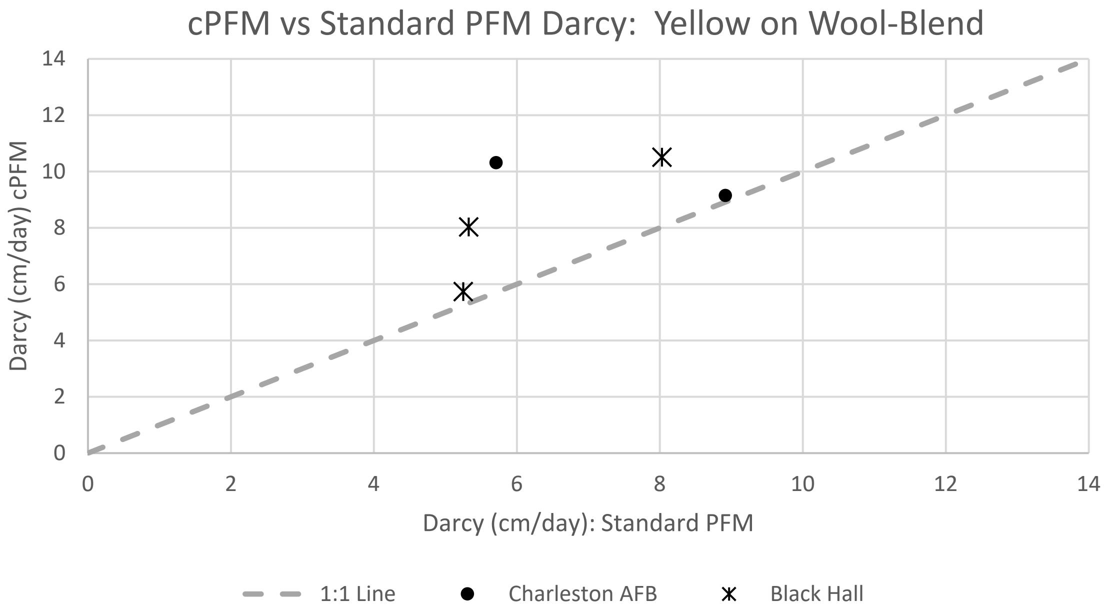


Figure 5-11. cPFM Darcy flux versus standard PFM Darcy flux: field site data: yellow on wool-blend sorbent fabric

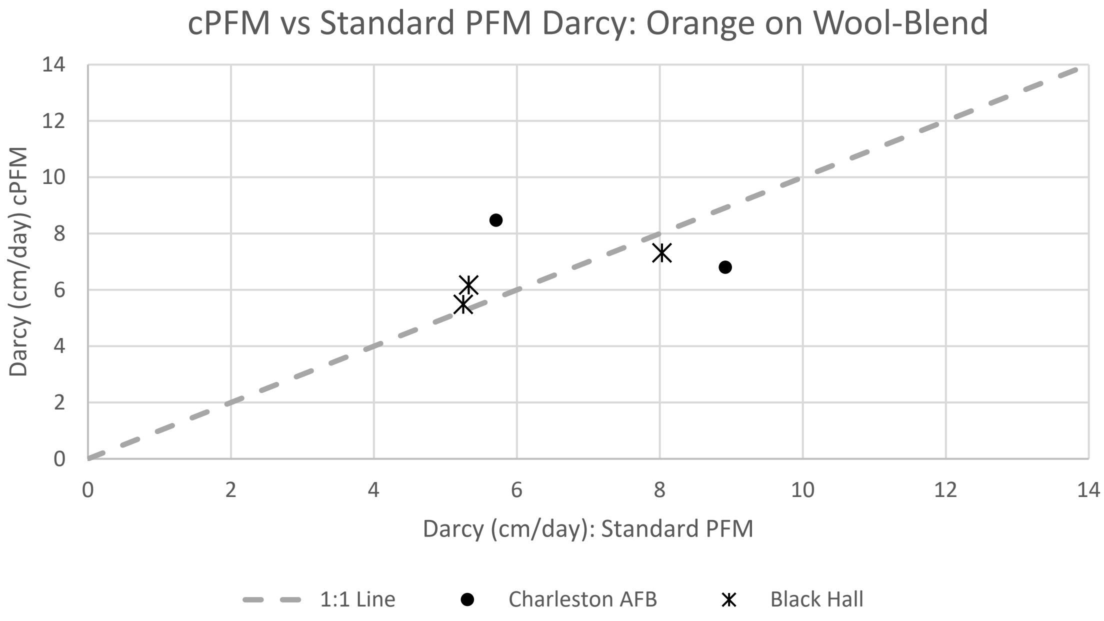


Figure 5-12. cPFM Darcy flux versus standard PFM Darcy flux: field site data: orange on wool-blend sorbent fabric

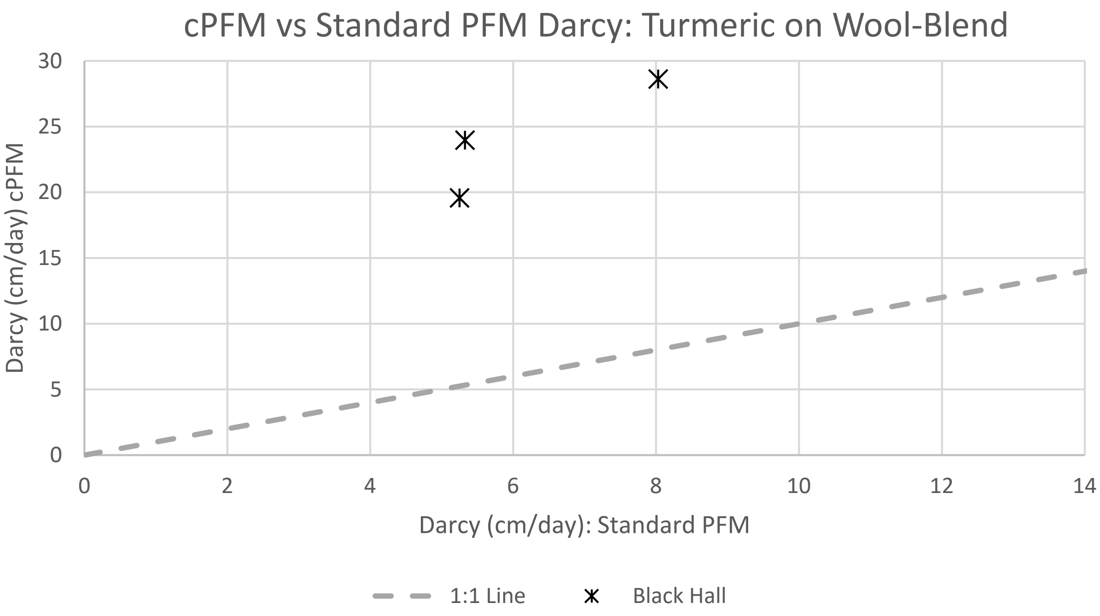


Figure 5-13. cPFM Darcy flux versus standard PFM Darcy flux: field site data: turmeric on wool-blend sorbent fabric

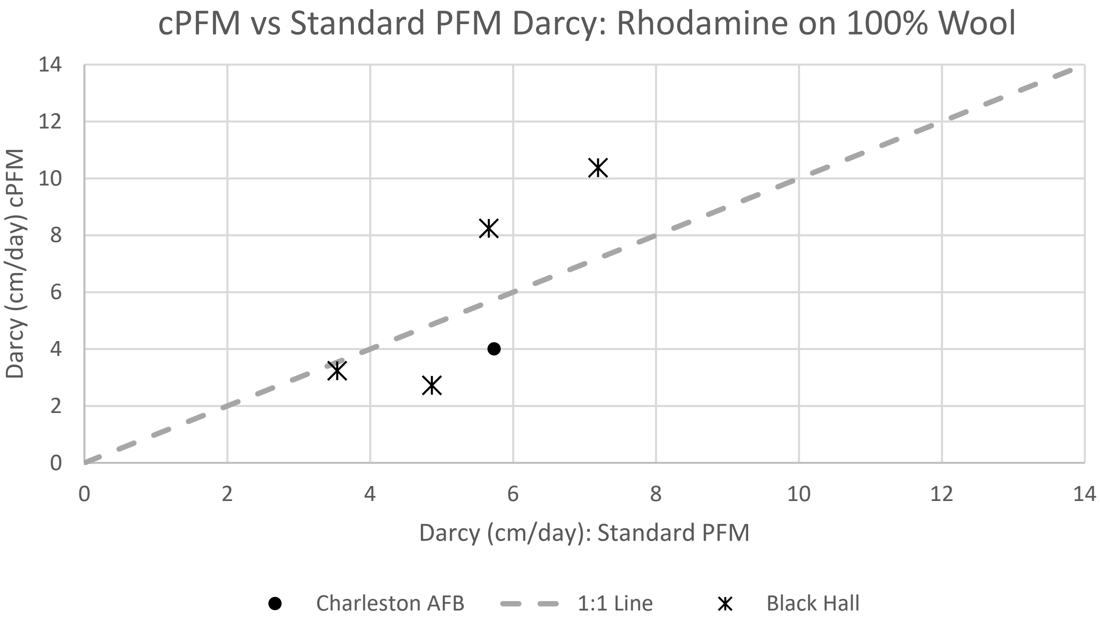


Figure 5-14. cPFM Darcy flux versus standard PFM Darcy flux: field site data: rhodamine on 100% wool sorbent fabric

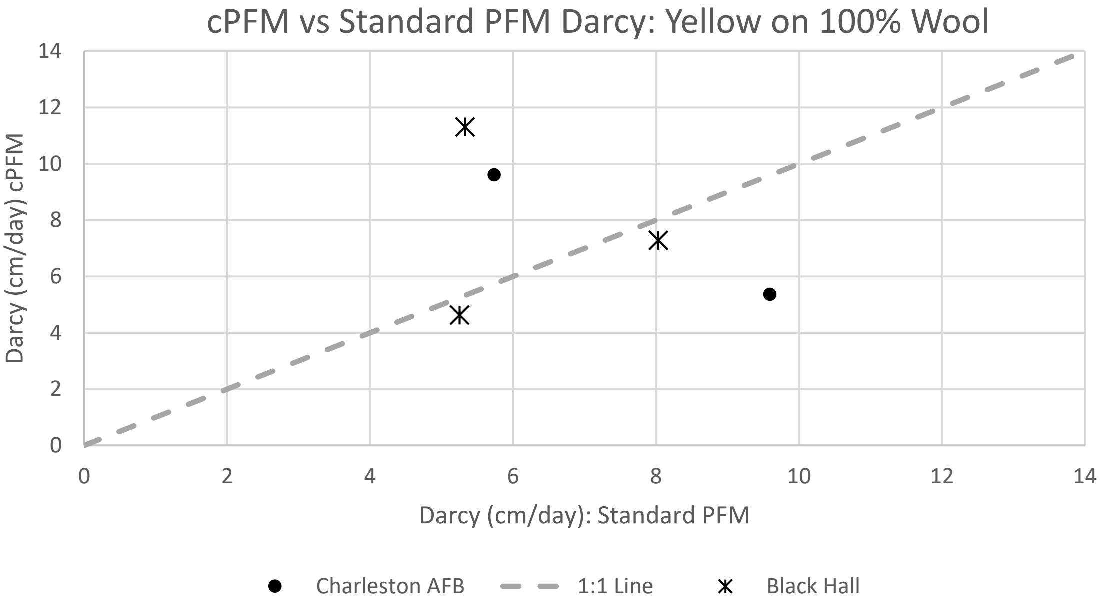


Figure 5-15. cPFM Darcy flux versus standard PFM Darcy flux: field site data: yellow on 100% wool sorbent fabric

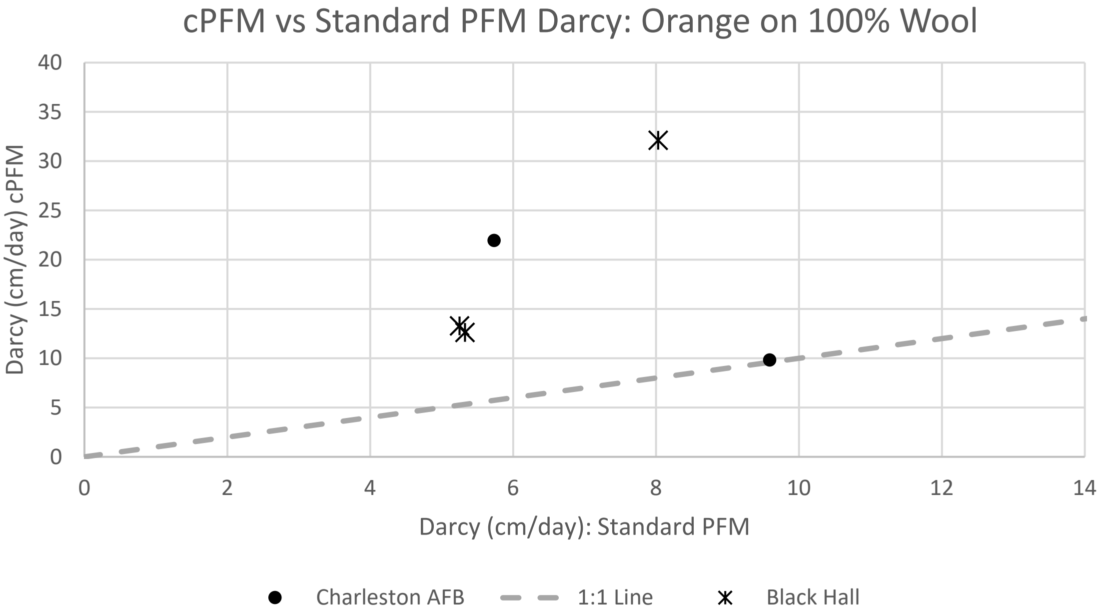


Figure 5-16. cPFM Darcy flux versus standard PFM Darcy flux: field site data: orange on 100% wool sorbent fabric

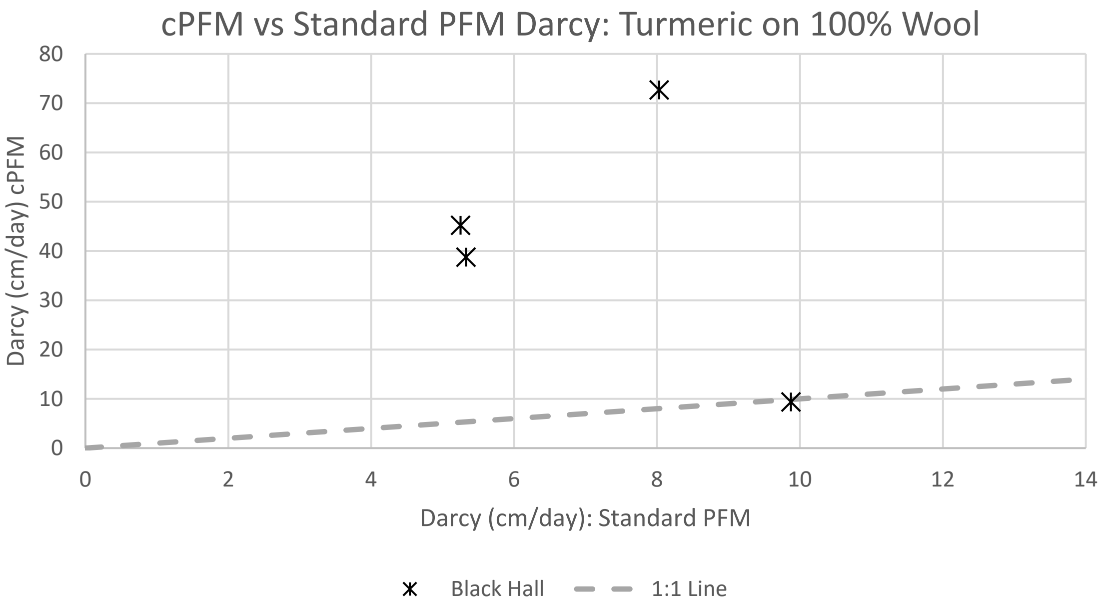


Figure 5-17. cPFM Darcy flux versus standard PFM Darcy flux: field site data: turmeric on 100% wool sorbent fabric

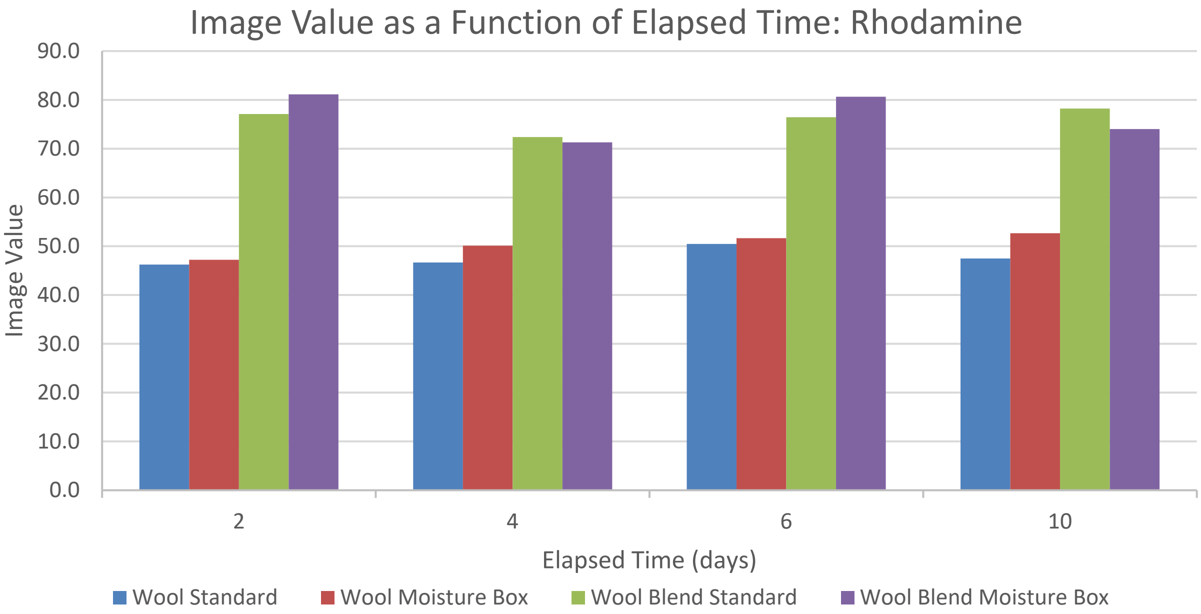


Figure 5-18. Moisture content analysis: image value of reference disk storage over time and storage type: rhodamine

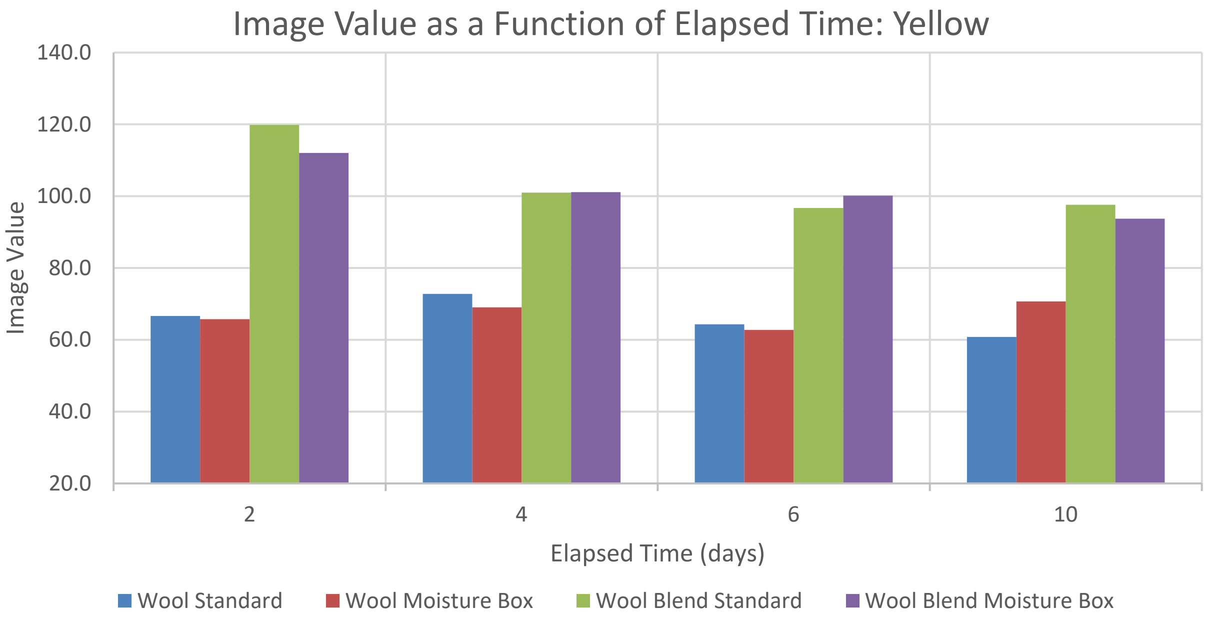


Figure 5-19. Moisture content analysis: image value of reference disk storage over time and storage type: yellow

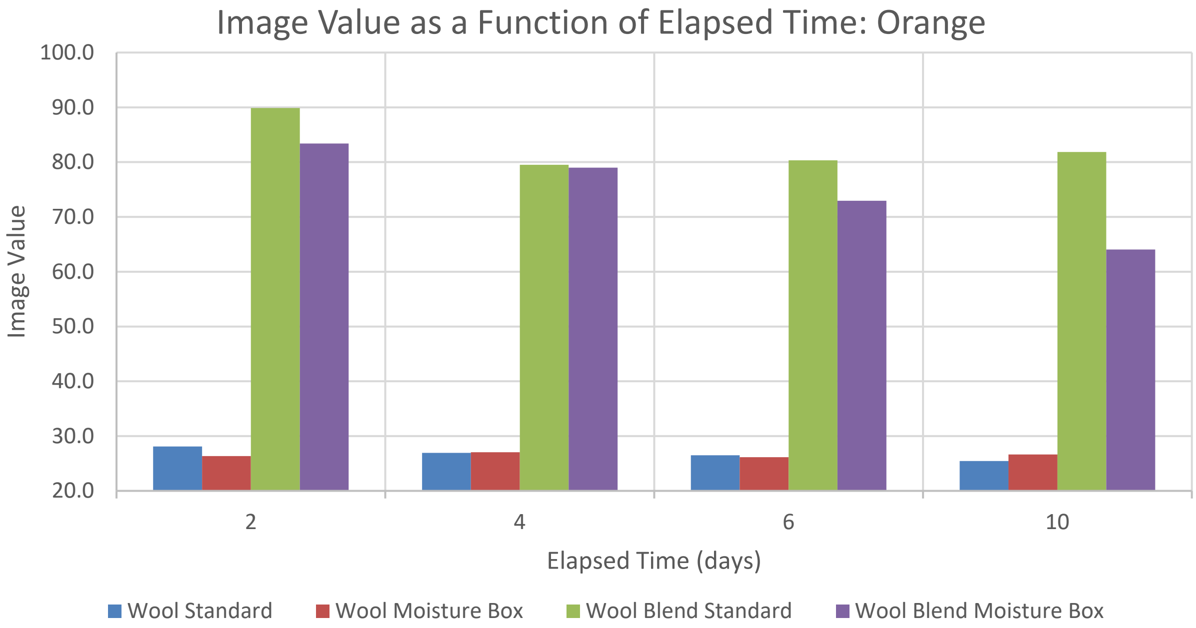


Figure 5-20. Moisture content analysis: image value of reference disk storage over time and storage type: orange

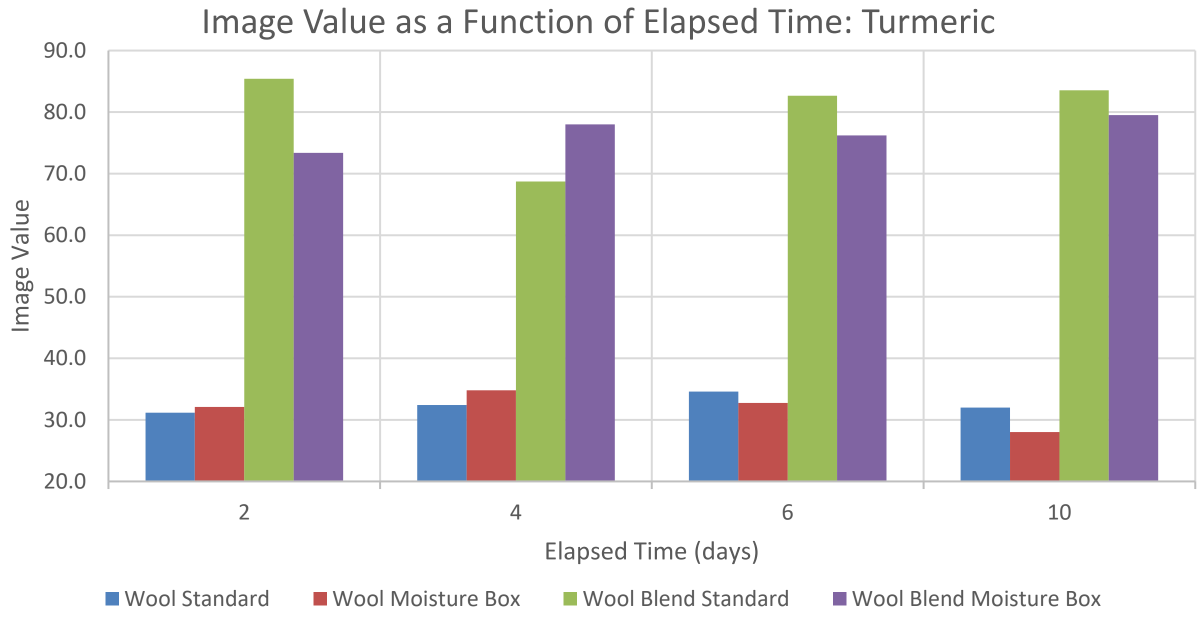


Figure 5-21. Moisture content analysis: image value of reference disk storage over time and storage type: turmeric

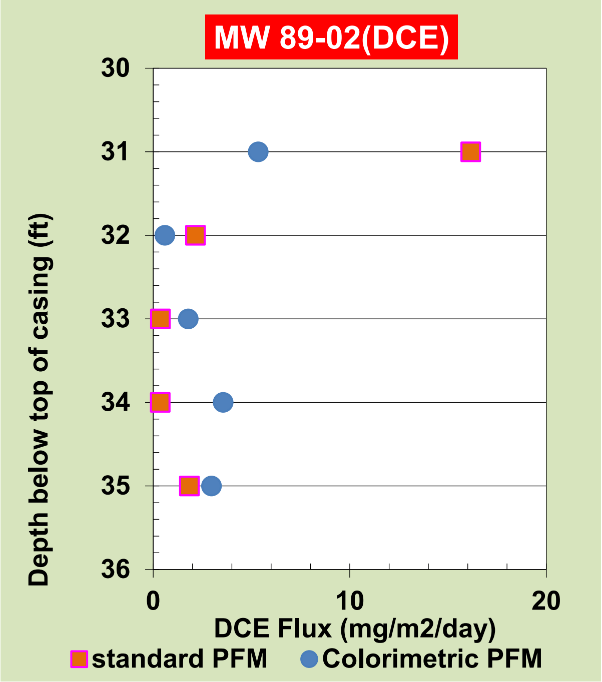


Figure 5-22. cPFM versus standard PFM contaminant flux measurement: Charleston AFB, South Carolina MW 89-02

Table 5-1. Values used to calculate alpha: wool-blend sorbent fabric

Variable	Value	Unit
kd, hydraulic conductivity of PFM sorptive media	140	(m/day)
ko, hydraulic conductivity of surrounding aquifer	18	(m/day)
ks, hydraulic conductivity of well screen	2	(m/day)
r, cPFM radius	0.0254	(m)
ro, well screen outside radius	0.0318	(m)
KD, ratio of kd/ko	7.78	-
Ks, ratio of ks/ko	0.11	-
Rs, ratio of ro/r	1.250	-
Alpha	0.78	-

Table 5-2. Values used to calculate alpha: 100% wool sorbent fabric

Variable	Value	Unit
kd, hydraulic conductivity of PFM sorptive media	980	(m/day)
ko, hydraulic conductivity of surrounding aquifer	18	(m/day)
ks, hydraulic conductivity of well screen	2	(m/day)
r, cPFM radius	0.0254	(m)
ro, well screen outside radius	0.0318	(m)
KD, ratio of kd/ko	54.44	-
Ks, ratio of ks/ko	0.11	-
Rs, ratio of ro/r	1.250	-
Alpha	0.81	-

Table 5-3. cPFM percent error summary of laboratory testing

	Percent Error: Laboratory Tests			
Sorbent Material	Rhodamine	Orange	Yellow	Turmeric
Wool-Blend	46%	26%	28%	55%
100% Wool	35%	63%	28%	162%

Table 5-4. cPFM percent error summary of field testing

	Percent Error: Field Tests			
Sorbent Material	Rhodamine	Orange	Yellow	Turmeric
Wool-Blend	36	22	33	225
100% Wool	25	166	43	589

Table 5-5. Adjusted R/∝ values based off of curve fitting of 3-D box aquifer data

Dye	Sorbent Material	R/∝	CF	(R/∝)*CF	% Error	Adjusted % Error	% Error Difference
Rhodamine	Wool-Blend	69	1.67	116	46%	21%	25%
	100% Wool	95	1.60	152	35%	37%	-2%
Orange	Wool-Blend	74	1.24	92	26%	29%	-4%
	100% Wool	370	1.12	415	63%	64%	0%
Yellow	Wool-Blend	110	1.04	114	28%	28%	0%
	100% Wool	143	1.02	146	28%	29%	0%
Turmeric	Wool-Blend	282	2.07	583	55%	64%	-8%
	100% Wool	900	0.33	299	162%	37%	125%

Table 5-6. Comparison of Darcy velocity between standard PFM and cPFM: Charleston AFB MW 25

Standard PFM Average Darcy Velocity (cm/day)	cPFM Darcy Velocity (cm/day)			Fabric Type
	Rhodamine	Orange	Yellow	
5.73	4.26	23.36	10.22	100% Wool
5.71	7.33	8.47	10.31	Wool-Blend

Table 5-7. Comparison of Darcy velocity between standard PFM and cPFM: Charleston AFB MW 89-02

Standard PFM Average Darcy Velocity (cm/day)	cPFM Darcy Velocity (cm/day)			Fabric Type
	Rhodamine	Orange	Yellow	
9.59	1.58	10.45	5.70	100% Wool
8.92	6.33	6.80	9.15	Wool-Blend

Table 5-8. Comparison of Darcy velocity between standard PFM and cPFM: Black Hall deployment 1

Standard PFM Average Darcy Velocity (cm/day)	cPFM Darcy Velocity (cm/day)				Fabric Type
	Rhodamine	Orange	Yellow	Turmeric	
5.33	3.45	13.43	12.03	41.23	100% Wool
5.25	2.90	14.14	4.92	48.10	
5.33	8.81	6.17	8.03	23.97	Wool-Blend
5.25	6.26	5.49	5.74	19.57	

Table 5-9. Comparison of Darcy velocity between standard PFM and cPFM: Black Hall deployment 2

Standard PFM Average Darcy Velocity (cm/day)	cPFM Darcy Velocity (cm/day) Rhodamine	Orange	Yellow	Turmeric	Fabric Type
8.03	8.77	34.17	7.75	77.31	100% Wool
8.03	5.32	7.32	10.51	28.62	Wool-Blend

Table 5-10. Comparison of Darcy velocity between standard PFM and cPFM: Black Hall deployment 2: rhodamine layer

Standard PFM Average Darcy Velocity (cm/day)	cPFM Darcy Velocity (cm/day) Rhodamine				Standard Deviation	Fabric Type
9.87	11	13	10	10	1.36	100% Wool
9.87	13.8	12.8	12.1	11.7	0.80	Wool-Blend

Table 5-11. cPFM detection range

Sorbent Material	cPFM Detection Range (cm/day) Rhodamine	Orange	Yellow	Turmeric
Wool-Blend	1.8 - 14.6	2.0 - 15.7	2.9 - 23.3	7.0 - 55.9
100% Wool	2.6 - 20.7	9.5 - 76.0	3.7 - 29.4	23.1 - 184.6

Table 5-12. Cost comparison analysis: PFM versus cPFM

Cost Comparison Analysis		
Cost Component	PFM	cPFM
Material	36	42
Labor	30	36
Analysis	70	15
Shipping	40	20
Total	176	113

APPENDIX A
HYDRAULIC CONDUCTIVITY: SPONGE

The hydraulic conductivity (K), shown in Equation A-1, of the sponges used in cPFM construction was determined through both falling head and constant head tests. This value is important in determining $\propto$, and therefore, understanding the flow field dispersion within and surrounding the cPFM deployed in the well.

$$K = \frac{Q}{i * A} \tag{A-1}$$

The falling head test yielded a K of 45 m/day and the constant head test yielded a value of 47 m/day, as seen in Tables A-1 and A-2 below, respectively. The falling head plot used to obtain the regression slope is shown in Figure A-1. These results can be compared to the hydraulic conductivities of the cPFM sorptive media, surrounding aquifer, and well screen to better assess the flow convergence or divergence.

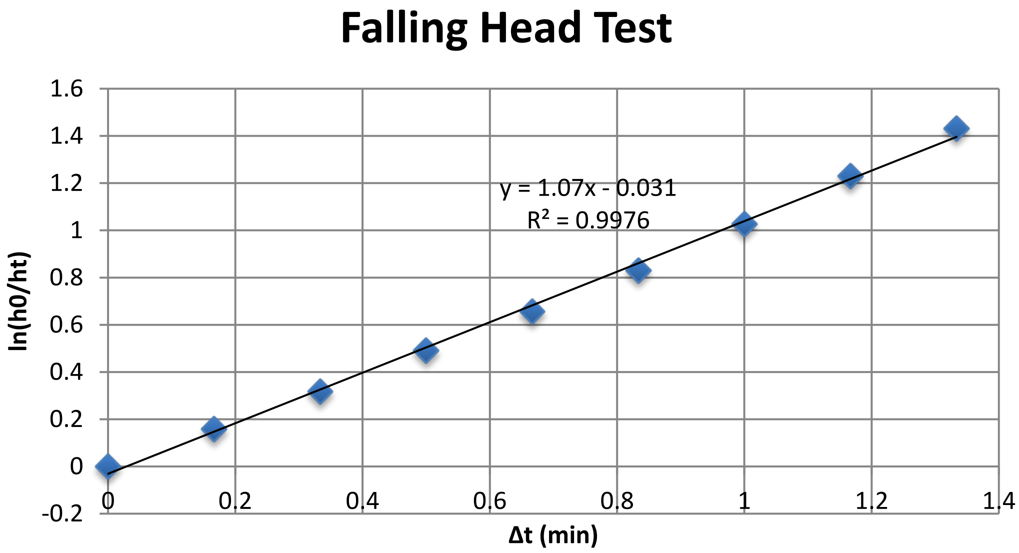


Figure A-1. Falling head test regression plot: sponge

Table A-1. Falling head test data: sponge

Falling Head Test		
Variable	Value	Unit
h0	97.5	cm
h1	83.2	cm
h2	71.0	cm
h3	59.7	cm
h4	50.6	cm
h5	42.5	cm
h6	34.9	cm
h7	28.5	cm
h8	23.3	cm
Δt	10	sec
L	2.9	cm
Di	3.8	cm
A	45.6	cm^2
k	3.1	cm/min
k	45	m/day

Table A-2. Constant head test data: sponge

Constant Head Test		
Variable	Value	Unit
Δt	0.5	min
h	81.0	cm
L	2.9	cm
Di	3.8	cm
A	11.4	cm^2
Q	1030	mL/min
k	3.2	cm/min
k	47	m/day

APPENDIX B
3-D BOX AQUIFER TEST: COTTON SORBENT MATERIAL

A preliminary 3-D box aquifer test was conducted on cotton acting as the sorbent material. Although no 2-D tests were preliminarily conducted on cotton to determine the retardation factor for each dye on cotton as the sorbent material, the range of MR values gives insight to which range of Darcy velocities would fall within the detection limit using cotton, notably the MR value for yellow being as low as 0.39 after only 50 pore volumes. These results are summarized in Table B-1. It is notable that both rhodamine and turmeric yielded MR values greater than 1, and therefore, are not viable results. This could have resulted from improper preparation of the sorbent material or other potential causes.

With a hydraulic conductivity of 70 m/day compared to 140 m/day and 980 m/day for wool-blend and 100% wool, respectively, it can be initially observed that cotton has the potential to show significant loss of resident tracer over short intervals of deployment or for aquifers with low hydraulic conductivities and Darcy velocities. This could allow for a lower detection limit in measuring Darcy velocities potentially.

Table B-1. MR results: 3-D box aquifer test: cotton sorbent fabric

Pore Volumes	Well Diameter	Delta t	Delta t	MR			
-	cm	hours	days	Rhodamine	Orange	Yellow	Turmeric
49.75	5.08	72	3	1.11	0.85	0.39	1.90

APPENDIX C
3-D BOX PFM DARCY CONFIRMATION

The Darcy flux was first tested with a standard PFM to ensure that the flow within the well screen was similar to the effluent flow from the box where flow measurements are made for each test. These flow measurements are averaged and then converted to a flux which is used as the reference for how accurate the cPFM performs for laboratory testing. In comparison, for field results the standard PFM results are used as the reference, actual Darcy velocities.

It can be seen from Figures C-1 and C-2 for boxes 1 and 2, respectively, that the standard PFM accurately estimates the actual Darcy flux. The Darcy flux for each sample within a given test and box were averaged together and then compared to the effluent actual flow from the box. In both cases the percent error of the actual Darcy to the measured Darcy by the PFM was 6%.

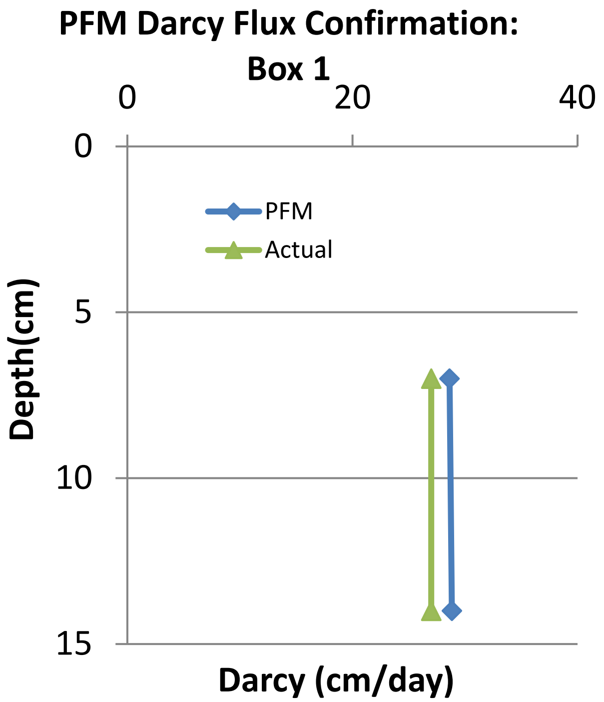


Figure C-1. Flow regime confirmation of 3-D box aquifer 1 using standard PFM

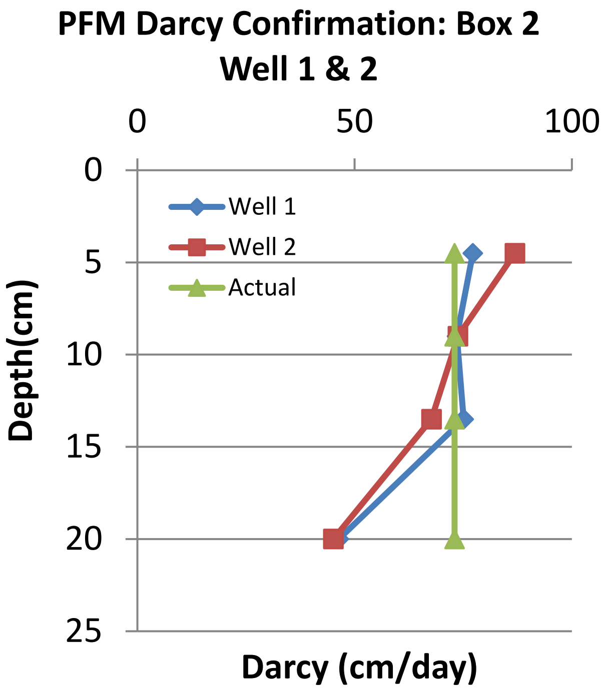


Figure C-2. Flow regime confirmation of 3-D box aquifer 2 in well 1 and 2 using standard PFM

APPENDIX D
ENVIRONMENTAL INFLUENCE ASSESSMENT

Contaminant Influence

When measuring groundwater flux in a contaminated aquifer, contaminant concentrations have the potential to influence the colorimetric response, therefore skewing the measured flux values. To determine this potential influence, laboratory-scale testing was conducted. Chlorinated solvents and alcohols were chosen as representative for the batch test, specifically Trichloroethylene (TCE) and Ethanol.

Sample and reference disks were created as per the approach described in this report for rhodamine dye on 100% wool and wool-blend. It is assumed here that rhodamine would react similarly to the other fluorescent dyes when in contact with contaminant concentrations. Sample disks were then individually placed in 50 mL containers in solutions of 0 ppm TCE, 100 ppm TCE, 1,000 ppm TCE, and 10% (vol.) Ethanol. TCE has a density of 1.46 g/mL and a solubility of 1,100 mg/L. Ethanol has a density of 0.79 g/mL and is miscible (Mackay et al., 1993). Reference disks were stored in the moisture regulating box for the test duration. The sample disks in contaminant solutions were statically stored for the duration of the test. After sitting for 14 days, the samples were removed and photographed alongside their reference disks as per the approach described above. The difference in MR between same dye and sorbent combinations at varying contaminant concentrations was assessed. This was done to determine contaminant presence potential influence on colorimetric response in sample disks under static conditions. Figure D-1 shows the sample disks after removal from their respective batch solutions for 14 days in order of 0 ppm TCE, 100 ppm TCE, 1,000 ppm TCE, and 10% (vol.) Ethanol from left to right.

The results of the batch test are shown in Table D-1 and D-2 for wool-blend and 100% wool, respectively. An additional row was added with hypothetical groundwater fluxes based off of the obtained MR values and a deployment duration of 14 days to better assess the effect of each contaminant solution. It can be seen that only a miniscule change in MR occurs to samples in varying batch test solutions. For wool-rayon blend the fluctuation in MR between samples was at most 0.10 with a standard deviation of 0.04, this would result in an underestimation of the groundwater flux by 1.7 cm/day. For 100% wool the fluctuation in MR between samples was at most 0.07 with a standard deviation of 0.03, this would result in an overestimation of the groundwater flux by 1.8 cm/day. This indicates that the presence of these specific contaminants at varying concentrations do not cause a significant influence on colorimetric response.

pH Influence

The pH within and across differing aquifers can vary greatly. The Floridan aquifer system, for example, is composed of a thick sequence of tertiary carbonate rock. These limestone layers will result in slightly basic environments. Contrastingly, infiltrating rainwater will result in slightly acidic environments. Changes in pH could have potential effects on the colorimetric responses from groundwater flows passing through the sorptive matrix. Rhodamine fluorescence is known to diminish at a pH value of 5 or below as well as 10 or higher (Wilson et al., 1986). Because of such, laboratory-scale testing was conducted to assess this influence on the upper and lower pH limits of potential influence on colorimetric response. These effects were assessed in a batch test for a pH of 4.5, 7, and 9.5. The acidic pH solution was made with diluted hydrochloric acid (HCl) while the basic pH solution was made with diluted sodium hydroxide (NaOH).

Sample and reference disks were created as per the approach described in this report for rhodamine dye on 100% wool and wool-blend. It is assumed here that rhodamine would react similarly to the other fluorescent dyes when in contact with pH fluctuations. Sample disks were then individually placed in 50 mL containers in solutions of pH of 4.5, 7, and 9.5. Reference disks were stored in the moisture regulating box for the test duration. The sample disks in contaminant solutions were statically stored for the duration of the test. After sitting for 14 days, the samples were extracted from the pH solution and photographed alongside their reference disks as per the approach described above. The difference in MR between same dye and sorbent combinations at varying pH was assessed. Figure D-2 shows the sample disks after removal. The results of the batch test are shown in Table D-3 and D-4 for wool-blend and 100% wool, respectively. An additional row was added with hypothetical groundwater fluxes based off of the obtained MR values and a deployment duration of 14 days to better assess the effect of each pH solution. It can be seen that minimal change in MR occurs to samples across the tested spectrum of the pH scale. For wool-rayon blend the fluctuation in MR between samples was 0.05 with a standard deviation of 0.02, this would result in an underestimation of the groundwater flux by 0.9 cm/day. For 100% wool the fluctuation in MR between samples was 0.10 with a standard deviation of 0.04, this would result in an underestimation of the groundwater flux by 2.6 cm/day. It is notable that the lowest MR values resulted from a pH of 7 and that the highest MR values resulted from a pH of 4.5, with pH of 9.5 samples falling in between, for both wool-blend and 100% wool. Although these differences are minor, it shows that changes in pH, especially more acidic solutions, could cause less dye to elute from the sorbent. While this effect is minimal at the pH values tested, further testing could be conducted to see the extent of influence at more acidic and basic pH values.

Figure D-1. Contaminant influence samples. Exposure medium from left to right: 0 ppm TCE, 100 ppm TCE, 1000 ppm TCE, 10% EtOH.

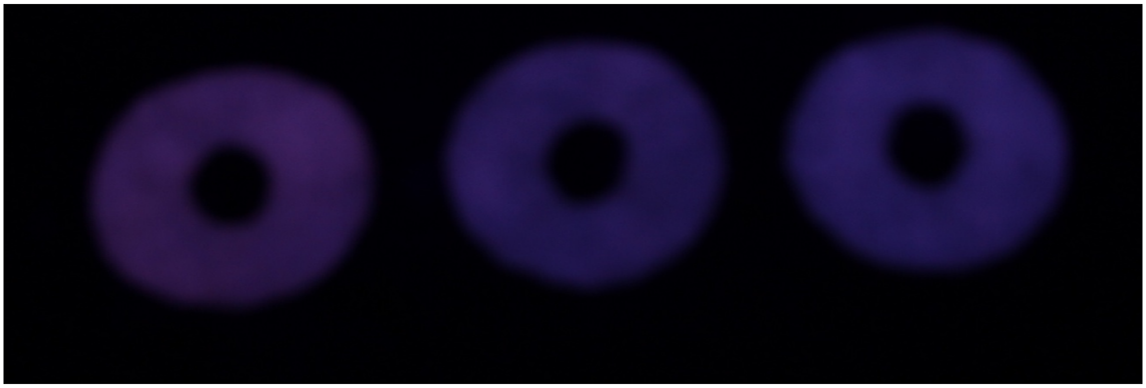


Figure D-2. pH influence samples. Exposure medium from left to right: pH 4.5, pH 7, pH 9.5.

Table D-1. Contaminant influence batch test: comparison of MR and q_D values after exposure to contaminant solutions: wool-blend

Variable	Wool-Blend Sorbent Contaminant Influence				Standard Deviation
	0 ppm TCE (tap water)	100 ppm TCE	1,000 ppm TCE	10% EtOH	
MR	0.42	0.51	0.47	0.41	0.04
q_D (cm/day)	10.6	8.9	9.7	10.8	0.76

Table D-2. Contaminant influence batch test: comparison of MR and q_D values after exposure to contaminant solutions: 100% wool

Variable	100% Wool Sorbent Contaminant Influence 0 ppm TCE (tap water)	100 ppm TCE	1,000 ppm TCE	10% EtOH	Standard Deviation
MR	0.71	0.66	0.64	0.66	0.03
q_D (cm/day)	7.5	8.8	9.3	8.8	0.67

Table D-3. pH influence batch test: comparison of MR and q_D values after exposure to pH solutions: wool-blend

Variable	Wool-Blend Sorbent pH Influence pH 4.5	pH 7	pH 9.5	Standard Deviation
MR	0.50	0.45	0.47	0.02
q_D (cm/day)	9.1	10.0	9.7	0.37

Table D-4. pH influence batch test: comparison of MR and q_D values after exposure to pH solutions: 100% wool

Variable	100% Wool Sorbent pH Influence pH 4.5	pH 7	pH 9.5	Standard Deviation
MR	0.70	0.60	0.67	0.04
q_D (cm/day)	7.8	10.4	8.6	1.09

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