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Designing a Permeable Reactive Barrier for the Remediation of Copper Contaminated Groundwater.

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DESIGNING A PERMEABLE REACTIVE BARRIER FOR THE REMEDIATION OF

COPPER CONTAMINATED GROUNDWATER.

By

Christopher C. Walkons

A THESIS

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I dedicate this thesis to my brother Curtis Walkons, whose courage, wisdom, and support

have been inspirational and instrumental in my pursuit of my academic goals.

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Preface

This project was made possible by the Michigan Department of Environmental Quality which provided funding under project tracking code 2014-004. Data collection and analysis was primarily performed by the author of this work, Christopher Walkons. Other contributors, (listed alphabetically), include Dr. Rod Chimner who provided edits for this document. Dr. Rupali Datta provided edits and developed the synthetic groundwater formula as listed in the supporting material. Dr. Alex Mayer provided edits, assisted in developing the procedures for running the column experiments as listed in the Methods section, and developed the groundwater contours in the Results section. Huiling Piao calculated groundwater elevations and the hydraulic conductivity values for soil samples as listed in the supporting material. Dr. Dibyendu Sarkar developed procedures for running batch reactor and kinetics experiments as listed in the Methods section. Dr. Eric Seagren also assisted in developing the column experiment procedures and provided edits for this document.

Acknowledgements

[1]Abstract

This project details the design of a sorption based pilot-scale permeable reactive barrier (PRB) for the removal of copper from groundwater. The reactive material for the barrier is the residual of coagulants used in drinking water treatment operations. Physical and chemical properties of these water treatment residuals (WTR) have been studied to optimize PRB design. Batch reactor tests have shown that equilibrium sorption of copper can be fit to a Langmuir type isotherm. Kinetic and column experiments have been conducted to understand the significance of chemical and physical mass transfer limitations. A leaching test indicated the concentrations of hazardous elements leached from the residuals do not exceed specified limits. Permeameter tests were performed with various mixtures of the WTR and an inert support material (pea gravel) to determine the ideal mix for matching the hydraulic conductivity of the field site. Additional work has been conducted at the site to determine groundwater flow direction, pore water velocity, and contaminant concentration for designing the optimal dimensions and placement of the PRB.

Introduction

The presence of excessive metals in groundwater is often a long-term environmental problem in regions where metal mining has occurred. Traditional solutions to this problem have included groundwater pumping and treating, soil excavation, and contaminant isolation. Permeable reactive barriers (PRBs) offer several advantages as a remediation method. Permeable reactive barriers operate without the energy inputs,

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[1] The material contained in this document is in preparation for submission to a journal.

greenhouse gas emissions, or noise pollution associated with conventional methods. The volume of materials used in constructing a PRB is often lower than the volume used by other remediation processes (ITRC (2011). When constructed with recycled materials the measure of sustainability of the PRB is increased even further.

While PRBs were initially used to treat groundwater contaminated with organic solvents, their use has broadened so that they are now used to remediate a variety of contaminants. Metals that PRBs have been used to treat include, Am, As, Cd, Cr, ^{137}Cs, Cu, Fe, Hg, Mo, Ni, Pb, Pu, Se, ^{90}Sr, Tc, and U (Obiri-Nyarko, Grajales-Mesa, & Malina, 2014). The number of reactive materials used in PRBs has seen a similar expansion. The primary reactive material of choice in the early years of the technology development was zero-valent iron (ZVI), and this is still one of the most commonly used PRB materials. Although ZVI has been used to treat some metals, other materials including zeolites, apatite, oxides, organic matter, limestone, alkaline materials, and sulfate have also been used in PRBs for remediating metal contaminated groundwater (Obiri-Nyarko et al., 2014). The use of recycled materials is also becoming more prevalent in reactive barrier development. Laboratory tests on foundry sand and fly ash have been conducted for this purpose, while recycled concrete has been used in a PRB for the remediation of acidic water and metals in New South Wales, Australia (Morar, Aydilek, Seagren, & Demirkan, 2011) (Banasiak & Indraratna, 2012) .

Another recycled material that is potentially useful for groundwater remediation is water treatment residuals (WTR). In the process of treating drinking water, coagulants such as aluminum sulfate are added to assist in particle settling and removal. Over time the

settling tanks accumulate a residual sludge that is regarded as a waste product by water treatment facilities. The residual material consists of sediments from the raw water and amorphous masses of aluminum hydroxides and oxides (Dayton & Basta, 2001). The ability of hydrous metal oxides to develop both positive and negative surface charges allows them to complex a wide number of inorganic and organic chemical species (Essington, 2004).

Numerous laboratory and field studies on the sorption capacity of WTR have shown that these materials are capable of binding and immobilizing a range of potential environmental contaminants. In field experiments WTR have been shown to reduce P and NH_4^+ loading to surface water (Gallimore et al., 1999) (Habibiandehkordi, Quinton, & Surridge, 2015). Research has shown WTR to sorb anions such as perchlorate, (Makris, Sarkar, & Datta, 2006a) As(V) and As(III), (Makris, Sarkar, & Datta, 2006b) and Se(VI) and Se(IV) (Ippolito, Scheckel, & Barbarick, 2009). This material has also been found to remove or immobilize cations such as Cu, Pb, and Zn, (Hardy, 2008) Hg, (Hovsepyan & Bonzongo, 2009) Ni, (Elkhatib, Mahdy, & ElManeah, 2013) and Cr(III) and Cr(VI) (Zhou & Haynes, 2011). However, little research has been devoted to the application of WTR in a metal remediating PRB.

The goal of this research is to test the feasibility of a pilot-scale WTR based PRB for the remediation of copper contaminated groundwater at a specific field site. The selected site and choice of reactive media influence characteristics of the PRB's design such as placement, dimensions, and composition. Chemical and physical data about the site and

WTR which will be used to determine these design characteristics, are the project objectives.

Method and Materials

Designing a sorption based PRB requires an understanding of key characteristics of the site and the media of which the barrier will be composed. This is necessary for deciding on PRB placement and for calculating PRB dimensions and lifetime. Site characteristics including hydraulic conductivity, soil porosity, hydraulic gradient, and the chemical make-up of the groundwater are required to determine the site's suitability for PRB treatment (Gavaskar, Gupta, Sass, Janosy, & Hicks, 2000). These same properties are then used for the selection of the PRB's reactive material (Obiri-Nyarko et al., 2014). Additionally it is necessary to determine if the reactive material placed in the environment will be prone to leach contaminants. This section discusses the methods used for calculating the PRB dimensions and lifetime, as well as the methods applied for collecting the field and laboratory data needed for those calculations.

Dimension and lifetime calculations

A critical factor in determining the feasibility of the PRB is the dimensions required to achieve reduction of the contaminant to a specified level. Here, we assume that the PRB is shaped as a rectangular prism of dimensions defined in Figure 1.
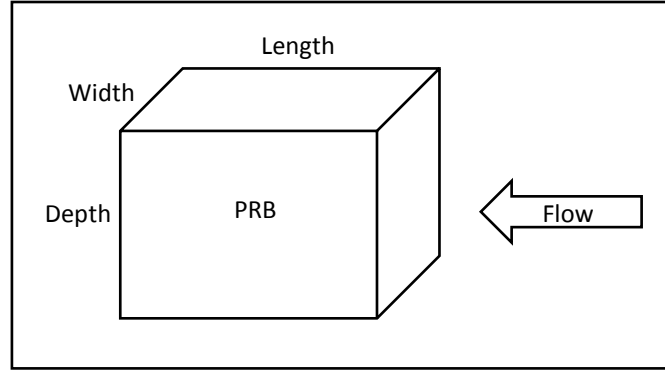
Figure 1: Depiction of PRB dimensions in relation to groundwater flow.

Assuming that the flow and transport through the PRB is one-dimensional in the direction of flow, the dimensions of width and depth are determined by the same dimensions of the contaminant plume to be captured by the PRB. Thus, the critical design dimension of the PRB is length with the assumption being that one-dimensional contaminant transport can be described by a variation of the advective-dispersive equation (Fetter, 1999) as shown below:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - \frac{B_d}{\theta}\frac{\partial q_e}{\partial t} + \left(\frac{\partial C}{\partial t}\right)_{rxn} \tag{1}$$

In our application of equation (1), C is copper concentration in groundwater, t is time, D is the longitudinal dispersion coefficient, x is distance in the length dimension, v is pore water velocity, B_d is the PRB media bulk density, θ is the PRB media porosity, and q_e is the mass of copper sorbed per mass of the PRB media. While this equation accounts for a reaction term, (subscript rxn), we are assuming no other reactions beside sorption are affecting the copper concentration, thus making this term equal to zero.

Assuming instantaneous equilibrium and a linear relationship between aqueous and

sorbed concentrations, the following equation (Fetter, 1999) can be applied to the system:

$$K_d = \frac{q_e}{C} \tag{2}$$

In this case the distribution coefficient, K_d is equal to the slope of the linear portion of the

sorption isotherm derived from experiments testing the capacity of the WTR to sorb

copper. The distribution coefficient can be used to calculate a retardation factor (R)

(Fetter, 1999) as shown below:

$$R = 1 + \frac{B_d}{\theta} \times K_d \tag{3}$$

Applying Equations (2) and (3), Equation (1) can be re-organized as:

$$R \frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2} \tag{4}$$

Initial and boundary conditions for this equation can be defined using the notation C(x, t)

= C(t). For the design, we assume an initial condition of zero concentration in the PRB

or, C(x, 0) = 0. Boundary conditions are a constant influent concentration (C_0) or, C (0, t)

= C_0, and a zero-gradient downstream boundary condition located at an infinite distance

from the influent location or, $\frac{\partial C}{\partial x}\big|$ x→∞ = 0. With these conditions, the solution to the

advective-dispersive equation (Ogata & Banks, 1961) which accounts for retardation can

be expressed as follows:

$$C = \frac{C_0}{2} \left[\operatorname{erfc} \left(\frac{L - \frac{v}{R}t}{2\sqrt{\frac{D}{R}t}} \right) + \exp \left(\frac{v\,L}{D} \right) \operatorname{erfc} \left(\frac{L + \frac{v}{R}t}{2\sqrt{\frac{D}{R}t}} \right) \right] \tag{5}$$

Field work including groundwater sampling and gradient measurements provided the values for C_0 and v, while column tests provided data for D and R values. The remediation target copper concentration, C, is based on criteria set by the Michigan Department of Environmental Quality (MDEQ) and is specific for the selected site as described below. When the values for equation (5) of C_0, v, D, and R are specified, the time (t) before C exceeds the remediation target value, (or PRB lifetime), can then be related to PRB length (L). Design of the PRB is therefore focused on determining a reasonable length that allows for contaminant reduction throughout a reasonable lifetime.

Site characteristics

Groundwater chemistry and flow

The location for this research is in northern Michigan's Keweenaw Peninsula, an area that has been severely impacted by the deposition of copper laden mine tailings (Jeong, Urban, & Green, 1999). The specific site selected for the pilot PRB is a riparian area of stamp sand deposits adjacent to Huron Creek located in Houghton, Michigan (Figures 2 & 3).

Figure 2: Location of Houghton, Michigan.
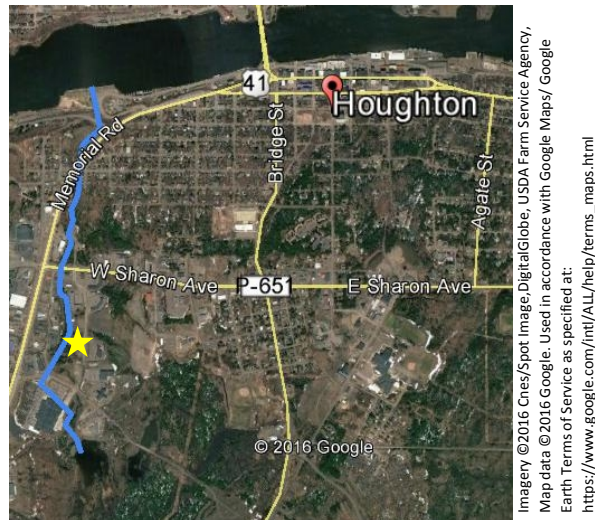
Figure 3: Location of site for pilot PRB design.
Blue line represents Huron Creek and star is field site.

Excessive copper levels in Huron Creek are thought to be due to groundwater flowing through nearby stamp sand deposits that discharges into the creek (Mayer, 2014). The MDEQ has specified that copper levels in the upper reaches of the creek should not exceed 0.031 ppm (MDEQ, 2016). Because the copper concentration in groundwater has been found to be one order of magnitude higher than that of the creek, some dilution can be expected as the groundwater and surface water mix. However, as a conservative

measure, the remediation target concentration has been decided upon assuming no dilution will take place. Therefore, the value of 0.031 ppm has been set as the target concentration for the groundwater exiting the PRB.

Orientation of the PRB is dependent on the direction of groundwater flow, which was determined using a grid of monitoring wells installed parallel to the creek (Figure 4).
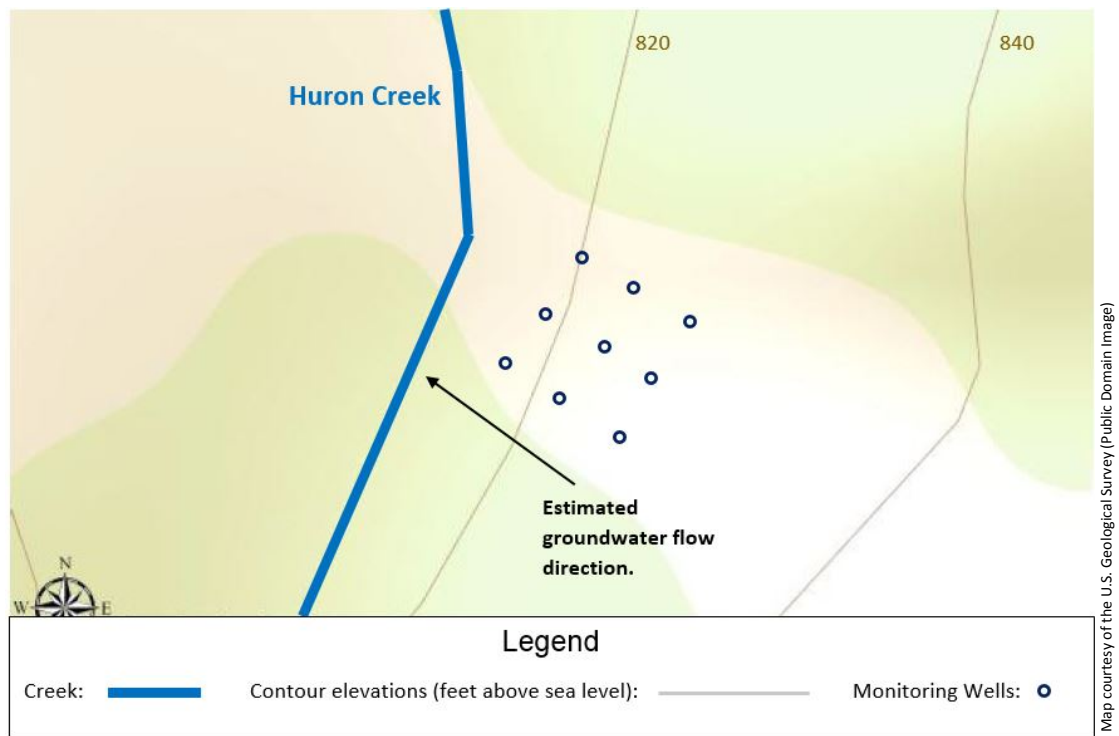
Figure 4: Depiction of monitoring well grid in relationship to Huron Creek.

Wells were constructed of 5.1 cm (2 inch nominal) diameter PVC pipe and installed to a depth of approximately 30 cm below the top of the water table. Groundwater elevation measurements were used to develop groundwater contour lines using the groundwater modeling software program Surfer. These contours were used to estimate direction of flow and hydraulic gradient. The wells were also used to sample groundwater for analysis of total copper, dissolved organic carbon (DOC), hardness, alkalinity, and concentrations

of chloride and sulfate. Elevation measurements and samples were taken approximately every three months, as weather allowed, over the course of one year.

Eighteen soil samples from the site were collected to determine porosity and hydraulic conductivity. Samples were taken from cores of approximately 0-15 cm, 15-30 cm, and 30-45 cm from the ground surface. Twelve of these samples were taken from within the well grid and six were taken between the grid and the creek. Soil porosity was estimated by measuring the volume of water filling soil voids when the water was added to a sample in a graduated cylinder. Each of the samples was run in triplicate through constant head permeameters using method ASTM D5856-15, Standard Test Method for Measurement of Hydraulic Conductivity of Porous Material Using a Rigid-Wall, Compaction-Mold Permeameter.

Media Characterization

The WTR in this project was acquired from the Ontonagon water treatment plant located in White Pine, Michigan. This plant uses aluminum sulfate as a coagulant and therefore generates aluminum-based WTR. The WTR was taken from lagoons, air dried, and crushed by hand to a size of 2 mm or less. Sorption capacity of the WTR was tested by batch reactor and kinetics experiments.

Batch sorption and sorption kinetics experiments

Two batch reactor experiments (BREs) were conducted to develop a sorption isotherm. A BRE using copper solutions across a high concentration range was run to determine overall sorption curve shape, while a second was run at a low concentration range

comparable to conditions in the field. For the higher concentration experiment twenty-one 50 mL polyethylene centrifuge tubes were filled with 2.5 g of WTR each. This allowed for samples containing seven different aqueous copper solutions to be run in triplicate. The solutions were made using groundwater taken from the site and had copper concentrations of 0, 50, 100, 500, 1000, 2000, and 3000 ppm. Copper nitrate hemi-pentahydrate (Acros Organics, CAS # 19004-19-4) was added to the groundwater to make the various concentrations. To maintain a constant ionic strength, potassium chloride (Fisher Scientific, CAS # 7447-40-7) was added to the samples to achieve a concentration of 0.01 M. The solutions were buffered with 4-Morpholineethanesulfonic acid (MES) (Sigma-Aldrich, CAS # 4432-31-9) to achieve a concentration of 0.01 M buffer in solution. The pH of the samples prior to the experiment was ~5.5. This process was duplicated with a set of control samples which contained no WTR. Samples were placed on a shaker and allowed to be mixed for 24 hours. The samples were filtered, diluted, acidified, and analyzed using a Perkin Elmer model 3100 atomic absorption spectrometer (AAS).

The low concentration experiment was conducted in a similar manner but with across a copper concentration range of ~0.15 to ~0.45 ppm. Other differences were that the samples were run in 250 mL amber glass bottles and that no buffer was added. The low amounts of copper salt used in this experiment resulted in a relatively consistent sample pH of ~8.45. These samples were analyzed using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) as was provided by Whitewater Laboratory in Amasa, Michigan.

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The kinetics experiment was conducted similarly to the high concentration batch reactor experiment but used only the 3000 ppm copper solution. To determine sorption kinetics, samples were removed from the shaker at the time intervals of 0.5, 1, 2, 3, 4, and 24 hours. These samples were also analyzed using the AAS.

Leaching test

A synthetic precipitation leaching procedure (SPLP) test (EPA method 1312) was performed to mimic the effect of acidic precipitation on the WTR and test for the leaching of elements of concern. Three 100 g samples of crushed and sieved WTR were exposed to extraction fluid in a rotary agitation apparatus for 18 hours. The leachate was then analyzed by Whitewater Laboratory for the following elements: Al, As, Ba, Cd, Cr, Cu, Pb, Hg, Se, and Ag. The MDEQ Cleanup Criteria Requirements for Response Activity, rule R 299.48 Generic soil cleanup criteria for nonresidential category, Groundwater Surface Water Interface Protection Criteria was used to determine if the concentration of the elements in the leachate were below acceptable limits.

Physical Media Characteristics

Because the PRB is a passive remediation system, one objective of its design is to ensure that the hydraulic conductivity (K) of the PRB is at least as high as that of the site (K_{site}) (Gavaskar et al., 2000). To achieve this, the media of the PRB is a mixture of the reactive media component, the WTR, and an inert media component intended to provide the desired hydraulic conductivity. Increasing the percentage of the inert component increases the mixture's hydraulic conductivity ($K_{mixture}$), but lowers the sorption capacity of the PRB. A conservative ratio of $K_{mixture}$ to K_{site} being greater than or equal to ten, was

used to select the mixture. Once the optimal mixture was selected, the measurements of bulk density and porosity of the mix were obtained to calculate the retardation factor.

The inert medium chosen for testing was 10 mm (3/8" nominal) washed pea gravel obtained from Superior Sand and Gravel located in Hancock, Michigan. A permeameter was used to measure the hydraulic conductivity of various mixtures, as discussed above.

Column testing

Column experiments were conducted to model the transport of copper through the mixture that would make up the PRB. Columns were constructed of 15.2 cm (6 inch nominal) diameter PVC pipe and were 45.7 cm long. Five sampling ports were placed at equal distances along the column's length. The sampling ports extended approximately 5 cm into the interior of the column. Three columns were constructed but only two were used in experiments. The columns were packed with the optimal mixture of WTR and pea gravel as is described in the Results section. Using positive displacement model QD FMI pumps, fluid was pumped from bottom to top at a velocity comparable to the pore water velocity of the site (0.07 cm/s). Figure 5 illustrates the column set-up.
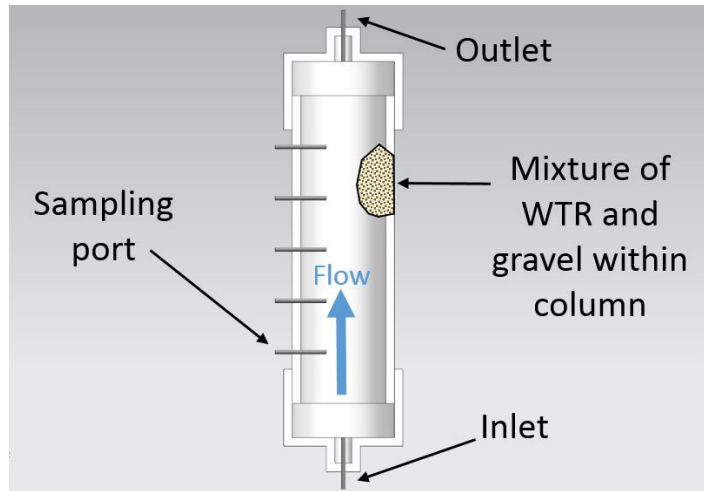
Figure 5: Depiction of column used in testing sorption capacity of PRB media mixture.

Conservative tracer tests were conducted with a tracer solution of 1000 ppm bromide, which was made using potassium bromide salt (Sigma-Aldrich, CAS # 7758-02-3). Effluent samples from the column were analyzed with an Orion 720A Benchtop Meter with bromide and reference electrodes. Using the code CXTFIT (Tang, Mayes, Parker, & Jardine, 2010), the advection-dispersion equation was fit to breakthrough curve data to obtain estimates of the porosity and dispersion coefficient of the mixture in the column.

The copper solution was pumped through the columns in the same manner as the tracer. The copper content of the influent solution was set at a concentration of 5 ppm using the same copper salt used in the BRE and kinetics experiments. The aqueous solution for these experiments was a synthetic groundwater mix made with various salts to mimic the chemistry of the natural groundwater. The details of the synthetic groundwater mixture are available in the supporting material to this project. No KCl salt or buffer was added and the pH of the mixture was around 8.0. Analysis of the column effluent was done at Michigan Technological University's forestry department using ICP-OES.

Results and Discussion

Site characteristics

Elevation data indicate that groundwater is flowing toward the creek and in a downstream

direction. A groundwater contour profile developed with Surfer is shown in Figure 6.

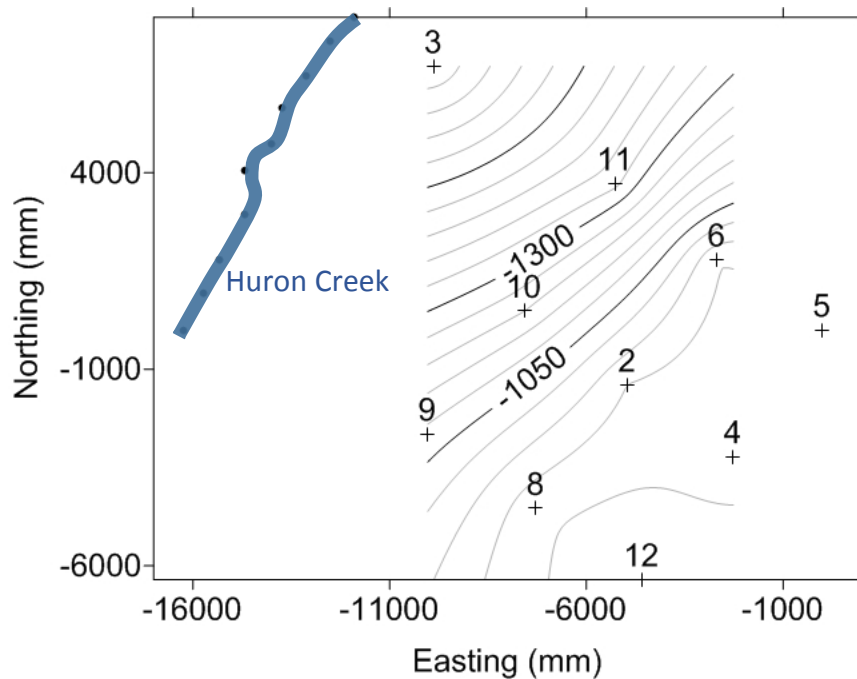*Figure 6: Groundwater contours at site relative to Huron Creek. Crosses represent wells, contours are in increments of 50 mm. Top of Well 4 is Z datum.*

Using profiles such as that in Figure 6, the site's hydraulic gradient is estimated to be

~0.1. Groundwater samples were taken between 2015 and 2016 in the months of October,

January, May, and July. Values for total copper are shown in Figure 7 with an overall

mean value of 0.273 ppm.
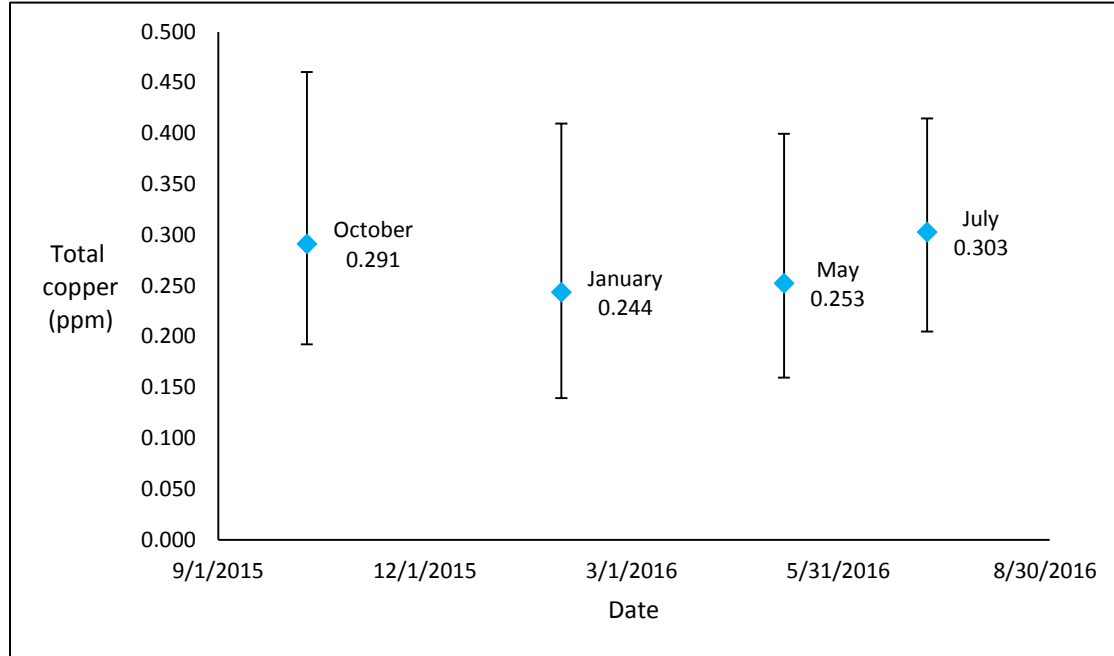
Figure 7: Total copper ppm from quarterly sampling. Note: The vertical bars depict the range of values used to compute the mean.

Porosity of the soil samples ranged from 31.8% to 60.3% with a mean of 36.5%. The K values ranged from 0.333 to 0.001 cm/s with the latter being an outlying value one order of magnitude less than the next. By calculating the geometric mean of the K values without the outlier and adding one standard deviation, a K value for PRB design of 0.240 cm/s was arrived at. The values for gradient, porosity, and K were used to calculate a design pore water velocity of 0.07 cm/s. Data from the site including groundwater elevations, surface water and groundwater chemistry, soil porosity, and site hydraulic conductivity calculations are available in the supporting material.

<u>Reactive media characteristics</u>

Batch reactor and kinetics experiments

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The results of the high and low concentration BREs are given in Table 1.

Table 1: High and low batch reactor experiment results.

High Concentration BRE			Low Concentration BRE		
Initial conc. C_0 (mg/L)	Equilibrium conc. C (mg/L)	Mass sorbate per mass sorbent q_e (mg/g)	Initial conc. C_0 (mg/L)	Equilibrium conc. C (mg/L)	Mass sorbate per mass sorbent q_e (mg/g)
2855	2268	12	0.440	0.045	0.079
1939	1402	11	0.420	0.054	0.073
1027	510	10	0.340	0.042	0.060
521	108	8	0.290	0.040	0.050
109	2	2	0.220	0.040	0.036
54	1	1	0.140	0.037	0.021
0	0	0	**Mean**	**0.043**	**0.053**

These data are plotted in Figures 8 and 9. As evident in Figure 8, the low concentration BRE does not shown a clear relationship between q_e and C. The C values from this experiment may be an underestimate of actual values. This may be due to copper being lost through sample filtration in the preparation for analysis.
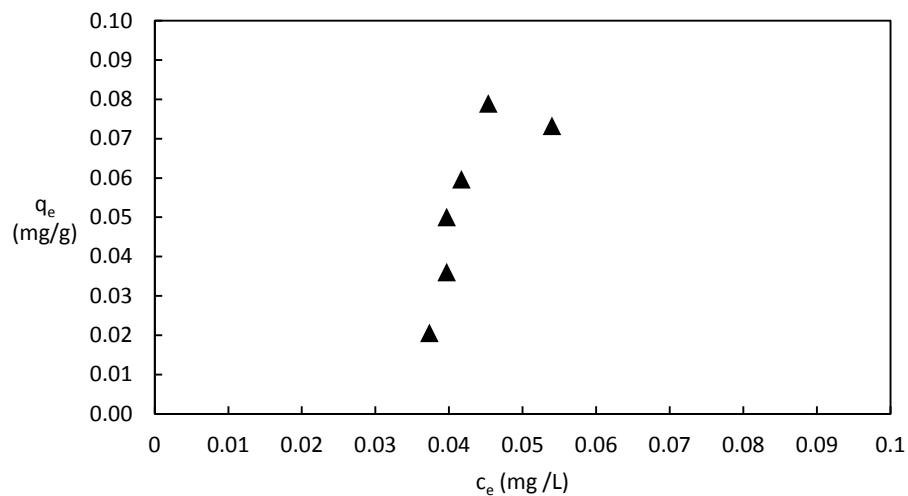

Figure 8: Plot q_e vs C values obtained from low concentration batch reactor experiment.

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In Figure 9, the q_e and C values of the low BRE were averaged into a single point (shown as a triangle) and plotted with points (shown as squares) from the high BRE. The data in this figure indicate that sorption follows a Langmuir type curve. Linearizing the Langmuir equation provides the parameters of a sorption maximum of 10 mg/g and a sorption constant of 0.121 L/mg. The two lower data points in Figure 9 are bounds for the aqueous concentration region where the column experiments were conducted. It is assumed that the q_e vs C relationship in this region is linear, with a K_d value calculated to be 1.21 L/g. Calculations for the sorption maximum, sorption constant, and distribution coefficient are available in the supporting material.
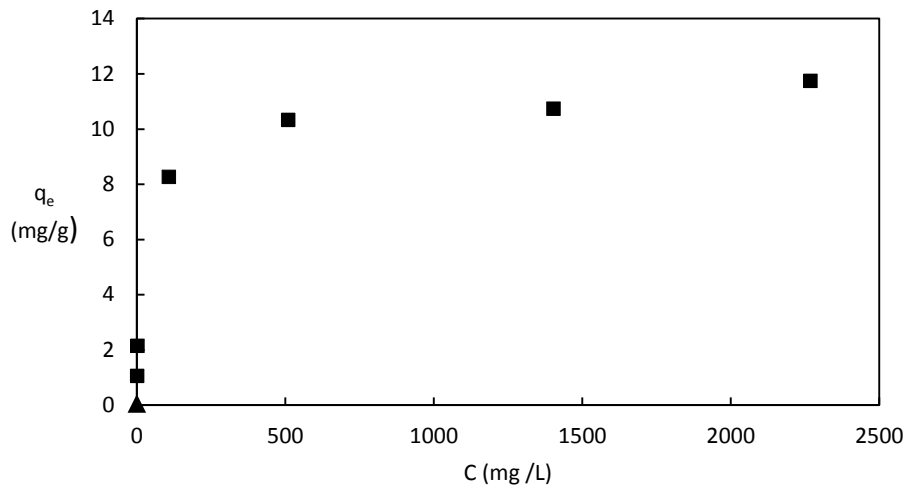

Figure 9: Isotherm comprised of all points from high BRE plus averaged point from low BRE.

The results of the kinetics experiment show that the sorption capacity of 10 mg/g is reached in approximately one hour as shown in Figure 10.
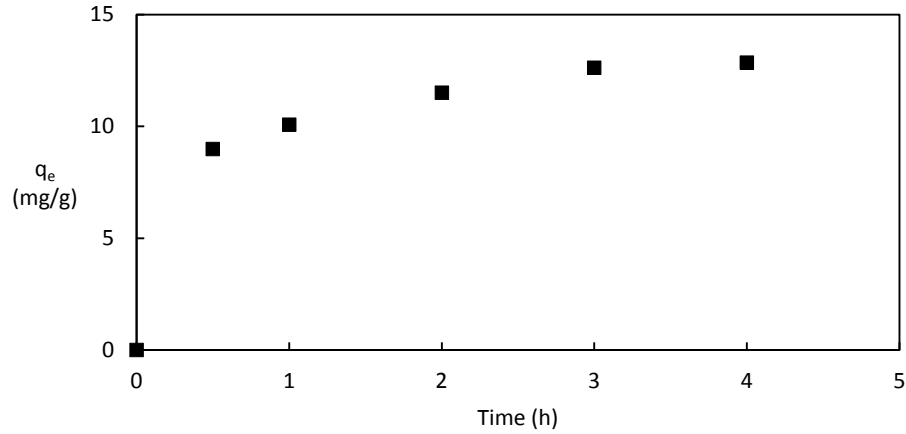
Figure 10: Sorption of copper to WTR over time.

Leaching test

Leaching limits were based on MDEQ established soil cleanup criteria values. Because these values are in units of µg/kg soil, the concentrations from the leachate were converted to the same units for comparison. This was done by multiplying the leachate concentrations by the ratio of liters of extraction fluid to sample mass, or 20 L/kg. The values for comparison are shown in the two right-most columns of Table 1.

Table 2: Comparison of metals leached from WTR and MDEQ soil cleanup criteria values.

Element	Concentration in leachate (µg/L)	Concentration in WTR (µg/kg)	Soil cleanup criteria values (µg/kg)
Aluminum	800	16000	N/A
Arsenic	<25	<500	4600
Barium	18	360	2400000
Cadmium	5.4	110	2400
Chromium	<0.8	<16	3300
Copper	54	1100	45000
Lead	<10	<200	3200000
Mercury	<0.1	<2.0	50
Selenium	32	640	400
Silver	16	320	100

The majority of elements tested for were found to be in concentrations far below cleanup criteria values. The exceptions are selenium and silver. However, since the PRB will be a mixture of WTR and pea gravel, the concentration of elements leached from the PRB will be reduced to the percentage of WTR in the mixture. This reduction places the concentrations of all tested elements below cleanup criteria values.

Hydraulic Conductivity

The permeameter tests revealed that the K values for a mixture of 90% gravel and 10% WTR (by mass) varied from 0.03 to 0.53 cm/s. Because of the order of magnitude difference in values, the mean of these values was calculated as the geometric mean which is 0.18 cm/s. The K values of the 95% gravel, 5% WTR mixture varied from 0.44 to 6.90 cm/s with a geometric mean of 2.64 cm/s. The mean K value of the 95% mixture met the design criteria of being ten times that of the site and was therefore selected as the material for the PRB. This mixture has a bulk density of 1.49 g/cm^3 and a porosity of 0.40. A retardation factor for each component of the mixture was calculated using Equation 3. These factors were then weighted by their respective mass ratios in the mix and summed to produce an overall retardation factor for the mixture of R= 290.

Column testing

A plot of the tracer samples compared to breakthrough curves using the porosity and dispersivity values generated with CXTFIT, is shown in Figure 11. The program gave porosity values of approximately 38% and dispersivity values of approximately 3.4 cm. The sum of the squared residuals (SSR) between the predicted values and the values of actual sample concentrations in Column 1 was 0.008 while the SSR of the values for

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Column 3 was 0.014. The closeness of fit suggest uniform grain distribution and the
absence of void spaces within the packed columns.
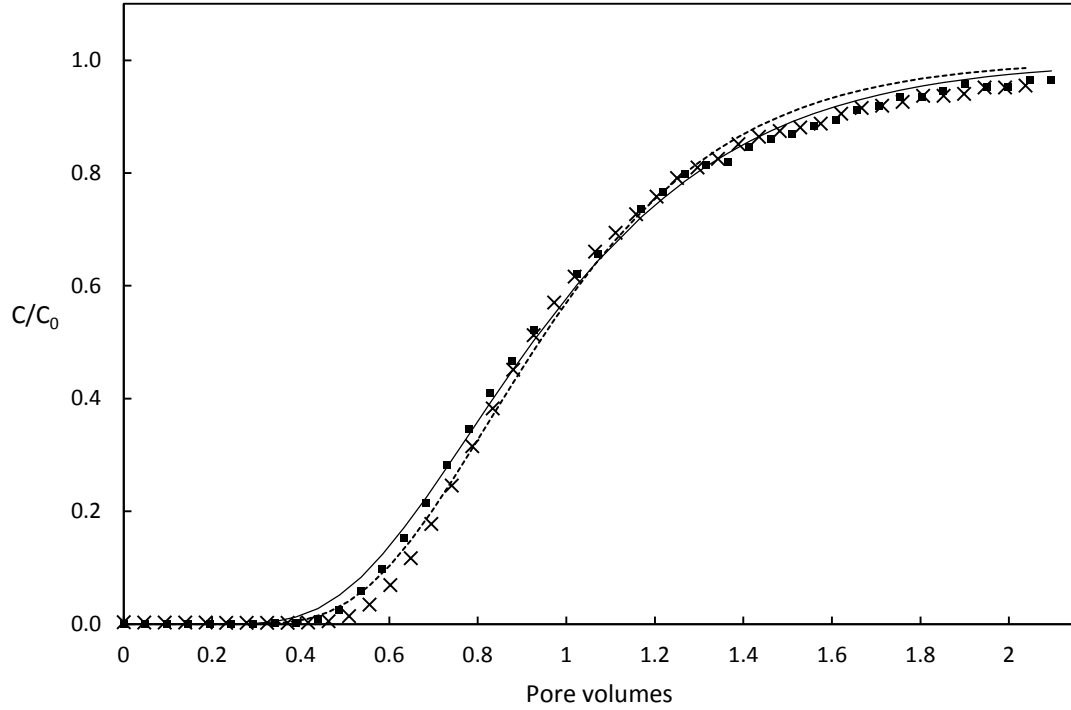

Figure 11: Comparisons of samples from tracer tests with curves predicted by CXTFIT. Squares
represent samples taken from Column 1 while the solid line represents the predicted curve for the
column with the specified porosity and dispersivity values. Crosses represent the samples taken
from Column 3 with the dashed line representing the predicted curve for this column.

The results of the copper experiment in Column 1 are shown in Figure 12.
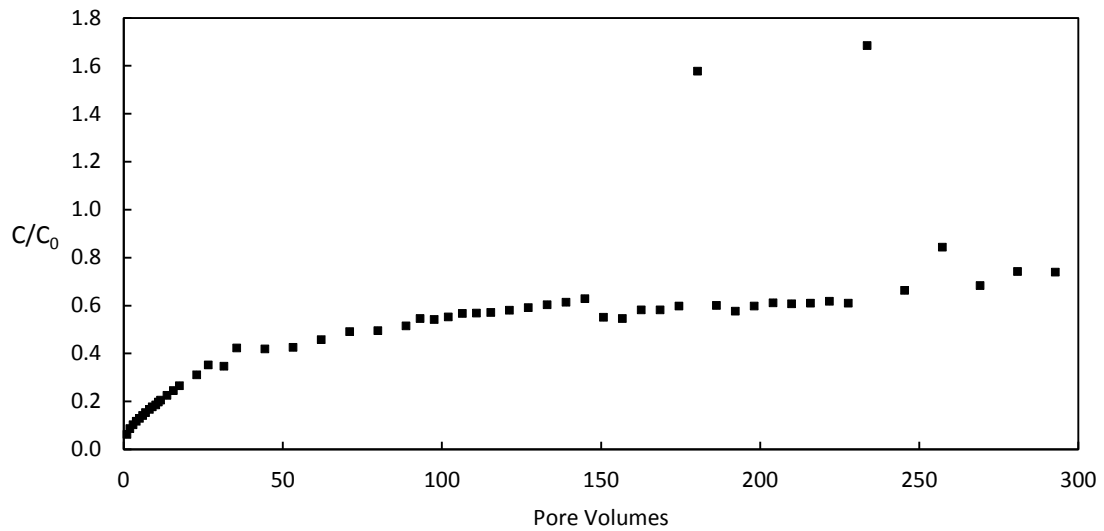
Figure 12: Copper concentration per pore volumes in Column 1.

The column experiments indicate that Equation 5 accurately models solute transport through the PRB media mixture with a conservative tracer but not with the copper solution. The C/C_0 value in the tracer experiment arrived at 1.0 after ~2 pore volumes. Applying the calculated retardation factor of 290, the concentration of the copper solution could be expected to achieve full breakthrough at ~580 pore volumes. However, as Figure 12 shows, the copper concentrations did not follow the expected S-shaped breakthrough trend, but instead rose quickly and then plateaued at $C/C_0 \approx 0.7$. Copper never achieved full breakthrough through the duration of the experiment which ended at ~600 pore volumes. (Plot available in the supporting information.) Because the residence time of solute in the column is only 10 minutes sorption equilibrium in the column is most likely not being achieved.

There were two instances where effluent values were higher than influent at approximately 180 and 235 pore volumes. Additionally, the influent concentration was found to fluctuate during the experiment. (Data available in supporting material.) This may be a sign of copper precipitation in the influent source. Since the column experiment was an attempt to mimic sorption at the pH of the natural groundwater (pH=8.0), no buffers were added to the synthetic groundwater used in this experiment. However, creating a 5 ppm copper solution at this pH could have resulted in precipitate formation. The concentration of 5 ppm was chosen so that samples could be analyzed using a copper-probe with a limited detection limit. This method of analysis was ultimately not used. The problem with precipitate formation may have been avoided if the influent had been made at a concentration comparable to that of the natural groundwater.

Although copper transport in the column was not well modeled by Equation 5, the data from this experiment can still be used to calculate the length of a PRB with the given pore velocity and media mixture conditions. The point at which $C/C_0 = 0.10$ is approximately three pore volumes. The design pore velocity at the field site was calculated as being 0.07cm/s or ~22km/year. Designing a PRB for this pore velocity with a one year lifetime means that the barrier must not allow for more than three pore volumes to pass through annually. Required length would be about 7 kilometers.

A more reasonable length for design can be calculated if the system were to be implemented at a site where the design pore velocity is lower. Using the media characteristics and changing certain site characteristics, two scenarios have been developed for which more reasonable lengths of a PRB have been calculated. Scenario 1

considers a hypothetical site in which pore water velocity is one order of magnitude

lower than that of the Huron Creek site. In this scenario, the PRB mixture is made of 75%

gravel and 25% WTR and a remediation target concentration is set as 20% of the

incoming groundwater concentration ($C/C_0 = 0.20$). Scenario 2 is the same except that

pore water velocity is two orders of magnitude less than the original site. Both of these

scenarios assume that the advective-dispersive equation accurately models contaminant

transport and that sorption equilibrium is instantaneous. The resulting lengths of the

required PRB having various lifetimes are presented in Table 3.

Table 3: Lengths for PRBs of various lifetimes in alternative scenarios.

Lifetimes (y)	1	5	25	50
	Lengths (m)			
Scenario 1	1.75	7.5	35.25	50+
Scenario 2	0.25	1	3.75	7.5

A graphic comparison of the length and lifetime relationships is shown in Figure 13.
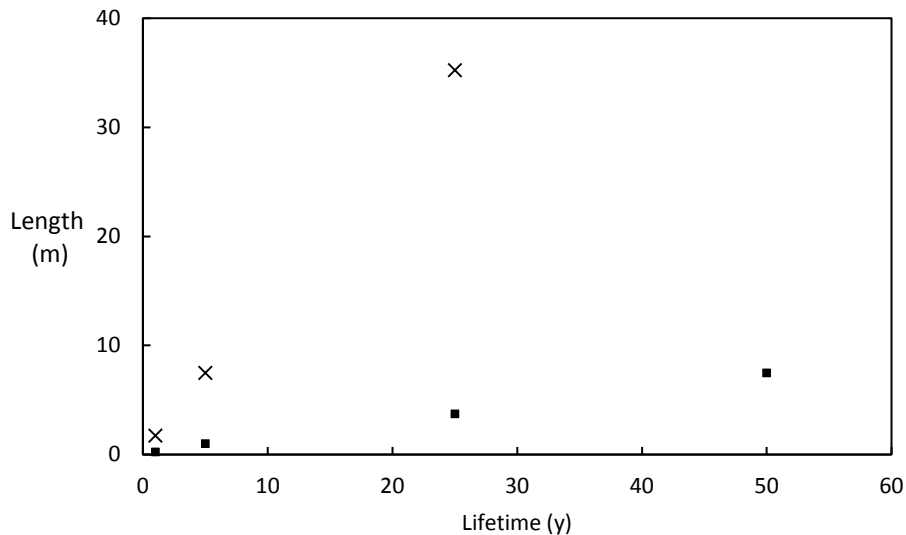
Figure 13: Graphic comparison of length and lifetime relationships for alternative scenarios. Crosses represent data from Scenario 1 while squares represent data from Scenario 2.

As evident from Figure 13, selecting at a site with a much lower pore water velocity would allow for the design of a PRBs with lengths of <10 meters and lifetimes on the order of decades.

Conclusions

The field data revealed that the groundwater at the site is flowing toward the creek in the downstream direction with a hydraulic gradient of ~0.1. The mean total copper concentration in groundwater was found to be 0.273 ppm. This is approximately ten times the limit established by the MDEQ. A hydraulic conductivity design value for the PRB based on mean K values from soil at the site was calculated to be 0.240 cm/s. Soil porosity was found to be 36.5%. A design pore water velocity value was calculated to be 0.07 cm/s.

The high BRE showed that copper sorption to the WTR appears to follow a Langmuir isotherm with a sorption maximum of about 10mg/g. An accurate understanding of isotherm shape at low concentrations could not be gained using the methods employed in this project. The K_d value in the region of natural groundwater concentration was calculated to be 1.21 L/g. A sorption kinetics test revealed that sorption equilibrium was reached in approximately 1 hour.

The synthetic precipitation leaching procedure test on the WTR indicated that the leached concentrations of most elements were below the criteria set for the project. The elements of selenium and silver had concentrations above the criteria but these concentrations per mass will be reduced when the WTR is mixed with pea gravel in the PRB.

To achieve a PRB mixture K value one order of magnitude greater than that of the site, a mixture of 95% gravel and 5% WTR by mass was selected for design. Data from the sorption tests were used to calculate a retardation factor for this mixture of 290.

Column tracer tests revealed that the advective-dispersive equation could accurately model transport of a conservative tracer through the columns. However, the copper test revealed that this model did not give results that the equation could predict. This may be caused by the residence time of solute in the column being too short to allow for sorption equilibrium. The results may also be affected by copper precipitation which presented a problem in controlling influent concentration.

Scenarios were developed that considered installing a WTR based copper remediating PRB at sites which have more favorable groundwater flow condition. In a scenario with pore water velocity two orders of magnitude lower than the test site, a PRB of less than 10 meters in length was calculated to provide remediation to a target level for a period of decades.

Future Work

Future work could entail barrier design based on a test site with hydrogeological characteristics better suited to the use of a PRB. Sorption at low concentrations could be predicted better if a method were developed that completely separated the copper sorbed to WTR from copper left in solution. Alternatively, a method of analysis which does not require filtration may be helpful. Future column studies could use a solution of lower copper concentration that may reduce the chance of precipitation at the natural groundwater pH. A sensitivity analysis considering the relationship between pH and

sorption could be run in either a batch or column set-up. Additionally, evaluating the

effects of pH on copper precipitation, dominant species presence, and hydroxide

complexation may be helpful in better understanding the factors affecting sorption of

copper to the WTR.

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