Evaluation of Soil Aquifer Treatment in a Laboratory-Scale Soil Column Experiment

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ABSTRACT

Soil aquifer treatment (SAT) during managed aquifer recharge has been studied as a method of providing additional environmental barriers to pathogens and contaminants in indirect potable reuse (IPR) applications. A soil column study was conducted by Hampton Roads Sanitation District in order to evaluate the effectiveness of SAT, as a component of its IPR project involving the replenishment of the Potomac Aquifer System (PAS), in providing a sustainable source of drinking water. Four packed soil columns were constructed with sand from the PAS and were designed to simulate the travel time of 3 days and 30 days. The tests conducted aimed at evaluating pathogen removal (MS2, *E. coli* and *Cryptosporidium* oocysts); evaluating attenuation of regulated (nitrate, nitrite, bromate, trihalomethane (THM), haloacetic acids (HAA), organic carbon) and unregulated contaminants of concern that affect drinking water quality. Effective pathogen removal was observed with 6 to 7-log removals of MS2 and *E. coli* and 3 to 5-log removals of microbeads, used as a surrogate for *Cryptosporidium*. Removal across 3 day columns was comparable to 30-day columns but the potential to achieve higher removal with longer retention time was acknowledged. Nitrate, bromate, THMs and HAAs were completely reduced in 30-day columns. Total organic carbon was removed at 25 – 35% in all four columns. Seven out of the 106 contaminants of emerging concern (CEC) tested were consistently detected in the column feed and effluent at concentrations greater than 100 ng/L; some compounds showed potential for removal while no conclusive results were drawn for the remaining compounds.

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GENERAL AUDIENCE ABSTRACT

Potable reuse is a sustainable solution to the increasing water demands of the present and more so the future. Hampton Road Sanitation District (HRSD) aims to treat effluent from its wastewater treatment plants using advanced treatment process for direct recharge of the Potomac aquifer system. This is a method of indirect potable reuse termed as managed aquifer recharge (MAR). MAR can provide additional environmental barriers to contaminants present in water through a process of natural attenuation called soil aquifer treatment (SAT). A soil column study was conducted at HRSD's pilot scale facility in order to asses SAT under controlled conditions at a meaningful scale. Attenuation of pathogens; regulated contaminants (nitrate, nitrite, bromate, etc.) and contaminants of emerging concern was evaluated through the soil columns. The results showed effective removal of most contaminants of interest which demonstrated that SAT potentially improves water quality and meets public health standards in potable reuse applications.

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1. INTRODUCTION

Water is a valuable resource which is consumed and replenished back into the environment by the natural water cycle. However, meeting the current water demands and tackling the issues of pollution is becoming increasingly strenuous. The rate at which water naturally replenishes may not be sufficient to exceed the rapid rate of consumption while also maintaining the quality required for potable use. Potable water reuse is a sustainable solution to the problem of increasing water demands of the present and more so the future. This area has been gaining momentum in recent years as the need for water reclamation is getting wider recognition.

Water treatment processes including reverse osmosis and ultraviolet advanced oxidation process (UV/AOP) among other processes, have been adopted for potable water reuse applications often in combination. Managed aquifer recharge (MAR) is a method of indirect potable reuse in which treated wastewater effluent is used to replenish groundwater resources. Aquifer recharge provides a way of natural storage and an additional environmental barrier for some contaminants that persist in the water after undergoing an advanced treatment train. This natural attenuation of organics, contaminants and pathogens as water percolates through aquifer material during MAR is termed soil aquifer treatment (SAT). (Bouwer and Rice, 1984; Idelovitch and Michail, 1984; Trussell et al. 2018)

1.1 Project Background

The Sustainable Water Initiative for Tomorrow (SWIFT) project is a Hampton Road Sanitation District (HRSD) initiative to replenish the Potomac aquifer system (PAS) using MAR. A pilot study to treat HRSD wastewater treatment plant secondary effluent using advanced water treatment (AWT) to meet drinking water standards and to recharge the PAS at 1 MGD was initiated in 2018. Additional aims of SWIFT are to decrease nutrient load on the Chesapeake Bay and to reduce land subsidence and salt intrusion.

Before implementing the replenishment program in full scale, HRSD conducted soil column experiments to collect scientifically defensible data and perform analysis for the evaluation of SAT as a requirement of the Underground Injection Control (UIC) permit. Soil column study was the first phase of the SWIFT project. The SWIFT program extends to Phase II which involves the construction of a 1 MGD demonstration facility at HRSD Nansemond Treatment Plant. The demonstration facility is constructed with the view to carry out the replenishment program at a meaningful scale and demonstrate that the finished water meets primary drinking water standards and is compatible with the PAS. The demonstration facility is an extension of the pilot scale with a recharge well and monitoring wells at different radial distances from the point of injection.

The recharge well screens the upper, middle and upper portion of the lower zones of the PAS referred to from hereon as Upper Potomac aquifer (UPA), Middle Potomac Aquifer (MPA) and Lower Potomac aquifer (LPA) respectively. The first multi-aquifer monitoring well is at a radial distance of 3 day from the recharge well. There are three other conventional monitoring wells for the UPA, MPA and LPA at a distance of 400 – 500 ft. After roughly 18 months of data collection and analysis from the demonstration facility, HRSD plans to implement and construct full scale SWIFT facilities.

The first monitoring well at a 3 day distance influenced the design decisions for the soil columns. Soil column experiments are designed to simulate aquifer properties thereby allowing the study of different solute transport mechanisms through the aquifer on a laboratory scale. SWIFT soil column study involved a total of four columns out of which two soil columns were designed and constructed to simulate the time required for recharge water to travel from the injection well to the first monitoring well. These columns are referred to from hereon as “3-day columns”. The other two soil columns were used to simulate a travel time of 30 day, and these columns are referred to here as the “30-day” columns. For the latter, column design was motivated by the UIC-based target of at least 1 log removal per month of travel time.

1.2 Objectives

The primary objectives of this soil column study were:

1. To evaluate removal of pathogens and pathogen indicators demonstrating at least 1 log removal of viruses per month of aquifer travel time and consider removal of *Cryptosporidium* and *E. coli*.

2. To evaluate adsorption, transformation and degradation of total organic carbon (TOC), dissolved organic carbon (DOC), nitrogen species, and contaminants of emerging concerns (CECs).

3. To evaluate removal of disinfection by-products (DBPs) with the injection of free chlorine and mono-chloramine as disinfectant through the soil columns

The first step in the experimental plan was conducting tracer tests on each column to determine properties of the columns such as porosity, dispersivity and actual travel times. The second step was carrying out pathogen tests which involved spiking the feed water with MS2 (representative virus), *E. coli* (representative bacteria) and microbeads (surrogate for Cryptosporidium) along with sampling and analyzing the column effluent for breakthrough. After the pathogen challenge tests, the plan was to disinfect the feed to a set of 3-day column and 30 day column with chlorine and the other set with monochloramine at a residual concentration that provides the required Ct value. This allowed for the evaluation of the formation and subsequent reduction of DBPs across the columns along with the evaluation of the fate and transport of solutes such as nitrogen species, organic matter and emerging pollutants while simulating recharge conditions.

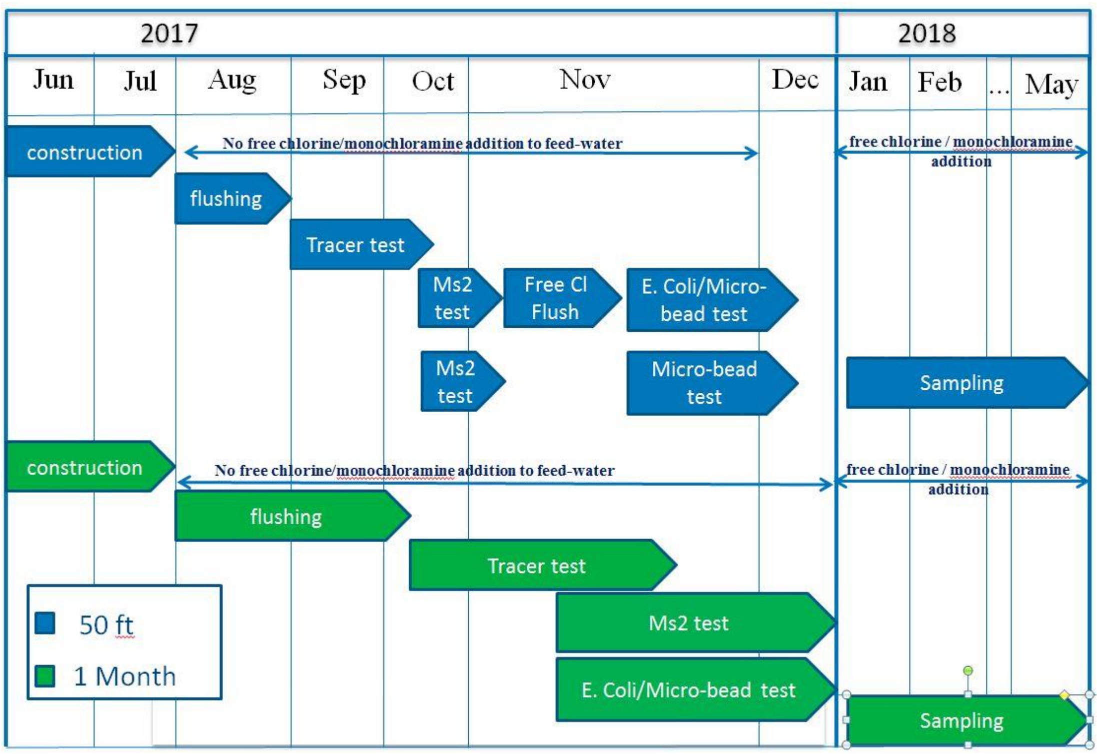


Figure 1: Experimental Schedule for Soil Column study

2. LITERATURE REVIEW

As the water demands are exponentially increasing, the focus is increasingly shifting towards potable reuse practices. Managed aquifer recharge (MAR) is one of the methods of indirect potable reuse which involves replenishment of the groundwater using engineered conveyances (EPA, 2017). MAR can be done with surface spreading basins or by direct injection into the aquifer. Few facilities like Los Alamitos Barrier Water Replenishment District of Southern California/Leo J. Vander Lans Advanced Water Treatment Facility (LVLAWTF) are conducting MAR through injection of reclaimed water; other facilities like Orange County Groundwater Replenishment System (GWRS) Advanced Water Treatment Facility have recharge basins for MAR application (EPA, 2017). MAR provides additional environmental barrier for contaminants in water through soil aquifer treatment (SAT).

SAT allows for the natural attenuation and removal of organics, contaminants, and microorganisms as water injected through managed aquifer recharge percolates through aquifer material. As managed aquifer recharge is gaining more attention, increasing number of studies have evaluated the effectiveness of SAT in potable reuse applications. The scale ranges from lab scale soil column experiments to field studies at aquifer recharge sites. These studies primarily focus on figuring out the fate and transport of various pollutants during MAR process; determination of the reactions that occur in the aquifer and mechanisms that contribute to attenuation of these pollutants; and understanding the conditions in which the attenuation takes place. Trussell et al. (2018), Burke et al. (2013), and Patterson et al. (2009), to name a few, have investigated the removal of selected micro-pollutants in soil columns while Scheurer et al. (2009), Drewes et al. (2002) conducted field studies to look at pharmaceuticals and trace organics removal through SAT. Wang et al. (2018) looked at bromate reduction in lab scale column. Organic matter removal and transformation has been studied with soil columns by Zhao et al. (2007) and in the field by Quanrud (2002). Several others have focused on the role of specific conditions like the composition of organic substrate in the attenuation of trace organics (Alidina et al. 2014) and the temperature and redox on organics and nutrients removal (Abel et al. 2012).

2.1 Soil Column Design

Soil column experiments are designed to simulate aquifer properties thereby allowing the study various solute attenuation mechanisms applicable to the aquifer. Several soil column studies have been conducted in the past to evaluate attenuation of different pathogens and contaminants. Optimizing the design and construction of soil columns requires several considerations.

There are primarily two types of soil columns: packed (disturbed) and monolithic (unpacked). In the case of packed columns, sand is extracted and homogeneously compacted with water. The unpacked columns are intact extracts from the aquifer and do not need repacking (Lewis et al. 2010). Although monoliths would provide the closest simulation of aquifer conditions, undisturbed samples are difficult to obtain and comprise of more heterogeneity compared to packed columns (Gibert et al., 2015). Packed soil columns ensure homogeneity and can be constructed with bulk density similar to the natural site conditions (Lewis et al., 2010).

The exterior of the columns are typically made of rigid inert and non-corrosive material to reduce any reaction with soil or water. Transparent material is preferred especially for the construction phase since it allows visual inspection of the slurry (soil and water) while packing the column. Most popular materials used for column construction are glass, PVC, acrylic and stainless steel (Gibert et al., 2015). During operation, however, the columns can be covered to avoid light penetration to prevent photolytic degradation of solutes.

The tubing used as influent and effluent lines of the columns also should be inert to contaminants of interest. Tubing made of Polytetrafluoroethylene (PTFE) also called Teflon is commonly used. Other types of tubing that may be used are made of high density polyethylene (HDPE), polypropylene (PP), silicone, Tygon © etc. Hebig et al. (2013) conducted a study on different tubing materials assessing their interaction with micro-pollutants. According to their results, using silicone, Tygon ©, Pharmed ©, NBR70, and low density polyethylene (LDPE) caused removal of some micro-pollutants tested; majority of the compounds were recovered while using other materials. PTFE, PP, HDPE are therefore the recommended tubing material.

For the simulation of saturated aquifer conditions, the flow through the columns is recommended to be in an upward direction. This allows for entrapped air bubbles to escape from the top during construction and operation of the columns. High precision peristaltic pumps have been typically used to produce pressurized up-flow of column influent.

Column set up, dimensions and operational procedures vary widely among different experimental studies. The diameters of the columns reported in literature range from 0.02-0.36 m and the heights are in the range of 0.05-2.4 m (Banzhaf and Hebig 2016). Ideally, the flow through the columns is uniformly distributed across the diameter and unidirectional. It is imperative to choose a suitable column height and diameter. Flow across the inner column boundaries can create problems of preferential pathways in long columns with small diameters while transversal dispersion can occur in columns with large diameter (Banzhaf and Hebig 2016). A diameter to height ratio of 1:4 has been recommended in a few column experiment reviews. (Lewis and Sjorstorm, 2010, Gibert et al. 2015). In order to prevent preferential flow paths or sidewall flows, the column diameter should be at least 40 times the average grain diameter of the soil/sand (Fand and Thinakaran, 1990). A 40–100 grain diameter is a good estimate for a representative elementary volume (REV) such that there is uniformity in volume, shape and orientation across REVs in porous media. Subsequently the height is determined to obtain the targeted travel time in the columns. Columns have been run in series as a means of simulating extended travel times without increasing column dimensions (e.g., length but also diameter).

2.2 Tracer Tests

Tracer tests are conducted in soil column experiments to determine properties of the media such as effective porosity and dispersivity and to confirm an observed travel time through the column. A tracer is a non-reactive dissolved constituent that is not subject to attenuation through sorption or biological transformation and is used to determine the physical transport properties of the soil column (Lewis and Sjorstorm, 2010). Anions are the most commonly used conservative tracer (i.e., bromide, introduced as KBr). Sodium chloride and lithium chloride are other ionic compounds used for tracer tests (Burke et al, 2013; Schyett et al., 2004).

2.3 Fate and Transport of Pathogens

Pathogen removal during aquifer recharge has important implications for advanced water treatment and MAR. Gaining pathogen log removal credits can take off the load from treatment processes like ozonation and disinfection. California, an early developer of regulations on recycled water, requires 12-log reduction of viruses and 10-log reduction of both *Cryptosporidium* and *Giardia* for potable reuse applications. California regulations published in

June of 2014 state that recycled municipal wastewater can be credited with 1-log virus removal for each month that the recycled water is in the aquifer up to a 6-log reduction (CDPH, 2014).

Removal is a function of retention time, water quality (pH, organic matter concentration, temperature, etc.), size of the pathogens, aquifer characteristics (porosity, homogeneity) among others. Pathogens can be attenuated via different mechanisms namely straining, adsorption, and decay. Several experiments have been conducted in the lab with columns and in the field at managed aquifer recharge sites to study the effectiveness of soil aquifer treatment in removing pathogens. Sidhu et al. (2015) has reported the average time for 1-log removal required for bacteria as <3 days, oocysts as <120 days, and enteric viruses as 18 to >200 days for different MAR sites. Elkyam et al. (2016) studied 30 years of aquifer recharge site in Israel and reported >5 log-removal of Fecal coliform and complete removal of Enteroviruses in around 370 days of travel time. Log removals of enteric viruses, bacterial pathogens and parasites vary across different studies owing to the different travel times and site/column characteristics. Pang (2009) compiled the average log removal achieved in various column experiments for different microbes including *E. coli*, MS2, protozoa, etc.; a summary has been shown in Table 1.

Table 1 Summary of Lysimeter studies compiled by Pang (2009)

Microbe	Average Log Removal/Meter
E. coli	8.2 – 9.6
MS2 phages	2.6 – 6.8
2.9 µm microspheres	8.47
Protozoa	4.87

2.3.1 Characteristics

MS2 (Male-specific) is a single stranded RNA virus. It is a bacteriophage with a particle diameter that ranges from 24-26 nm (Syngouna and Chrysikopoulos, 2011). The particle surface is coated with hydrophobic protein; altering the bonds present in this coating can result in inactivation. Since it cannot reproduce outside its host cell, MS2 will not replicate in waters with negligible bacterial concentration. MS2 is used as a surrogate for waterborne viruses because it is morphologically similar to pathogenic viruses such as poliovirus and hepatitis A virus (Nasser et al. 1995) and is non-pathogenic.

E. coli is a gram-negative rod-shaped bacteria with the typical dimensions of 2 um length and 0.25 – 1 um diameter. The optimum condition for *E. coli* to grow is at a temperature of 37°C with the presence of carbon source (preferably glucose) and nitrogen source (preferably ammonia). It is a facultative anaerobe. It inhabits the gut of mammals but it can also survive outside the mammalian body. *E. coli* is a fecal coliform and acts as an indicator of fecal contamination and of bacterial pathogens in water. There are different strains of *E. coli* some of which are pathogenic. *E. coli* K12, MTCC433, and DH5α are some of the non-pathogenic strains (Naganandhini, 2015).

Cryptosporidium is an obligate intracellular parasite. It resides in epithelial cells of host organisms and is dependent on the host for survival. However, it can survive outside of the organism for an extended time period forming an oocyst, which is a hard outer shell. *Cryptosporidium* oocysts are 4-6 um in diameter and are resistant to chemical disinfectants including chlorine (Carpenter et al., 1999). Using it for pathogen challenge tests requires high concentration spikes which may not be feasible. *Cryptosporidium* oocysts are naturally lower in concentration than other pathogens and culturing a high seed stock is difficult. They are also less viable because of high cost and more stringent requirement for safe handling. Many studies have used fluorescent microspheres as surrogates for pathogens (Harvey et al., 2015). Microspheres are non-reactive and are available in different sizes with charged or uncharged surfaces. So microspheres that are similarly sized as a *Cryptosporidium* oocyst can be used. Negatively charged microspheres like fluorescent carboxylated microspheres would be able to closely mimic the physical and physicochemical removal mechanism of *Cryptosporidium* oocysts that are also negatively charged (Dai and Hozalski, 2003). The uncharged microspheres would explain the removal as a result of physical mechanisms only. Microspheres would also not demonstrate inactivation and would act as conservative surrogates for pathogens like *Cryptosporidium*.

2.3.2 Transport and Attenuation Mechanisms

Advection is the transport of solutes with the bulk water. It is the dominant method of transport in groundwater and in soil columns simulating groundwater flow (Banzhaf and Hebig, 2016). Dispersion occurs due to the porous media characteristics (Schwartz 1977). Flow through porous media undergoes baffle effects which results in different flow pathways. Dispersion causes the spreading of the solutes in both transverse and longitudinal directions. The effect of dispersion increases with flow rate and scale of study (Banzhaf et al., 2016). Diffusion is a mechanism driven by concentration gradient. At a low flow rate and/or a small scale, transport through diffusion can play a significant role in the persistence of solutes in groundwater. The combined effect of dispersion and diffusion together is termed as hydrodynamic dispersion.

Retardation is a measure of the extent to which the velocity of a solute is accelerated or delayed compared to the velocity of the solvent. The formulaic definition of retardation is the velocity of solvent divided by the velocity of solute (i.e., pore water). If the retardation value is less than 1, the solute advective transport is greater than the rate of bulk fluid transport. In soil column studies, this could result in a breakthrough of the solute prior to the residence time of the column as determined by tracer breakthrough. Retardation is primarily a result of sorption (Banzhaf and Hebig, 2016). Sorption is a combination of adsorption and absorption mechanisms.

Desorption is the reverse mechanism in which compounds are released from the surface of the adsorbent or the absorbent. Concentration of the compound, organic carbon content, ionic charge, temperature, and pH of the fluid are some of the factors that affect sorption.

Straining is a mechanism in which particles cannot pass through pores smaller than their size. It is a function of grain size of the media and the size of the particle. According to Updegraff et al. (1983), when the average cell size of bacteria is greater than 5% of the grain size that makes up the media, removal by straining is significant. Straining is also affected by the flow rate through the porous media. The effects of straining decrease with the increase in pore velocity. Relatively large flow rates in a soil column increase occurrence of flow through macro-pores. Therefore, uniform distribution with constant loading rate is recommended to offset the effects of high flow rate (Stevik et al. 2004). However, Sirivithayapakorn (2003) studied size exclusion effect on transport of colloids and reported that the smallest pore throat to colloid size ratio required for colloids to pass through was 1.5. This implies that even in the presence of pores bigger than their size, compounds can be retained by the media.

Decay/Inactivation is a biological removal mechanism for pathogens. As discussed earlier, different pathogens have different optimum conditions for growth. In the absence of substrate for bacterial growth or host cells for viruses and parasites to replicate, they get inactivated after a time period. The rate of decay is temperature dependent and typically is a first order decay, although some studies have reported pseudo first order inactivation (Anders and Chrysikopoulos, 2006; Sim and Chrysikopoulos, 1996; Chrysikopoulos and Vogler, 2004). Inactivation rate of a pathogen in its suspended phase may be different than the rate in attached phase.

A number of studies have reported values of retardation factors, inactivation rates in the suspended and/or attached phase of different pathogens including MS2, *E. coli* and *Cryptosporidium*. Syngouna and Chrysikopoulos (2011) observed the retardation factors for MS2 in the range of 0.81 – 1.05. Kinner et al. (1993) conducted experiments on microbeads in the field at MAR sites and in the lab with soil columns and found the retardation value for microbeads in the field to be 1.5 -1.7 and 0.53 – 0.63 in the soil columns.

Peng et al. (2008) reported the inactivation rate of *Cryptosporidium* in sterilized water at a temperature of 4ºC to be 0.0029 d^{-1} and in soil to be 0.011 d^{-1}. Blausteina et al. (2013) studied the temperature dependence of *E. coli* inactivation in different water matrices and found out the k_{20} values for groundwater, wastewater, agricultural, pristine, lake, river and coastal water. The k_{20} values ranged from 0.063 d^{-1} for pristine water to 0.725 d^{-1} for river water. Similarly, several other studies have experimentally determined the rates for MS2 at different temperatures (see Table 2).

Table 2: MS2 inactivation rates in the aqueous and solid phase reported in papers

Temp (°C)	**k (d^{-1})**	
	Aqueous	**Solid**
4	0.026[a] (static batch experiment)	0.15 (new sand)[d]; 0.03 (old sand)[d]
15	0.060[a], 0.091[a]	n/a
5	0.082[b]	n/a
25	0.12[a], 0.576[c]	0.288 [c]

[a] Anders and Chrysikopoulos (2006); [b] Schijven et al. (2003); [c] Syngouna and Chrysikopoulos (2011); [d] Mayotte et al. (2017)

2.4 Fate and transport of solutes

Apart from pathogen removal, soil columns have been also studied for a range of contaminants. These contaminants typically include nitrogen species, organic carbon, trihalomethanes, haloacetic acids and various contaminants of emerging concern for MAR studies. These are a combination of regulated and unregulated drinking water quality parameters which is of significance to the evaluation of MAR as a method of potable reuse.

Nitrogen species including ammonia, nitrite, nitrate and Total Kjeldahl Nitrogen (TKN) contribute to the nutrient loading to water sources. Furthermore, National Primary Drinking Water Regulations imposes MCL of 10 mg/L for nitrate and 1 mg/L for nitrite in drinking water. Elevated nitrate concentrations are known to cause methemoglobinemia, also commonly called blue baby syndrome in infants (Bouchard et al. 1992). Nitrite can also cause damage to cells and may be carcinogenic at high concentrations. Most utilities monitor and regulate their Total Nitrogen (TN) level which encompasses regulation of all the nitrogen species. The transformation of nitrogen species at MAR sites has been an area of interest for a few studies (Miller et al. 2006 and Lee et al. 2005). Transformation reactions that are possible in the aquifer are nitrification, denitrification, and dissimilatory nitrate reduction to ammonia. Nitrification is carried out by autotrophic bacteria which convert ammonia to nitrite then nitrate under aerobic conditions. It may take place in the vadose zone or in the upper layers of the aquifer's saturated zone where oxygen concentration has not been completely consumed. The conversion of nitrate to nitrogen gas by denitrifying bacteria is called denitrification. The other pathway of nitrate removal mechanism is dissimilatory nitrate reduction to ammonia (DNRA). Denitrification is reported as the more common nitrate reduction mechanism compared to DNRA, although Teidje (1988) states that DNRA is not as rare as is usually reported and has been observed to take place in anaerobic digesters (Kaspar et al. 1981) and anoxic sediments (Boon et al. 1986). Although both mechanisms occur in anaerobic environments, there are conditions that select denitrifiers over microbes that carry out DNRA or vice versa. A high total carbon to nitrogen ratio with a low concentration of electron acceptors is reported to favor DNRA while the opposite is true for denitrification. The vertical gradient of temperature, dissolved oxygen concentration, and substrate availability in the aquifer provides a spectrum of conditions conducive for both oxidizing and reducing microorganisms at different depths (Misra et al. 1974).

Organic matter in reuse systems can be characterized as natural organic matter (NOM) already present in drinking water, synthetic organic compounds and soluble microbial products (Drewes et al. 1999). TOC and DOC are used as parameters to measure organics in water. Investigation of organics removal by soil aquifer treatment of wastewater effluent has shown reductions in TOC ranging from 50 to 90% (Quanrud et al. 2003, Amy et al. 1993, and Wilson et al. 1995). In another study conducted at the Sweetwater recharge facility in Tuscon, Arizona, DOC attenuation of about 55 to 60% removal in 3 m depth was observed which increased to 80 – 90% removal in 38 m depth (Yoo et al., 2006). Attenuation of the relatively degradable portion of TOC can occur in the soil columns through its utilization by microorganisms or through media adsorption.

The concern related to TOC is that organic matter can be precursors for disinfection by product formation. Recharge water is typically chemically disinfected with chlorine or monochloramine to avoid biofouling in recharge wells and in some cases to achieve additional disinfection. This leads to formation of disinfection by products which are potential risks to human health. Total trihalomethanes (TTHM) and haloacetic acids (HAA5) are disinfection by products suspected to be carcinogenic and are regulated at MCLs of 80 µg/L and 60 µg/L, respectively. While they can be formed in the recharge water, DBPs have also been observed to be bio-transformed during aquifer recharge (Thomas et al. 2000). HAAs are more readily degraded in the aerobic environments while anaerobic conditions favor THM degradation which is a relatively slower process. (Quanrud et al. 2016). Formation of brominated DBPs is driven by the bromide concentration in the water; chlorination of water with humic material is reported to produce more brominated or mixed halogenated trihalomethanes (Pourmoghadas and Kinman, 2013). Brominated DBPs are known to be more toxic than chlorinated DBPs (Yang et al., 2014).

Table 3: Compounds categorized under TTHM and HAA5

	Compounds
Total Trihalomethane (TTHM)	Chloroform
	Bromoform
	Bromodichloromethane
	Dibromochloromethane
Haloacetic acids (HAA5)	Monochloroacetic acid
	Dichloroacetic acid
	Trichloroacetic acid
	Monobromoacetic acid
	Dibromoacetic acid

Bromate is also considered carcinogenic and is a disinfection by product of ozonation. Bromide in the water is quickly oxidized to bromate in the presence of ozone. Ozonation has been commonly used in conjunction with biofiltration in the upstream treatment process of aquifer recharge in order to provide benefits of disinfection and assimilable organic carbon (AOC) formation and subsequent oxidation in downstream biofilters (van der Kooij et al. 1989). Bromate levels exceeding its 10 μg/L MCL can be formed and is not easily removed through adsorption. Wang et al. (2018)[a] reported effective removal of bromate by denitrifying bacteria in anoxic conditions in a lab scale study of MAR. Furthermore, bromate was also observed to be reduced (abiotic reduction) by Iron (II) in MAR systems (Wang et al. 2018)[b]. Chairez et al.

(2010) reported bromate reduction by biogenic sulfide in batch bioassays which implies it can potentially be removed by sulfide present in the aquifer though not much literature that have investigated this reaction in soil aquifer treatment can be found.

A fraction of the solutes in highly treated water comprises of mostly refractory compounds of emerging concern (CECs). These natural and synthetic compounds can be categorized into pharmaceutical and personal care products, pesticides, herbicides, flame retardants, hormones, food additives, and surfactants. Some of these compounds are not easily biodegraded and hence persistent in the water systems. They have already been detected at very low levels in various water sources. MCLs for emerging pollutants do not exist although some are classified into candidate contaminant lists (CCL) and reviewed for regulatory requirements as more information is gathered about their impact. There are also advisory limits indicated by states like California for a few of these compounds; ex. NDMA and 1,4-dioxane. The attenuation of these persistent, potentially harmful compounds has drawn a lot of research attention. Several studies have focused on the contaminants of emerging concern (CEC) and their possible attenuation in the aquifer. Banzhaf et al. (2012) studied sorption and biodegradation of carbamazepine, sulfamethoxazole and diclofenac. Strauss et al. (2011) and Fan et al. (2011) observed removal mechanisms for sulfamethoxazole and its metabolites. Other CECs that have been considered in soil column experiments are Bisphenol A, 17 β-estradiol, 17 α –ethynyl estradiol (Patterson et al, 2010), primidone, atenolol, meprobamate (Burke et al., 2013), perfluoroalkyl acid (PFAA) (McKenzie, et al., 2016).

The dominant mechanisms of CEC attenuation in the soil columns are biodegradation and adsorption. Sorption of compounds is a function of physico-chemical properties of the compounds as well as the media. Low K_{ow} hydrophilic compounds adsorb less easily than compounds with high K_{ow}. Many of the emerging contaminants of interest are organic and hence the organic carbon content in the subsurface affects the adsorption rate of the compounds; the higher the organic content higher the adsorption rate. Biodegradation is dependent on the microorganisms carrying out the degradation and the conditions that favor their growth. Retention time also plays a significant role in the biodegradability of compounds or rather the ability of microbes to biodegrade. Longer retention times allow micro-organisms to be acclimatized and be able to metabolize the compounds.

Several studies have focused on the attenuation of CECs during subsurface recharge. Nham et al. (2015) studied the transport behavior of 16 emerging contaminants including clofibric acid, ibuprofen, iohexol and carbamazepine in soil aquifer treatment by plotting breakthrough curves for each compound using one-dimensional 1st order reactive transport model. Attenuation mechanisms studied for some broad categories of emerging contaminants have been enlisted in Table 4.

Table 4: Removal Mechanisms for emerging pollutants

Compounds	Removal mechanism
1,4-dioxane	No anaerobic biodegradation observed in experiments or in microcosms created with samples collected from two different aquifers. Negligible effect of extended retention time on 1,4 -dioxane degradation (Steffan, 2007). Advanced oxidation processes such as UV- ozonation causes lysis (Stepien et al., 2014)
Artificial Sweeteners (Sucralose and Acesulfame-K)	Generally found to be persistent even after soil aquifer treatment. Under aerobic conditions, slow and incomplete mineralization of sucralose observed in lake water and in sewage. Little to no mineralization observed under anaerobic conditions (Scheurer, 2009). Partial mineralization by microbes through co-metabolic processes has also been reported. (Labare and Alexander, 1994). No effective sorption of sucralose (<5%) to soil reported in a test using autoclaved soil. Acesulfame-K degraded up to 20% after chlorination (Soh et al. 2011)
Iodinated compounds (Iohexal, Iopromide)	Negligible removal observed in aerobic conditions. Partial removal observed in anoxic conditions. (Drewes et al. 2001)
NDMA	Mineralization possibly carried out by microbes since it occurred under both aerobic and anaerobic incubations. Conditions that favor removal – microaerobic and neutral pH. Sorption was insignificant in soil samples from aquifer. (Gunnison et al. 2000)
Estrogens (Estradiols, estrones, estriol, xenoestrogen)	Potential degradation by nitrifiers (Layton et al. 2000)
Antiepileptic drugs (Carbamazepine, Primidone)	Fairly persistent and no significant indication of removal even after 6 years of subsurface recharge (Drewes et al. 2002), advanced oxidation processes might be effective
Analgesic and anti-inflammatory drugs (Ibuprofen, diclofenac, acetaminophen, Ketorolac)	Good removal via biodegradation demonstrated in SAT (Drewes et al. 2002)
Flame retardants (TCEP, TCPP)	Negligible removal in short travel times in the vadose zone (travel time <3 days); 50 – 80% removal in the lower aquifer with travel time of 60 days (Laws et al. 2011). This may be indicative of biodegradation occurring in anaerobic conditions.
Perfluorinated compounds (PFOA/PFAS)	Resistant to chemical or biochemical degradation. Possible attenuation mechanisms in groundwater are adsorption to aquifer solids or dilution caused by dispersion. (Xiao et al. 2015)
Caffeine	Non-conservative. Degraded after ozonation. (Soh et al. 2011). Quick degradation (~16 h) observed in MAR study; adsorption was seen but biodegradation was the dominant mechanism (Alidina et al. 2014).

3. MANUSCRIPT 1: EVALUATION AND MODELING OF PATHOGEN REMOVAL IN SOIL COLUMN EXPERIMENTS

ABSTRACT

Managed Aquifer Recharge (MAR) is a method of indirect potable reuse which can provide additional environmental barriers to contaminants present in water through a process of natural attenuation termed as Soil Aquifer Treatment (SAT). Evaluation of SAT is critical in assessing MAR as a means to provide a sustainable source of drinking water. Soil column study is one of the ways to evaluate SAT at a meaningful scale. Experiments with soil columns were conducted at a pilot facility in Hampton Road Sanitation District (HRSD)'s York River Treatment Plant with the view to determine the effectiveness of MAR in the removal of different contaminants of concern. Four soil columns were constructed using sediment from the Potomac Aquifer System and were designed to simulate two different travel times of 3.2 days and 30 days. One of the primary objectives of the soil column study was to confirm that 1 log virus removal could be achieved with 1 month of aquifer travel time in accordance with California's regulation and to evaluate similar removal of *Cryptosporidium* and *E. coli*. Pathogen challenge tests including MS2 as a representative virus, *E. coli* as a representative bacteria and microbeads as a surrogate for *Cryptosporidium* were conducted on all four columns. 6 to 7-log removals of MS2 and E. coli and 3 to 5-log removals of microbeads were observed. Log reduction values were higher for longer retention time of 30 days. A model using advection-dispersion equation and analytical solution for reactive solute was also used to fit the measured pathogen data for a better understanding of pathogen attenuation mechanisms. The model could not accurately quantify the removal rates attributed to adsorption and decay of the pathogens primarily because the

measured column effluents were either very low or were below detection. Nonetheless, effective pathogen removal was seen in the soil columns, which has important implications in terms of getting disinfection credits for potable reuse applications. Data from this soil column study provided a basis for the future implementation of the recharge program at full scale SWIFT facilities.

3.1 Introduction

Potable reuse is a sustainable solution to the problem of increasing water demands of the present and more so the future. Water treatment processes including reverse osmosis, ultraviolet advanced oxidation processes (UV/AOP) have been adopted for potable water reuse applications often in combination. Managed aquifer recharge (MAR) is a method of indirect potable reuse in which water from various sources including reclaimed water is used for groundwater replenishment. Aquifer recharge provides a way of natural storage and an additional environmental barrier for some contaminants that persist in the water even after undergoing an advanced treatment train. This natural attenuation of organics, contaminants and pathogens as water percolates through aquifer material during MAR is termed Soil Aquifer Treatment (SAT). (Bouwer and Rice, 1984; Idelovitch and Michail, 1984; Trussell et al. 2018)

As managed aquifer recharge is gaining more attention, increasing number of studies have evaluated the effectiveness of SAT in potable reuse applications. The studies range from laboratory-scale soil column experiments to field studies at aquifer recharge sites. Soil columns enable the evaluation of SAT at a manageable scale which then provides a basis for implementation on a full scale. Ideally soil columns are designed to be homogeneously packed with longitudinal direction of flow and uniform distribution across the column diameter in order to get a close representation of the aquifer conditions while also maintaining the analysis manageable at a lab scale. Several considerations are required in the design of the columns to achieve this. These include the construction aspects such as the material used to make column exteriors, pumps and tubing; method of packing; dimensional considerations like diameter and height as well as operating conditions such as flow rate and travel times.

There are primarily two types of soil columns: packed (disturbed) and monolithic (unpacked). In the case of packed columns, sand is extracted and homogeneously compacted with water. The unpacked columns are intact extracts from the aquifer and do not need repacking (Lewis et al. 2010). Although monoliths would provide the closest simulation of aquifer conditions, packed soil columns ensure homogeneity and can be constructed with bulk density similar to the natural site conditions (Lewis et al., 2010).

Pathogen contamination in drinking water is a serious health issue and subsequently pathogen attenuation during MAR is a pivotal area of interest from a health regulatory standpoint. MAR provides additional environmental barriers to pathogens present in the water. The state of California, which is currently at the fore front of potable reuse regulations, requires 12-log removal of virus and 10-log removals of both *Cryptosporidium* and *Giardia* for potable reuse. According to California regulations published in June 2014, 1-log virus removal can be credited for each month the recycled water is in the aquifer, up to 6-log reduction (CDPH, 2014). In the light of this regulation, several experiments conducted with soil columns and in the field at managed aquifer recharge sites have focused on studying the effectiveness of soil aquifer treatment in removing pathogens. Log removals of enteric viruses, bacterial pathogens and parasites vary across different studies owing to the different travel times and site/column characteristics. The findings for pathogen removals as observed by different studies have been tabulated in Table 5.

Table 5: Removal of different pathogens observed in various studies

Reference	Scale of study	Observation
Sidhu et al. (2015)	Field study including four different aquifer recharge sites	Average time for 1-log removal for bacteria:<3; oocysts:<120 days; enteric virus:18 to >200 days
Elkayam et al. (2016)	Aquifer recharge site in Israel operating for 30 years	Fecal coliform:>5-log removal after 17 days of travel time; Enterovirus: complete removal in 370 days of travel time
Santamaria et al. (2011)	Column study with lysimeter and packed column	Cryptosporidium: 2 to 5-log. Reduction increased with increase in residence time.
Hijnen et al. (2005)	Soil columns with soil extracted from aquifer recharge (AR) site and river bank filtration (RBF) site	MS2: 3.3-log, 2.2-log; *E. coli*: 4.7-log, 4.2-log; Cryptosporidium: 3.9-log, 3.3-log; Giardia: 6.2-log, >6.2-log @ 0.5 m/d, 0.9 m/d in columns filled with soil from AR site; higher removals observed in soil from RBF site

These attenuations are primarily attributed to effects of straining adsorption and biological inactivation. Although field studies better represent the fate and transport of pathogens during MAR, the low concentration of pathogens on site and the risk associated with contaminating the sites with high concentrations of pathogens required for attenuation studies, makes them less feasible compared to soil columns (Hijnen et al. 2005).

Column set up, dimensions and operational procedures vary widely among different experimental studies. The diameters of the columns reported in literature range from 0.02-0.36 m and the heights are in the range of 0.05-2.4 m (Banzhaf et al., 2016). Ideally, the flow through the columns is uniformly distributed across the diameter and unidirectional. It is imperative to choose a suitable column height and diameter. Flow across the inner column boundaries can create problems of preferential pathways in long columns with small diameters while transversal dispersion can occur in columns with large diameter (Banzhaf et al. 2016). A diameter to height ratio of 1:4 has been recommended in a few column experiment reviews. (Lewis and Sjostrom 2010, Gibert et al. 2014). Also for the simulation of saturated aquifer conditions, the flow through the columns is recommended to be in an upward direction. This allows for entrapped air bubbles to escape from the top during construction and operation of the columns. After the construction, analysis is also required to verify important parameters of the soil column such as effective porosity, dispersivity and the actual retention time in the columns. This is done with the help of tracer tests where non-reactive compounds such as chloride and bromide are spiked in the influent of the columns and their breakthrough is observed and analyzed in the column effluent. In order to prevent preferential flow paths or sidewall flows, the column diameter should be at least 40 times the average grain diameter of the soil/sand (Fand and Thinakaran, 1990).

Soil columns enable the evaluation of soil aquifer treatment at a manageable scale which then provides a basis for implementation on a full scale. This column study was the first phase of Hampton Road Sanitation District (HRSD) Sustainable Water Initiative for Tomorrow (SWIFT) project. HRSD plans to treat effluent from seven of its wastewater treatment plants with advanced water treatment processes to comply with drinking water standards for indirect potable reuse. Four soil columns were built at HRSD’s York River Treatment Plant pilot facility to simulate two different travel times of 3 days and 30 days. The primary objective of this soil column study was to simulate the conditions in the Potomac Aquifer System (PAS) with the view to confirm the CA regulation of crediting at least 1 log virus removal for 1 month of aquifer travel time during subsurface recharge and to evaluate similar removal of *Cryptosporidium* and *E. coli*. Although there have been several soil column experiments conducted to study pathogen removal through porous media, there are few that have been conducted at a scale comparable to this study. Demonstration of effective pathogen removal data at a meaningful scale has important implications in terms of getting disinfection credits for potable reuse applications. The results of this study provided scientifically defensible data for the implementation of aquifer recharge program at a 1 MGD demonstration facility at HRSD's Nansemond Wastewater Treatment Plant and the long term goals of constructing and operating full scale SWIFT facilities

3.2 Materials and Methods

3.2.1 Experimental Design

The set up for the soil aquifer treatment experiments consisted of four soil columns designed to simulate two travel time intervals in the aquifer. Two columns were constructed to match the estimated travel time of 3.2 days associated with the first monitoring well at a radial distance of 15 m (50 ft.) from the SWIFT pilot recharge well (henceforth referred to as 3 day columns). Two additional columns were constructed to represent 30 days of travel time (henceforth referred to as 30 day columns). The decision of simulating 30 days of travel time was made to evaluate California's regulation of crediting 1 log-virus removal for a month that water is in the aquifer. The diameter of all four columns was 0.305 m (1 ft.). The 3 day columns were constructed 2.4 m in height and filled with aquifer sediment, primarily sand, to 2.3 m. The 30 day columns were 3.9 m in height and filled with aquifer sediment to 3.6 m. The column properties for all four columns have been summarized in Table 5.

Table 6: Design parameters for soil columns

Column	Travel Time in days	Flow rate in mL/min	Total height in meters (ft.)	Depth of sand in meters (ft.)	Diameter in meters
#1 (30 day)	30	2.2	4.0	3.7	0.305
#2 (30 day)					
#3 (3 day)	3.2	13	2.4	2.3	
#4 (3 day)					

The sediment used to fill the columns was extracted from the Potomac Aquifer. Aquifer sediment collected from the Potomac aquifer was washed thoroughly in a cement mixer and then sieved through a 4 mm screen to remove drilling mud, clay, and larger debris. As the columns were being filled with sediment, finished water from the SWIFT pilot was also added to saturate the sand. The columns were tapped with a rubber mallet to improve compaction and release trapped air. The exterior is comprised of 12-inch schedule-40 clear PVC. Clear PVC was valuable during the construction of the columns to ensure that all air bubbles were removed. The columns were then covered with 6-mm thick polyethylene plastic to prevent light penetration that may have encouraged algal growth or photolytic chemical transformations not representative of subsurface conditions.

The columns were designed for the study of saturated aquifer conditions. Influent water was stored in 76 L (20 gal) PVC containers by Ace Roto-Mold, a division of Den Hartog Industries, Inc. The containers were kept inside a refrigerator by Frigidaire with the capacity of 473 L (17 cu. ft.) and with temperature maintained below 4°C. The refrigerators were modified to allow tubing to pass through the side walls. As shown in Figure 1, tubing ran from the containers to the bottom of the soil columns and Masterflex ® L/S ® digital peristaltic pumps fed water through the columns in upward direction. The type of tubing used for the experiment was polytetrafluoroethylene (PTFE) semi-clear tubing (6.35 mm OD, 3.175 mm ID) by Teflon ®, the peristaltic pumps used Masterflex ® L/S ® Tygon tubing EW-06509-14 for 3 day columns and EW-06509-13 for 30 day columns. The rate of the feed pump was 13 mL/min for the 3 day columns and 2.2 mL/min for the 30 day columns. The flow rates were determined for the specific travel times using a Lagrangian approach.

The effluent emanated from the top of columns through the aforementioned, PTFE semi-clear tubing that was connected to a fitting on the flange of the columns. Column effluent was collected and stored in 19 L (5 gal) cubic containers in a separate refrigerator maintained at a temperature of less than 4°C. Dissolved oxygen (DO) probes were installed at the top of each column that allowed for continuous, real-time DO and temperature measurement of the effluent. Ambient temperature was also measured to keep track of the changes in temperature. The temperature in the columns was at a higher range of 26 – 30°C in the beginning of the experiment (Oct. – early Nov.) and dropped to ranges of 25 – 21°C towards the end of the experiment (Dec). The ambient temperature was consistently about 2°C lower than the temperature recorded in the columns.

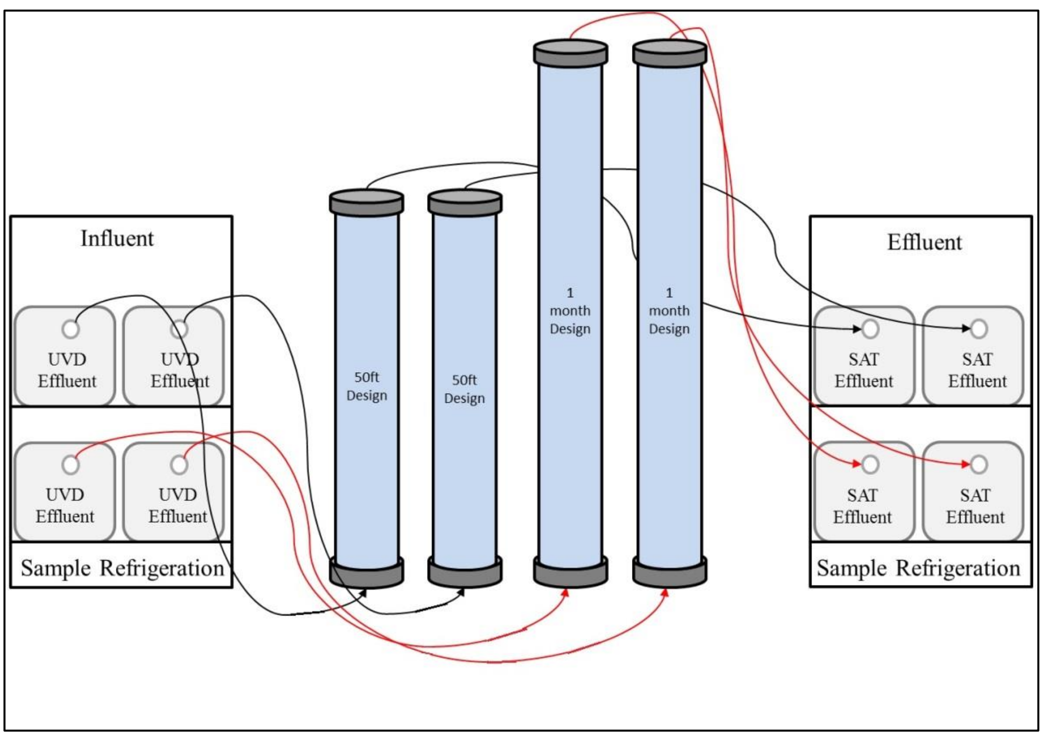


Figure 1: Soil column set up

The effluents from all four columns were collected in separate 19 L (5-gal) collapsible containers stored in a refrigerator. The weight of the containers was measured for known time intervals, typically 24 hours.

The influent to the soil columns was the SWIFT finished water derived from the pilot advanced water treatment systems. The feed for the SWIFT pilot was the HRSD York River Water Resource Recovery Facility effluent. SWIFT finished water undergoes several treatment processes, including flocculation/sedimentation, ozonation, biofiltration, and UV- disinfection that provided a source of highly-treated column influent consisting mostly of recalcitrant organic compounds and nutrients.

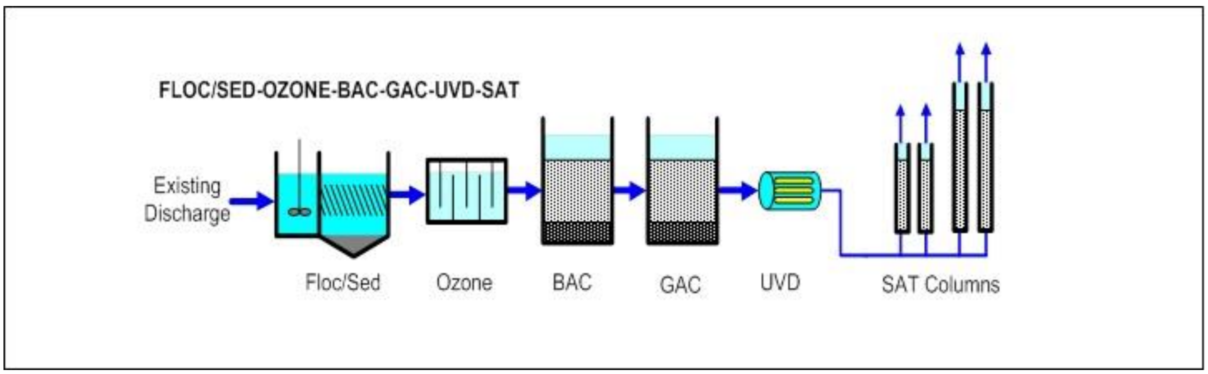


Figure 2: SWIFT pilot treatment process

3.2.2 Tracer Test

Tracer test was conducted on the columns after they were flushed at three times the designed flow rates. Sodium chloride was used as a conservative tracer. Prior to the introduction of the tracer, the feed water was first analyzed to determine the background concentration of chloride and determine the amount of chloride to be added. The background chloride concentration ranged from 150 to 225 mg/L. The influent was spiked with sodium chloride to obtain a concentration higher than the background (~500 mg/L). The duration of the continuous feed of tracer was 4 days for the 3 day columns and 10 days for the 30 day columns. Following the tracer addition, the columns were supplied continuously with SWIFT finished water.

Column effluent samples were collected for chloride analysis over a time interval to capture the expected breakthrough of the chloride concentration for each of the four columns. These samples were collected directly from the effluent tubing in 250 mL Nalgene bottles. Column effluent was sampled and monitored until the chloride concentration decreased to within 10% of the background value.

Prior to the start of the tracer test, a linear correlation between conductivity and chloride concentration was determined for the finished water. In a step-wise method, a known mass of sodium chloride was added to a known volume of the finished water, and the conductivity was measured. This step was repeated to obtain a range of chloride concentrations and the corresponding conductivity values (Appendix- Figure 27). This established correlation was used to calculate the chloride concentrations from the observed conductivity values of the column effluents during the tracer test.

Tracer tests were conducted in two soil columns simultaneously. An online conductivity probe by s::can (Vienna, Austria) was used to obtain continuous conductivity measurements of one of the column effluents. The probe was connected to a meter which logged data into the online PLC system at York River's Pilot Plant. For the second column effluent, HACH CDC401 conductivity probe was used and conductivity readings were logged onto HACH HQ40D multi-meter every 30 minutes. The column effluents were collected in 250 mL Nalgene bottles.

3.2.3 Pathogen Test

Tracer tests were followed by microbial challenge tests. The study of the removal of pathogens and pathogen indicators is a critical objective of this project. MS2 coliphage, *Cryptosporidium* and *E. coli* were the pathogens and pathogen indicator of interest, respectively. For all three pathogen tests, the spiked influent was prepared in batches by adding the required stock volume to the feed and mixing manually with a plastic rod. The duration of the spiked feed was 5 days for the 3-day columns (#3, #4) and 30 days for the 30-day columns (#1, #2). Influent samples were collected every time a new batch was prepared until the duration of the spike.

3.2.3.1 MS2

A stock of MS2 with the concentration of 3.5×10^{11} PFU/mL was purchased from a lab called GAP EnviroMicrobial Services Ltd. (Canada). The influent was spiked with MS2 coliphage to a concentration of 10^{7} PFU/mL in a 75 L (20 gal) polyethylene tank. Columns were fed from a single source of influent to avoid variability. The background influent concentration of MS2 was not measured but assumed to be negligible. Since MS2 has been reported to have quick breakthroughs (Syngouna and Chrysikopoulos, 2011) the effluent sampling started a day after the MS2 feed for the columns #3 and #4, and after 12 days of feed for column #1. Samples were collected at a frequency of 2x/day. Samples were collected in 1L autoclaved HDPE bottles and analyzed by HRSD's Technological Services Division (TSD).

3.2.3.2 *E. coli*

E. coli test was conducted after the MS2 test in one of the 3 day columns. There was concern that following the MS2 test, MS2 adsorbed on the column media would interfere with the *E. coli*. MS2 is a bacteriophage that infects *E. coli* and in the presence of MS2, *E. coli* degrades at a faster rate. To avoid this, the 3 day column (#3) was amended with free chlorine for around 3.5 days, equivalent to one pore volume of injection in order to inactivate the attached MS2. This was followed by flushing at twice the designated flow rate for an additional 3.5 days, which was equivalent to flushing two pore volumes. This step was not required in the 30 day columns, since the *E. coli* test and the MS2 test were simultaneously carried out in two different columns.

For this test, a non-pathogenic strain of *E. coli* K-12 was used which was cultured at HRSD's Central Environmental Laboratory (CEL). The influent was spiked to the concentration of 10^6 MPN/mL. For the effluent, a sampling schedule similar to MS2 was followed, again due to possibility of an earlier breakthrough. Samples were collected in autoclaved 250 mL glass containers and analyzed by CEL.

3.2.3.3 Microspheres

Microsphere test was conducted simultaneously in both of the 3-day columns and one of the 30-day columns (#2). 3 µm fluorescent microspheres were used as surrogates for *Cryptosporidium* oocysts. These fluorescent microspheres are similar to *Cryptosporidium* oocysts in molecular size. They act as conservative surrogates because they do not carry any surface charge and hence would only be removed by physical mechanisms as opposed to the *Cryptosporidium* oocysts which have negative surface charge and can be removed by physical as well as physicochemical filtration. Fluorescent microspheres are less expensive and relatively easier for safe handling. 3 µm green colored fluorescent microspheres were purchased from Thermo Fisher Scientific. Stock of microspheres was added to the finished water and stirred manually to achieve the targeted concentration of 10^5 count/mL. The effluents were sampled. The sampling frequency for effluent was once per day. . Samples were collected in 250 mL HDPE bottles. In order to prevent the microbeads from sticking to the walls of the container, Polysorbate 20 (TWEEN 20) was added to the bottles prior to sampling. 2.5 mL of Polysorbate 20 was added to each bottle to achieve the recommended volume of 10 mL/L of sample collected. The samples were analyzed by Biological Consulting Services (BCS) in Gainesville, Florida.

Table 7: Concentrations of the influent for MS2, microspheres and *E. coli* and their respective Method Reporting Limit (MRL)

	Concentration of feed	MRL	Duration of spike	
			3-day columns	**30-day columns**
MS2	10^7 PFU/mL	1 PFU/100 mL	3 days	30 days
Microspheres	10^5 count/mL	1 count/10 mL		
E. coli	10^6 MPN/mL	1 MPN/100 mL		

3.2.3.4 Biological Inactivation test

A separate experiment was conducted in order to determine the endogenous inactivation rate of MS2 and *E. coli* in the aqueous phase. The experiment was conducted in a span of 9 weeks. Two different solutions were prepared for the two pathogens. Finished water was taken in a container and spiked to around 10^6 PFU/mL of MS2; similar process was followed to obtain a concentration of 10^6 MPN/mL of *E. coli.* The prepared MS2 and *E. coli* solutions were poured into 500 mL autoclaved HDPE containers and 250 mL sterilized glass containers respectively. All containers used in this experiment were wrapped in aluminum foil to avoid light penetration. They were kept in a water bath set at the temperature of 20^oC. One sample container each for MS2 and *E. coli* was sent to the lab for analysis every week for 9 weeks. The time that the container was taken out of the foil for analysis was recorded and used to calculate the time elapsed between the sample analyses. The concentration data were then plotted with respect to time and a first order decay curve was obtained.

3.2.4 Data Analysis and Modeling

A one dimensional solute transport model was prepared in Microsoft Excel to analyze transport and attenuation of the tracer and the pathogens. The model was comprised of the advection-dispersion equations of mass balance for transport in porous media.

3.2.4.1 Non-Reactive Model

A conservative model was used for the tracer data analysis. Because the tracer is a non-reactive solute, this model only accounted for advective-dispersive solute transport and did not incorporate adsorption or transformation as removal mechanisms.

The general equation is:

$$D_L \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} = R\frac{\partial C}{\partial t} \qquad (1)$$

BC $\quad C(0,t) = C_o \qquad$ for $t \geq 0$

$C(\infty,t) = 0 \qquad$ for $t \geq 0$

IC $\quad C(x,0) = 0 \qquad$ for $x \geq 0$

The equation incorporates the velocity of the water (v_x), concentration of solute (C), time elapsed (t), longitudinal distance (x), and dispersion coefficient in liquid (D_L). The dispersion coefficient is a product of the dispersivity value (α_L) and the velocity of the water.

$$D_L = \alpha_L \,.\, v_x \qquad (1.1)$$

The additional parameter is the retardation factor (R). The equation that defines the retardation factor is:

$$R = \frac{v_x}{v_c} \tag{1.2}$$

Retardation factor accounts for the lag in the velocity of solutes (v_c) compared to the velocity of water (v_x) due to the effects of adsorption. Using this relation, Equation (1) can be modified as:

$$D_c \frac{\partial^2 C}{\partial x^2} - v_c \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \tag{2}$$

However, the tracer does not get adsorbed to the media. So the retardation factor in the case of the tracer test was considered to be equal to 1. Therefore equations (1) and (2) would essentially be the same in this case.

The exact solution of the differential equation (2) when the influent is continuous and the influent concentration (C_o) is constant is:

$$C(x,t) = \frac{C_o}{2}\left[erfc\left(\frac{x - v_c t}{2\sqrt{D_c t}}\right) + exp\left(\frac{v_c x}{D_c}\right).erfc\left(\frac{x + v_c t}{2\sqrt{D_c t}}\right)\right] \tag{2.1}$$

The exact solution for a varying source concentration ($\Delta C_o \neq 0$) has an additional term and can be expressed as:

$$C(x,t) = \frac{C_o}{2}\left[erfc\left(\frac{x-v_c t}{2\sqrt{D_c t}}\right) + exp\left(\frac{v_c x}{D_c}\right).erfc\left(\frac{x+v_c t}{2\sqrt{D_c t}}\right)\right] - \frac{\Delta C_o}{2}\left[erfc\left(\frac{x-v_c(t-t_o)}{2\sqrt{D_c(t-t_o)}}\right) + \exp\left(\frac{v_c x}{D_c}\right).erfc\left(\frac{x+v_c(t-t_o)}{2\sqrt{D_c(t-t_o)}}\right)\right] \tag{2.2}$$

Where, ΔC_o is the reduction in the source concentration at time $t = t_o$ relative to the starting boundary condition (C_o). The concentration of the source varied in the four days and ten days that tracer was fed to the 3-day and 30-day columns respectively. Therefore solution (2.2) was used for the data analysis.

The breakthrough of the model-predicted chloride concentration was a function of the two primary input parameters namely effective porosity and dispersivity (ft.). Effective porosity was used to directly calculate velocity. The input for each column was estimated using total porosity and then adjusted to match the breakthrough time. Dispersivity was used to fine-tune the match of the model to the rate of rise of the tracer concentration. Altering these parameters altered the concentration of the solute and the values were plotted to obtain a breakthrough curve. The influent and effluent concentration data analyzed by the lab were also put into the model. The concentration of chloride calculated from the chloride-conductivity correlation was also plotted. The goal was to match the concentrations predicted by the model with the actual concentrations determined through analysis. The set of values that resulted in the best fit breakthrough curve were considered the best estimates of these parameters.

3.2.4.2 Reactive model

For the reactive compounds, a modified form of equation (2) is used. This equation has an additional parameter, λ_c which is the effective first order decay rate of the compound. The general equation is:

$$D_c \frac{\partial^2 C}{\partial x^2} - v_c \frac{\partial C}{\partial x} - \lambda_c C = \frac{\partial C}{\partial t} \tag{3}$$

This decay rate constant accounts for decay of the solute in both aqueous phase (λ_a) and in solid phase (λ_s) along with removal via adsorption (R). It can be expressed as

$$\lambda_c = \lambda_s - \frac{\lambda_a}{R} \tag{3.1}$$

The exact solution of this differential equation for a varying source concentration ($\Delta C_o \neq 0$) is:

$$C(x,t) = \frac{C_o}{2}\left\{exp\left[\frac{v_c x}{2D}(1-\Gamma)\right].erfc\left(\frac{x-v_c t\Gamma}{2\sqrt{D_c t}}\right)+exp\left(\frac{v_c x}{2D}(1+\Gamma)\right).erfc\left(\frac{x+v_c t}{2\sqrt{D_c t}}\right)\right\} - \frac{\Delta C_o}{2}\begin{bmatrix} exp\left[\frac{v_c x}{2D}(1-\Gamma)\right].erfc\left(\frac{x-v_c(t-t_o)\Gamma}{2\sqrt{D_c(t-t_o)}}\right)+ \\ \exp\left(\frac{v_c x}{2D}(1+\Gamma)\right).erfc\left(\frac{x+v_c(t-t_o)\Gamma}{2\sqrt{D_c(t-t_o)}}\right)\end{bmatrix} \tag{3.2}$$

The parameter Γ in the above equation can be expressed as

$$\Gamma = \frac{\sqrt{{v_c}^2+4\lambda_c D_c}}{v_c} \tag{3.3}$$

With the knowledge that pathogens are subjected to removal through physical, chemical and biological mechanisms, a non-conservative model was used for the pathogen test analysis. The model was based on Solution (3.2). It predicted the concentration of pathogen depending on the input parameters. The best estimates of effective porosity and dispersivity determined from the tracer test analysis were used for all the following analytical models. The influent and effluent concentration values analyzed by the lab were put into the model. The decay rate in aqueous phase for MS2 and *E. coli* were experimentally determined through a biological inactivation test the procedures of which has been detailed in Section 3.2.3.4, the decay rate in solid phase and the retardation factors were values consulted from published literature.

3.3 Results and Discussion

3.3.1 Tracer test

The results from the tracer test provided estimates of effective porosity and dispersivity along with the verification of the actual travel times in the soil columns. The values for the four columns have been summarized in Table 8. The estimated values of dispersivity, effective porosity and the calculated travel times for all four columns were in accordance with expectation.

Table 8: Dispersivity, effective porosity values and travel time of the soil columns estimated by the model

	30 day column (#1)	30 day column (#2)	3 day column (#3)	3 day column (#4)
Dispersivity in m (ft.)	0.12 (0.41)	0.08 (0.27)	0.13 (0.42)	0.05 (0.15)
Eff. Porosity	0.35	0.35	0.35	0.38
Travel time in days	29.6	30.2	3.1	3.4

Dispersivity in lab scale soil columns with uniform grade size is usually close to 0.001 m. 0.0001 to 0.01 m is the typical range of longitudinal dispersivity values for column experiments (Domenico and Schwartz, 1998). This holds true for column experiments conducted using uniform grain size for the porous media. The higher dispersivity values in the range of 0.05 – 0.13 m observed in this study indicated that the porous media in the soil columns did not have a uniform grain size distribution. This was also supported by the uniformity coefficient of approximately 5 which was calculated by using sieve analysis data of the sand (Appendix – Figure 28).

The values of effective porosity were comparable for all four columns with the porosity values estimated to be 0.35 for three columns and 0.38 for one column. This attests to the similar compaction process used for all columns. Compared to the average porosity value determined for the core samples taken from the aquifer which was approximately 0.28, these values are slightly higher. The sand used to fill the columns was washed thoroughly to remove drilling mud removing fine grained particles along with it. This could have resulted in the higher porosity in the soil columns in comparison to the core samples which were undisturbed and had clay, interstitial silts.

Table 9: Porosity results from core sample analysis at different depths of the Potomac aquifer

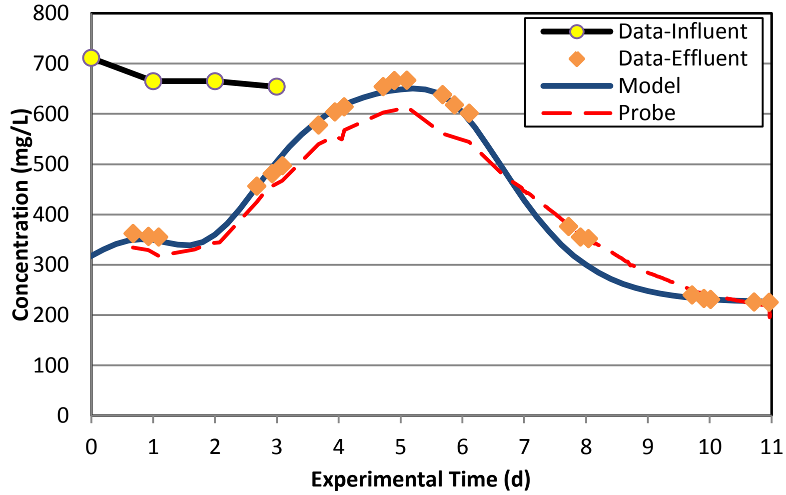
Grain varieties	Depth interval (ft.)			
	646 - 648	**1051.6 – 1063.6**	**1257 – 1258.4**	**1315 – 1316.5**
Intergranular porosity (%)	27	23	29.7	18.7
Secondary intragranular porosity (%)	3.3	4	2.7	0.3
Grain-moldic porosity (%)	1.3	1	0.3	
Intercrystalline microporosity (%)	1	0.3	0.3	1.3
Total porosity (%)	32.6	28.3	20.3	33
Average porosity (%)	28.6			

The travel times were calculated using the effective porosity values determined by the model and the experimental flow rates for each column. The calculated travel times for both the 30 day columns and the 3 day columns were very close to the design travel times of 30 days and 3.2 days respectively.

3.3.1.1 Data Analysis and modeling

The model using advection-dispersion equation and its analytical solution for a non-reactive solute worked well for the tracer test analysis. In general, there was concurrence between the lab measured chloride values, chloride concentrations derived from conductivity values and the values determined by the model for both the 3 day columns (see Figure 3) and 30 day columns (see Figure 4).It has to be noted that in the case of the 30 day columns, the tail end of the predicted chloride values were lower than the measured and conductivity derived chloride values. A possible explanation for the slight deviation of observed data from the model predicted curve was considered to be instrumental or analytical error in the measurement of chloride concentration. Background concentrations in the influent were measured throughout the experimental duration. When the background concentration measured on the 19th experimental day was increased by 50 mg/L the tail end of the model seemed to closely fit the observed values. Additionally, mass recovery calculation was conducted for the tracer tests. The percent difference in the mass of chloride in the influent and the effluent were determined to be in the range of 2 – 4% for the 3 day columns. For the 30 day columns, the difference was calculated to be 3 – 7%. The low values indicated that almost all the chloride fed to the columns during tracer tests was recovered in the effluent. This verified that the chloride indeed acted as a non-reactive solute and the tests were conducted with minimal error.

a.



b.

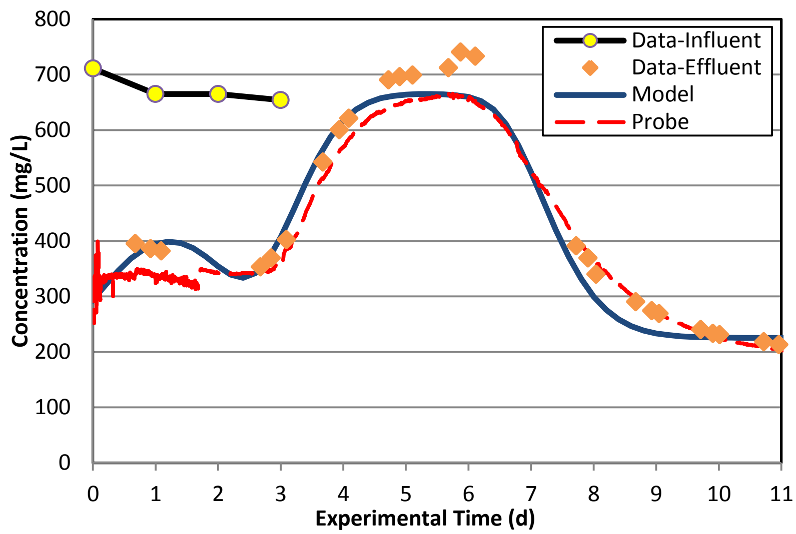


Figure 3: Tracer breakthrough curve for 3-day columns #3 (a) and #4 (b). The data-influent and data-effluent were chloride values measured in the lab and probe indicates chloride values derived from continuous conductivity measurements.

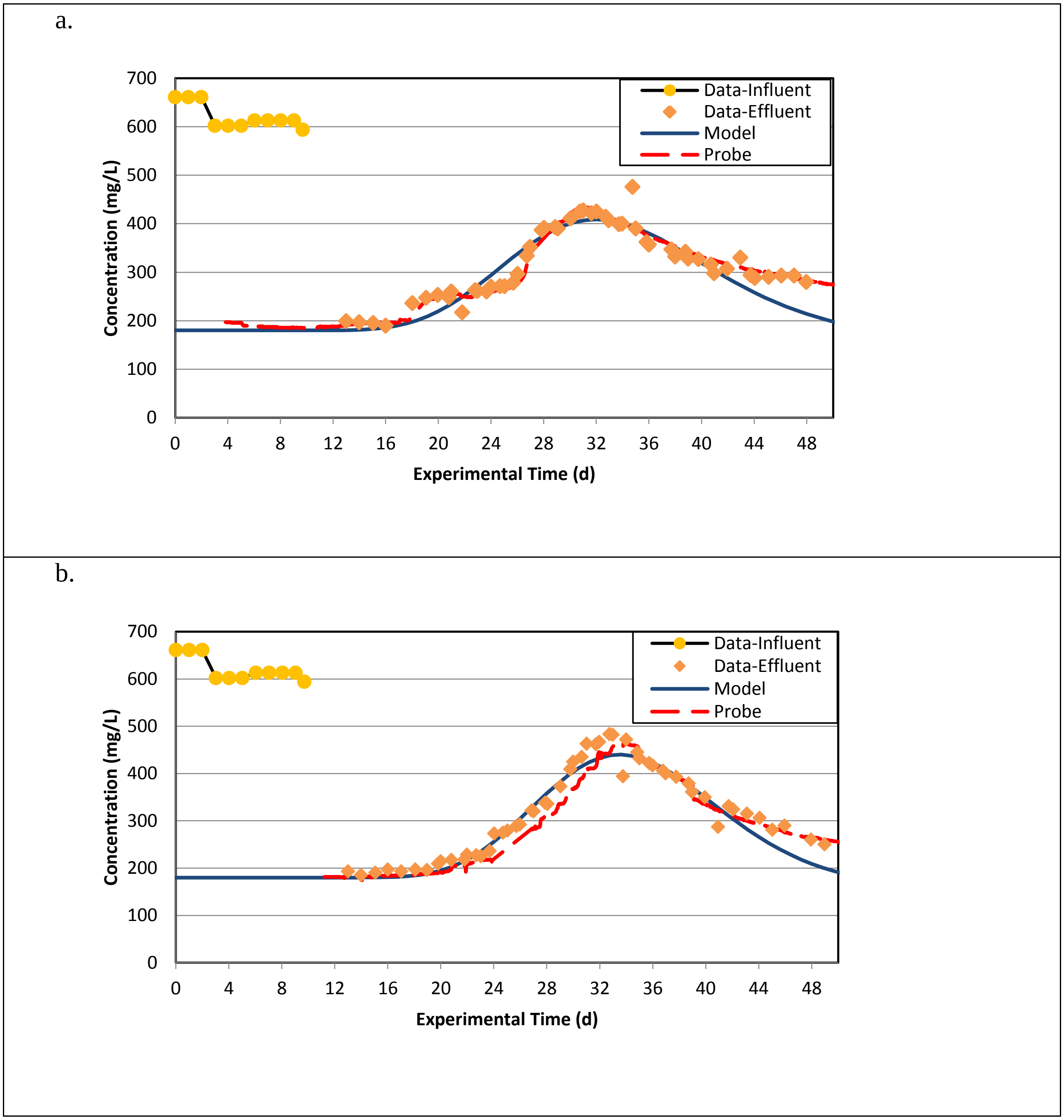


Figure 4: Tracer breakthrough curve for 30-day columns #1 (a) and #2 (b). The data-influent and data-effluent were chloride values measured in the lab and probe indicates chloride values derived from continuous conductivity measurements.

3.3.2 Biological inactivation test

The inactivation rates in the aqueous phase for MS2 and *E. coli* were experimentally determined in a separate batch inactivation test as has been detailed in Section 3.2.3. The natural log of the observed concentrations was plotted against experimental time. Assuming the biological inactivation of the pathogens to be first order decay the slope of these plots with linear regression were considered to be inactivation rates in the aqueous phase (see Figures 5 and 6). Aqueous phase inactivation rate for MS2 has been reported by various studies at various temperatures; 0.027 d^{-1} @ 4°C (Peng et al. 2008); 0.576 d^{-1} @ 25°C (Syngouna and Chrysikopoulos, 2011); 1.68 d^{-1} @ 28.8°C (Anders and Chrysikopoulos, 2006). The observed rate of 0.3 d^{-1} @ 20°C fell within the range of 0.027 – 1.68 d^{-1} for the temperature ranges of 4 – 28.8°C. As seen in Figure 5, an initial sharp decrease in the *E. coli* concentration was observed which then turned linear. This pseudo-first-order-decay like phenomenon was seen for MS2 inactivation by few other studies (Anders and Chrysikopoulos, 2006; Sim and Chrysikopoulos, 1996; Chrysikopoulos and Vogler, 2004). For the purposes of this study, a simplified approach was employed and only the linear portion of the plot was considered. Blausteina et al. (2013) reported the *E. coli* inactivation rates in various water sources including pristine and groundwater to be in the range of 0.063 – 0.725 d^{-1}. *E. coli* inactivation rate of 0.099 d^{-1} observed here was closer to the rate of 0.063 d^{-1} seen in pristine water. This was seen as reasonable since this experiment was conducted in highly treated water.

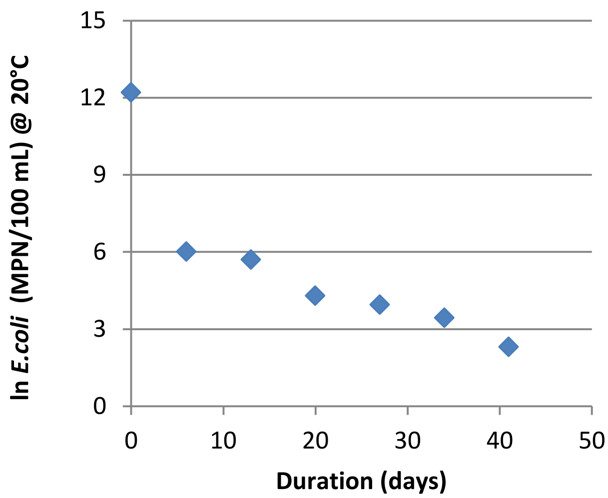


Figure 5: Semi-log plot of *E. coli* concentration over experimental time measured in a batch test conducted to determine biological inactivation rate of *E. coli* in aqueous phase

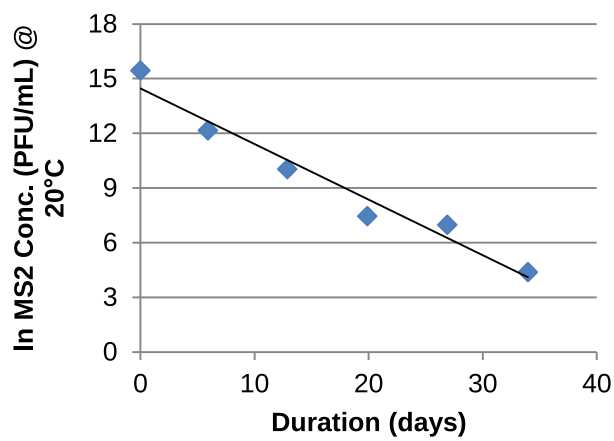


Figure 6: Semi-log plot of MS2 concentration over experimental time measured in a batch test conducted to determine biological inactivation rate of MS2 in aqueous phase

Table 10: Inactivation rates of MS2 and *E. coli* in aqueous phase determined at 20°C

Pathogen	k (d^{-1}) @ 20°C	C/C_o (Removal in %)	
		3 day column	30 day column
MS2	0.305	0.37 (63%)	0.0001 (99.99%)
E. coli	0.099	0.73 (27%)	0.051 (94.9%)

Accounting for solely biological inactivation in the aqueous phase and assuming that the decay rate stayed constant, there would be close to 100% pathogen attenuation in the columns with 30 days of retention time as indicated by the C/C_o values in Table 11. The columns with shorter retention time of 3 days would have less time to get inactivated and therefore a lesser fraction of the pathogen would have been inactivated in the aqueous phase in these columns.

3.3.3 Pathogen removal

The pathogen and pathogen indicator challenge tests demonstrated effective removals of MS2, *E. coli* and *Cryptosporidium* (microbeads) through the soil columns. The goal to demonstrate at least 1 log removal of virus for a month of travel time in the aquifer and to confirm removal of *Cryptosporidium* and *E. coli* at a similar scale in accordance with California regulations was met and exceeded by all four columns. Peak-concentration method of comparing the highest detected value in the effluent with the average spiked influent concentration was used for log removal determination in each case. This method has been used in a number of studies estimate log removal as pointed out by Pang (2009). Although the calculated removals using this method were reported to be usually higher than the ones calculated using mass recovery of pathogens, the use of peak concentration method for this study was considered reasonable since the pathogen levels in the effluent were mostly below detection. Close to complete removal of spiked MS2, *E. coli* and microbeads were seen in the 30-day columns. The removal data for the columns with 3 days of travel time also showed comparable reduction of the pathogens. It has to be noted that the influents to the 30 day columns were spiked to comparable concentration as the 3 day columns. Removal in higher orders of magnitude could be expected in the 30 day columns had the feed been spiked to a higher concentration. According to the soil column data, the 3 days of travel time was sufficient to meet the 1 log virus removal in the subsurface. However, it is also imperative to keep in mind that removals seen in lab scale soil column with controlled settings cannot necessarily be extrapolated to estimate removals in the field. Pang (2009) reported log-removals in columns to be one to three orders of magnitude higher than the ones for field studies. Nonetheless, high reductions in the range of 3 to 6-logs even in columns with short retention time displayed the effectiveness of SAT in pathogen removal.

Table 11: Log removals achieved in the 30 day and 3 day columns

	30 day (#1)	**30 day (#2)**	**3 day (#3)**	**3 day (#4)**
Travel time (days)	29.6	30.2	3.1	3.4
Log removals				
MS2	7	-	6	6
E. coli	-	6.5	6.6	-
Microbeads	-	4.8	3	3
Targeted	**at least 1 log removal per month of travel time**			

3.3.3.2 MS2

MS2 removal observed was about 6-log reduction in both the 3 day columns. It is not uncommon to observe an MS2 breakthrough earlier than the travel time in soil column studies (Syngouna and Chrysikopoulos, 2011) As expected, MS2 values in both 3-day columns were above the detection limit after a day of spike itself. 7-log reduction of MS2 was seen in the 30-day column with the potential to achieve higher removals if the concentration in the influent feed was higher. It was hard to decipher the occurrence of any breakthrough in the case of 30-day columns since there was only a single detect in the effluent. The dominant removal mechanisms for viruses such as MS2 are considered to be adsorption and inactivation (Anders and Chrysikopoulos, 2006; Gerba and Keswick, 1981; Sim and Chrysikopolous, 1999). The combination of both mechanisms along with the longer retention time in the 30 day columns resulted in very effective removal of the pathogen. MS2 is considered to be a good model virus because it is relatively more persistent and is attenuated to a lesser extent than other viruses

(Anders and Chrysikopoulos, 2009). So, good MS2 removal was considered an indicator of good removal of viruses, overall.

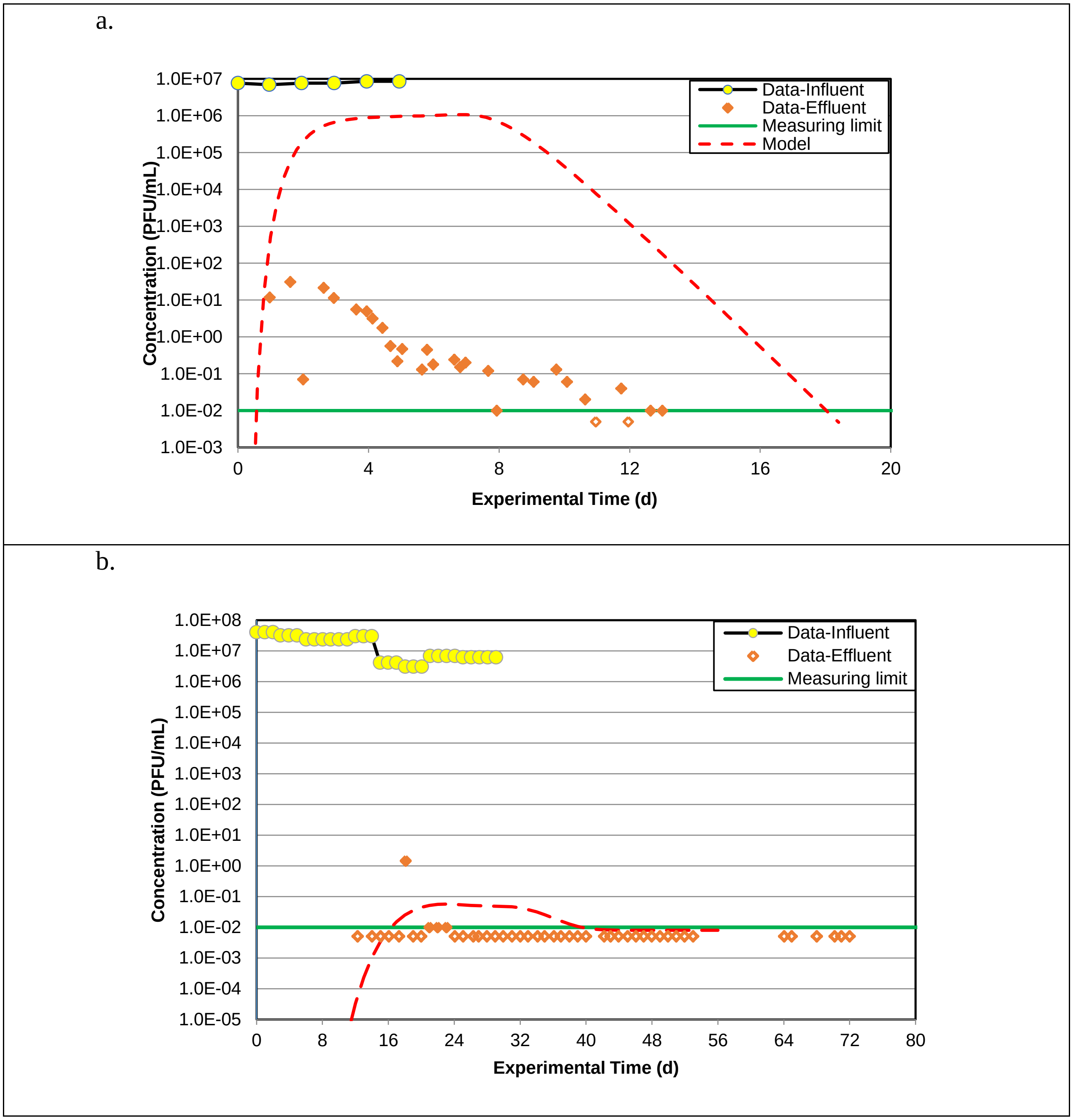
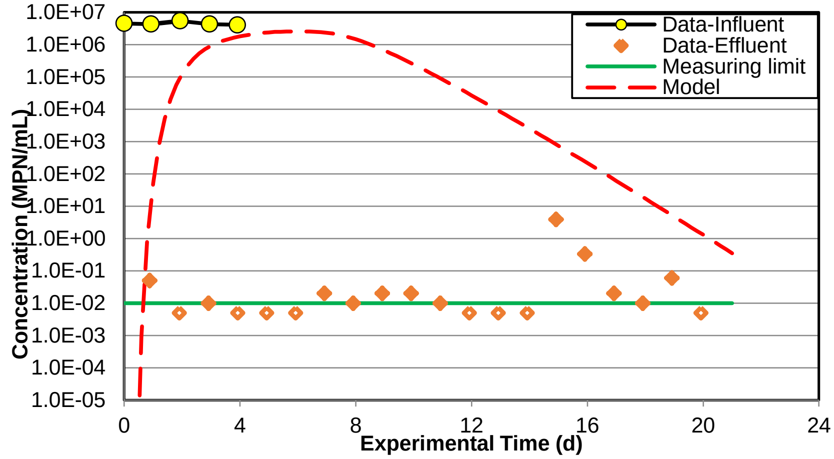


Figure 7: Breakthrough curve of observed and simulated MS2 concentration in (a) 3-day column #3 effluent after spiking influent feed for 5 consecutive days and (b) 30-day column #1 after spiking influent for 30 days. Data points with no fill indicate they were

3.3.3.3 *E. coli*

Similar to MS2, *E. coli* has been reported to travel faster than a tracer in some studies (Syngouna and Chrysikopoulos, 2011). Although the first sample collected from the 3-day column right after a day of the spike was above the detection limit, a clear breakthrough was not observed in the first two weeks of sampling. There were intermittent detects at low concentrations and non-detects. However, the peak value was detected on the 15th day of testing and the values tapered down to non-detect levels in the following 5 days. This occurred later than the expected retention time and detachment of *E. coli* from media that was not inactivated could be a possible explanation for this occurrence. Detachment and remobilization of pathogens like *Cryptosporidium* and *Clostridium* oocysts has been observed in a few soil column studies (Hijnen et al. 2005; Schijven et al. 2002) and similar phenomenon possibly occurred in the case of *E. coli.* Nonetheless, good removal in the 3-day columns was observed with close to 6-log reduction. Similar to the case of MS2, all effluent values were non-detects expect one in the 30 day column. About 7-log reduction was observed. The dominant removal mechanisms for bacteria were attributed to straining, adsorption and inactivation (Stevik et al. 2004).

a.



b.

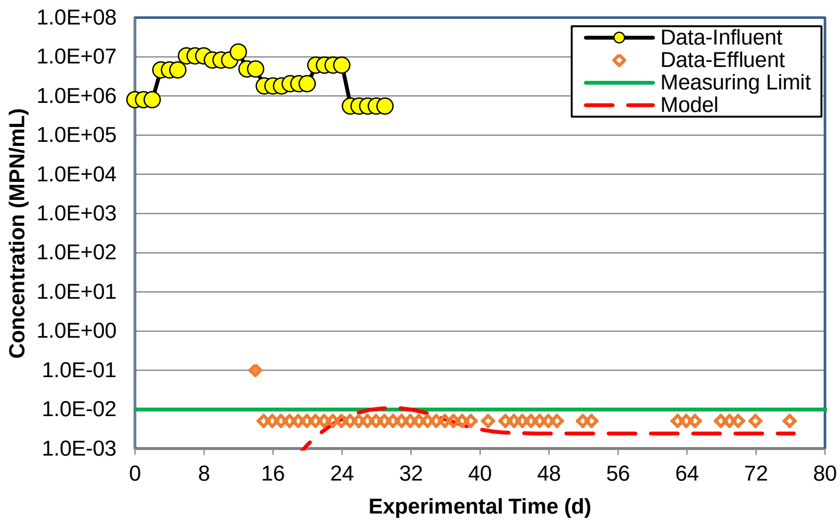


Figure 8: a. Breakthrough curve of observed and simulated E. coli concentration in (a) 3-day column #3 effluent after spiking influent feed for 5 consecutive days and (b) 30-day column #2 after spiking influent for 30 days. Data points with no fill indicate they were below the detection limit of 1 MPN/100 mL

3.3.3.4 Microbeads

Microbeads test on both the 3 day columns showed very similar trends. The first detect for both columns was observed on the second day after the spiked influent was fed and peak concentration occurred on the fifth day. All values after this peak were below the detection limit; an absence of a gradually declining limb was not of a typical breakthrough curve. Considering 3 µm microbeads were used in this study which is larger in size than 25 nm MS2 or 0.5 µm wide 2 µm long *E. coli*, straining was expected to play a greater role in its attenuation. However, the effects of straining did not seem to make its removal significantly better compared to MS2 or *E. coli* in the 3-day columns. There were no detects in the 30-day column effluent throughout the sampling duration. It has to be noted that the sampling period for microbeads was scheduled to be shorter than the other pathogen tests because of time and cost constraints. A longer sampling duration would have provided knowledge of occurrence of later breakthroughs due to detachment of the microbeads, though attachment would not be significant for microbeads removal. As aforementioned, microbeads were used as a surrogate of *Cryptosporidium* oocysts. The removal of these uncharged microbeads observed in these soil columns is a slightly conservative representation because straining is the primary removal mechanism. .The oocysts unlike the microbeads can have additional removal through inactivation as well.

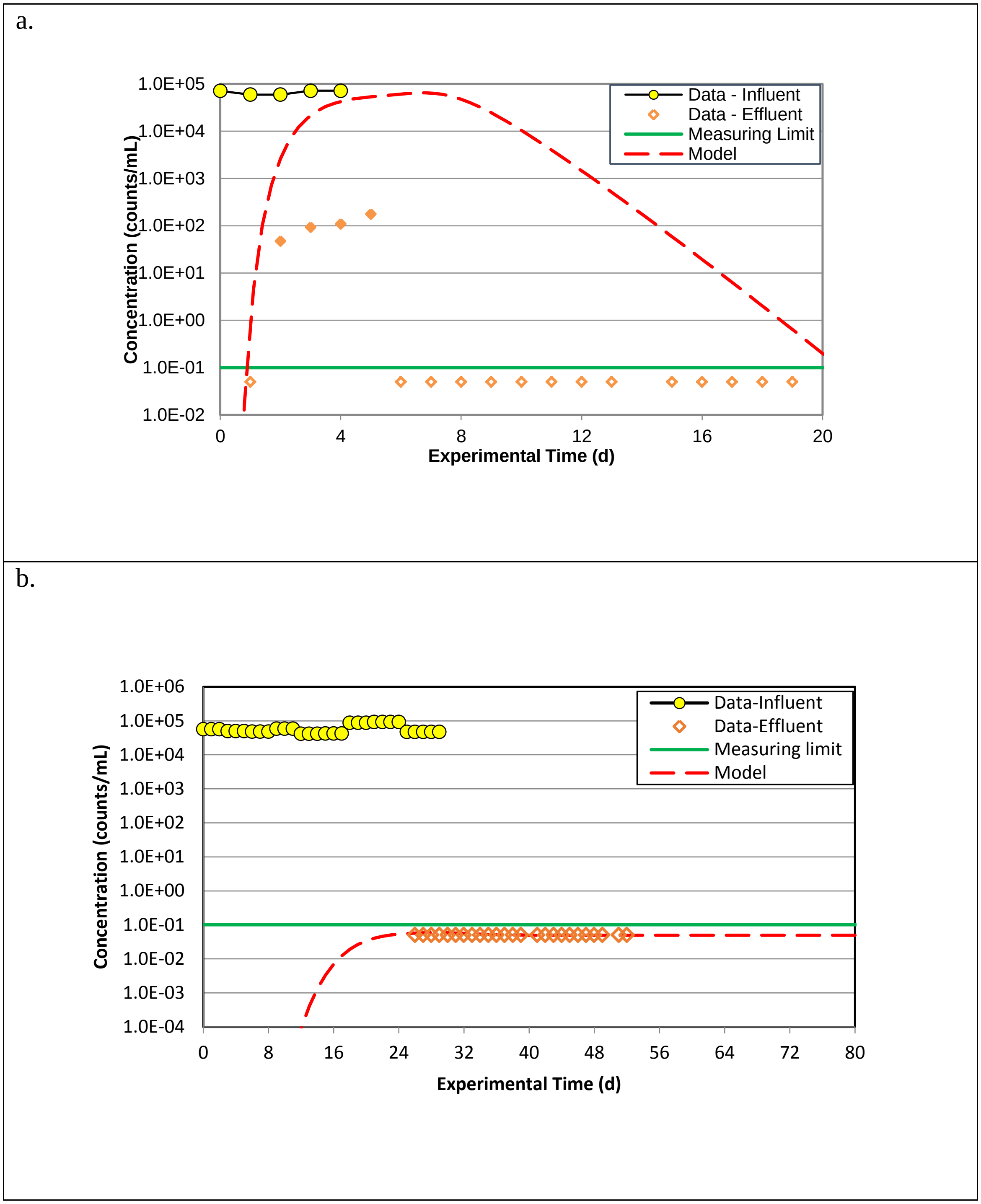


Figure 9: Breakthrough curve of observed and simulated microbeads concentration in (a) 3-day column #3 effluent after spiking influent feed for 5 consecutive days and (b) 30-day column #2 after spiking influent for 30 days. Data points with no fill indicate they were below the detection limit of 1 count/10 mL

3.3.3.1 Data analysis and modeling

Data analysis for removal of contaminants in soil column experiments has largely been conducted using some version of advection-dispersion. PHREEQC, CXTFIT and Hydrus-1D are available modeling software applicable for one dimensional flow characteristics (Gibert et al., 2015). CXTFIT uses the general advection-dispersion equation including sorption and first order removal. Hydrus-1D incorporates advection, dispersion inactivation in liquid and solid phases along with kinetic adsorption or desorption. (Frohnert et al. 2014). This study used advection dispersion model using analytical solution for reactive solutes to understand and determine removal rates for the pathogens. The values of retardation factor, inactivation rate in the aqueous phase and inactivation rate in the solid phase shown in Table 10 were used as inputs to the model.

Table 12: Retardation factors, inactivation rates for MS2, *E. coli* and microspheres

Pathogen	3 day columns			30 day columns		
	R	λ_a	λ_s	R	λ_a	λ_s
MS2	1.05, 0.85	0.305	0.15	ND	0.305	ND
E. coli	1.1	0.099	0.049	ND	0.099	ND
Microbeads	1.2, 1.5	0	0	ND	0	ND

- Most effluent samples for the 30 day columns were non-detects and thus R and λ_s were undeterminable through the model.

The decay rates in aqueous phase were experimentally determined as described in Section 3.3.2. For MS2 and *E. coli*, solid phase inactivation rates were considered as half the aqueous phase inactivation rate (Syngouna and Chrysikopoulos, 2011). Decay rates for microbeads were put in as zero since only physical removal was considered in this study. Retardation factors were the only inputs that were not pre-determined and were optimized to fit the data such that the predicted curve coincided with the first detected pathogen data point.

As can be seen in Figures 7 - 9, the model did not seem to fit the observed data very well. The difference between the values predicted by the model and the measured effluent values was more than three orders of magnitude for all the pathogen tests conducted in the 3 day columns. The model was ineffective in quantifying any removal rates in the 30 day columns because the majority of the effluent samples were below the method reporting limit. The predicted concentration were closer to the measured values when high decay rates, in the range of 7 to 9 d^{-1} were used as inputs to the model. These values were at least ten folds higher than the values reported in several studies and therefore considered improbable. Another significant consideration is also that changes in conditions such as pH, redox potential, and organic content affect inactivation and attachment of the microorganisms (Walshe et al. 2010, Klitzke et al. 2015). Models like the one used in this study assume constant removal rates for the entirety of the experiment for simplification. The predicted curve was also observed to overestimate the concentrations compared to the observed values after the peak concentration as seen in Figures 10 and 11. Schijven et al. (2002) discussed this failure of one site kinetic models in fitting the rising and declining limbs of the breakthrough curves. On the contrary, two-site kinetic model was discussed to effectively follow the observed values during breakthrough. Use of a two-site model with additional parameters of decay and sorption for a second kinetic site of pathogen attachment could potentially fit the observed data in this study.

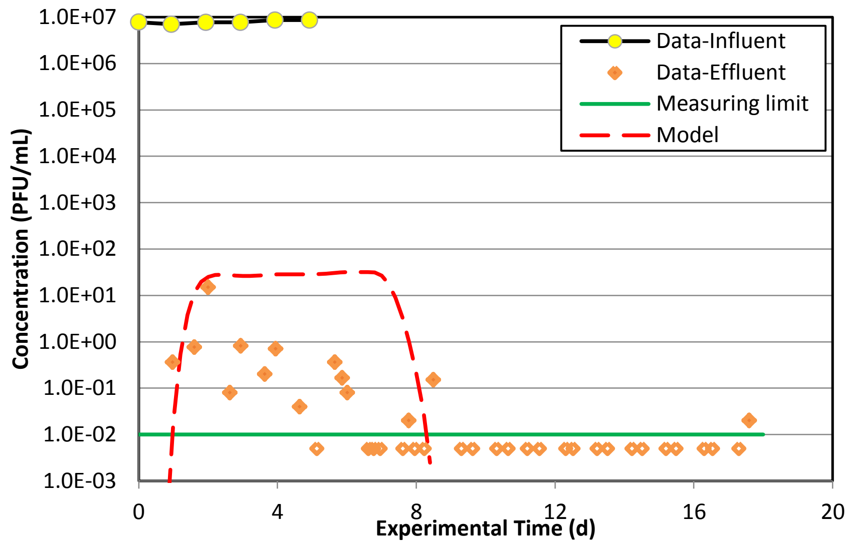


Figure 10: Breakthrough curve of observed and simulated concentration of MS2 in 3-day column #4 effluent using higher value (7 d^{-1}) for inactivation rate in solid phase

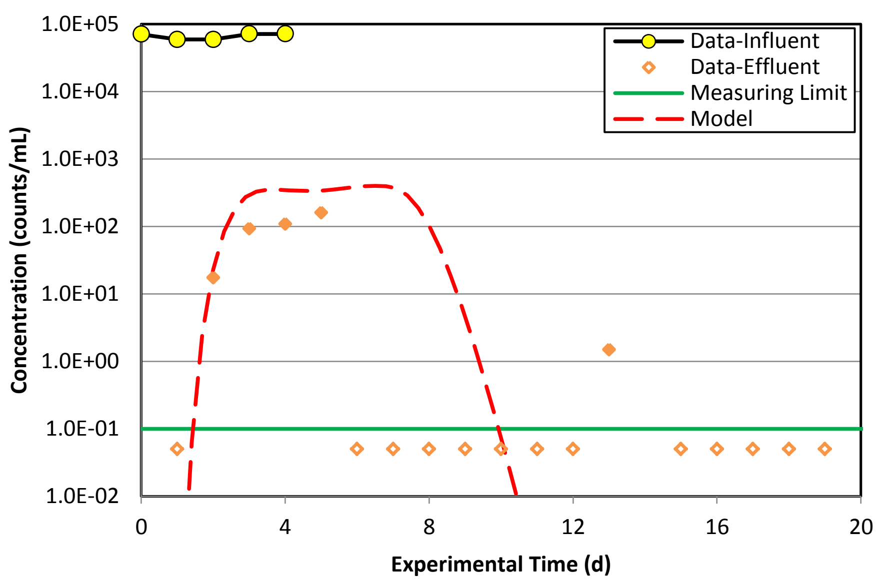


Figure 11: Breakthrough curve of observed and simulated concentration of microbeads in 3-day column #4 assuming inactivation in solid phase as 1.8 d^{-1} to better fit the data

The retardation factors of 0.85 and 1.05 estimated by the model were comparable to the range of 0.81 – 1.05 reported for MS2 by Syngouna and Chrysikopoulos (2011).The same paper also reported a range of 0.85-0.93 for *E. coli* retardation implying *E. coli* traveled faster relative to the solvent. However, a value of 1.1, estimated by this model, suggested it was slower compared to the fluid medium in this study. Microbeads had retardation values of 1.2 and 1.5 which were comparable to the observations of Harvey et al. (1993), in a study with microbial sized microsphere in the aquifer recharge sites with retardation values in the range of 1.5 – 1.7. Although the predicted values mostly agreed with values observed in published literature, one caveat to the retardation factor was that it only provided a numerical comparison between the velocity of compound and the velocity of fluid. In addition to retardation factors, incorporation of parameters such as attachment and detachment rates of each pathogen to the media in the modeling might enhance the understanding of the effectiveness and reversibility of pathogen retention (Fronhert et al. 2014).

No parameters were determined or estimated for pathogen removal in the 30-day columns. The model was ineffective because there was no observed breakthrough for any of the pathogens. Spiking the feed to these longer columns at higher orders of magnitude of pathogen concentration would have potentially resulted in detectable pathogen concentrations in the effluent. The increased time for inactivation and extended sites for sorption resulted in better removal in the 30-day compared to the 3-day columns. But it is hard to surmise whether the increase in retention time would have significant effects on retardation factors or on reactions that lead to pathogen inactivation.

3.4 Conclusion

The results of this experiment validate SAT as an effective barrier for pathogens including virus, bacteria and microorganisms such as *Cryptosporidium*, similar in size as the 3 µm microbeads. 6 to 7-log removals of MS2 and *E. coli* were achieved along with 3 to 5-log removals of microbeads. 3-day of travel time showed sufficient removal to meet the target of 1 log virus removal per month of aquifer travel time. Log reduction values were observed to be higher in the columns with longer retention time of 30 days and the potential to demonstrate higher log-reductions in these columns with higher levels of pathogen spike in the feed was acknowledged. The pathogen removal data provided defensible data to believe that facilities implementing indirect potable reuse can get additional disinfection credits through SAT. Further implications could be that the weight of disinfection can be slightly eased off of upstream treatment processes such as ozonation, UV disinfection, and chemical disinfection at a recharge facility. It is, however, imperative to keep in mind that the removals observed in the columns might not linearly scale up to removals observed at aquifer recharge sites in real time conditions with more variability. Soil column studies should be supplemented with regularly sampling and monitoring of pathogens in the field at recharge sites. Additionally, the limitation to the model using advection-dispersion equation and analytical solution for reactive solute, used in this study, in determining pathogen removal rates was realized. The model predicted values for pathogens were orders of magnitude higher than the observed data. Further research and study is required to grow the knowledge base regarding the pathogen attenuation mechanisms in varying conditions of pH, temperature, et al. that can prevail in the sub-surface. Incorporating all parameters for a comprehensive modeling and analysis would be ideal but may require several variable inputs.

Nevertheless, development of more robust predictive models may help address concern related to pathogen fate and transport in the subsurface during recharge.

3.5 References

Anders, R., & Chrysikopoulos, C. V. (2006). Evaluation of factors controlling the time-dependent inactivation rate coefficients of bacteriophage MS2 and PRD1. *Environmental sciencw & technology*, *40*(10), 3237-3242.

Anders, R., & Chrysikopoulos, C. V. (2009). Transport of viruses through saturated and unsaturated columns packed with sand. *Transport in Porous Media, 76(1),* 121-138.

Banzhaf, S., & Hebig, K. H. (2016). Use of column experiments to investigate the fate of organic micropollutants - A review. *Hydrology and Earth System Sciences*, *20*(9), 3719–3737. https://doi.org/10.5194/hess-20-3719-2016

Bitton, G., & Harvey, R. W. (1992). Transport of pathogens through soils and aquifers. *Environmental microbiology*, *19*, 103-123.

Blaustein, R. A., Pachepsky, Y., Hill, R. L., Shelton, D. R., & Whelan, G. (2013). Escherichia coli survival in waters: Temperature dependence. *Water Research*, *47*(2), 569–578. https://doi.org/10.1016/j.watres.2012.10.027

Bouwer, H., & Rice, R. C. (1948). Renovation of Wastewater at the 23rd Avenue Rapid Infiltration Project Renovation Avenue of wastewater rapid infiltration at the project. *Water Pollution Control Federation*, *56*(1), 76–83.

California Department of Health (CDPH) (2014). Retrieved from https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/documents/lawbook/RWregulations_20140618.pdf

Chrysikopoulos, C. V., & Aravantinou, A. F. (2012). Virus inactivation in the presence of quartz sand under static and dynamic batch conditions at different temperatures. *Journal of Hazardous Materials*, *233–234*, 148–157. https://doi.org/10.1016/j.jhazmat.2012.07.002

Chrysikopoulos, C. V., & Vogler, E. T. (2004). Estimation of time dependent virus inactivation rates by geostatistical and resampling techniques: application to virus transport in porous media. *Stochastic Environmental Research and Risk Assessment*, *18*(2), 67-78.

Domenico, P., and F. Schwartz. (1988). *Physical and Chemical Hydrogeology*. John Wiley and Sons, Inc., New York, NY.

Elkayam, R., Michail, M., Mienis, O., Kraitzer, T., Tal, N., & Lev, O. (2015). Soil aquifer treatment as disinfection unit. *Journal of Environmental Engineering*, *141*(12), 05015001.

Fand, R. M., & Thinakaran, R. (1990). The Influence of the Wall on Flow Through Pipes Packed With Spheres. *Journal of Fluids Engineering*, *112*(1), 84. https://doi.org/10.1115/1.2909373

Frohnert, A., Apelt, S., Klitzke, S., Chorus, I., Szewzyk, R., & Selinka, H. C. (2014). Transport and removal of viruses in saturated sand columns under oxic and anoxic conditions - Potential implications for groundwater protection. *International Journal of Hygiene and Environmental Health*. https://doi.org/10.1016/j.ijheh.2014.06.004

Gibert, O., Hernández Amphos, M., Vilanova, E., Cornellà, O., Wefer-Roehl, A., & Kübeck, C. (2012). *Guidelining protocol for soil-column experiments assessing fate and transport of trace organics Title: Guidelining protocol for soil-column experiments assessing fate and transport of trace organics.* Work Package: 12 Deliverable number: Partner responsible: CETaqua Deliverable author(s): Quality assurance. Retrieved from www.demeau-fp7.eu

Harvey, R. W., Kinner, N. E., MacDonald, D., Metge, D. W., & Bunn, A. (1993). Role of physical heterogeneity in the interpretation of small-scale laboratory and field observations of bacteria, microbial-sized microsphere, and bromide transport through aquifer sediments. *Water Resources Research*. https://doi.org/10.1029/93WR00963

Hebig, K. H., Nödler, K., Licha, T., & Scheytt, T. J. (2014). Impact of materials used in lab and field experiments on the recovery of organic micropollutants. *Science of the Total Environment*, *473–474*, 125–131. https://doi.org/10.1016/j.scitotenv.2013.12.004

Hijnen, W. A. M., Brouwer-Hanzens, A. J., Charles, K. J., & Medema, G. (2005). Erratum: Transport of MS2 phage, Escherichia coli, Clostridium perfringens, Cryptosporidium parvum, and Giardia intestinalis in a gravel and a sandy soil (Environmental Science and Technology (2005) 39 (7860-7868)). *Environmental Science and Technology*. https://doi.org/10.1021/es0580237

Idelovitch, E., & Michail, M. (1984). Soil-aquifer treatment: a new approach to an old method of wastewater reuse. *Journal (Water Pollution Control Federation)*, 936-943.

Klitzke, S., Schroeder, J., Selinka, H. C., Szewzyk, R., & Chorus, I. (2015). Attenuation and colloidal mobilization of bacteriophages in natural sediments under anoxic as compared to oxic conditions. *Science of the Total Environment*, *518–519*, 130–138. https://doi.org/10.1016/j.scitotenv.2015.02.031

Lewis, J., & Sjöstrom, J. (2010). Optimizing the experimental design of soil columns in saturated and unsaturated transport experiments. *Journal of Contaminant Hydrology*. https://doi.org/10.1016/j.jconhyd.2010.04.001

Mayotte, J. M., Hölting, L., & Bishop, K. (2017). Reduced removal of bacteriophage MS2 in during basin infiltration managed aquifer recharge as basin sand is exposed to infiltration water. *Hydrological Processes*, *31*(9), 1690–1701. https://doi.org/10.1002/hyp.11137

McCaulou, D. R., Bales, R. C., & Arnold, R. G. (1995). Effect of Temperature-Controlled Motility on Transport of Bacteria and Microspheres Through Saturated Sediment. *Water Resources Research*, *31*(2), 271–280. https://doi.org/10.1029/94WR02569

Murphy, E. M., & Ginn, T. R. (2000). Modeling microbial processes in porous media. *Hydrogeology Journal*, *8*(1), 142–158. https://doi.org/10.1007/s100409900043

Pang, L. (2009). Microbial Removal Rates in Subsurface Media Estimated From Published Studies of Field Experiments and Large Intact Soil Cores. *Journal of Environment Quality*, *38*(4), 1531. https://doi.org/10.2134/jeq2008.0379

Pang, L., Close, M., Goltz, M., Noonan, M., & Sinton, L. (2005). Filtration and transport of Bacillus subtilis spores and the F-RNA phage MS2 in a coarse alluvial gravel aquifer: Implications in the estimation of setback distances. *Journal of Contaminant Hydrology*, *77*(3), 165–194. https://doi.org/10.1016/j.jconhyd.2004.12.006

Peng, X., Murphy, T., & Holden, N. M. (2008). Evaluation of the effect of temperature on the die-off rate for Cryptosporidium parvum oocysts in water, soils, and feces. *Applied and Environmental Microbiology*. https://doi.org/10.1128/AEM.01442-08

Pham, M., Mintz, E. A., & Nguyen, T. H. (2009). Deposition kinetics of bacteriophage MS2 to natural organic matter: Role of divalent cations. *Journal of Colloid and Interface Science*, *338*(1), 1–9. https://doi.org/10.1016/j.jcis.2009.06.025

Runkel, R. L. (1996). Solution of the advection-dispersion equation: continuous load of finite duration. *Journal of Environmental Engineering*, *122*(9), 830-832.

Santamaría, J., Quinonez-Diaz, M. D. J., Lemond, L., Arnold, R. G., Quanrud, D., Gerba, C., & Brusseau, M. L. (2011). Transport of Cryptosporidium parvum oocysts in sandy soil: Impact of length scale. *Journal of Environmental Monitoring*, *13*(12), 3481–3484. https://doi.org/10.1039/c1em10390c

Sasidharan, S., Torkzaban, S., Bradford, S. A., Kookana, R., Page, D., & Cook, P. G. (2016). Transport and retention of bacteria and viruses in biochar-amended sand. *Science of the Total Environment*, *548–549*, 100–109. https://doi.org/10.1016/j.scitotenv.2015.12.126

Schijven, J. F., De Bruin, H. A. M., Hassanizadeh, S. M., & De Roda Husman, A. M. (2003). Bacteriophages and clostridium spores as indicator organisms for removal of pathogens by passage through saturated dune sand. *Water Research*, *37*(9), 2186–2194. https://doi.org/10.1016/S0043-1354(02)00627-9

Schijven, J. F., Hassanizadeh, S. M., & De Bruin, R. H. A. M. (2002). Two-site kinetic modeling of bacteriophages transport through columns of saturated dune sand. *Journal of Contaminant Hydrology*, *57*(3–4), 259–279. https://doi.org/10.1016/S0169-7722(01)00215-7

Schwartz, F. W. (1977). Macroscopic dispersion in porous media: The controlling factors. *Water Resources Research*, *13*(4), 743–752. https://doi.org/10.1029/WR013i004p00743

Sidhu, J. P. S., Toze, S., Hodgers, L., Barry, K., Page, D., Li, Y., & Dillon, P. (2015). Pathogen Decay during Managed Aquifer Recharge at Four Sites with Different Geochemical Characteristics and Recharge Water Sources. *Journal of Environment Quality*, *44*(5), 1402. https://doi.org/10.2134/jeq2015.03.0118

Sim, Y., & Chrysikopoulos, C. V. (1996). One-dimensional virus transport in porous media with time-dependent inactivation rate coefficients. *Water Resources Research, 32*(8), 2607-2611.

Sim, Y., & Chrysikopoulos, C. V. (2000). Virus transport in unsaturated porous media. *Water Resources Research, 36*(1), 173-179.

Stevik, T. K., Aa, K., Ausland, G., & Hanssen, J. F. (2004). Retention and removal of pathogenic bacteria in wastewater percolating through porous media: A review. *Water Research*. https://doi.org/10.1016/j.watres.2003.12.024

Syngouna, V. I., & Chrysikopoulos, C. V. (2011). Transport of biocolloids in water saturated columns packed with sand: Effect of grain size and pore water velocity. *Journal of Contaminant Hydrology*, *126*, 301–314. https://doi.org/10.1016/j.jconhyd.2011.09.007

Trussell, B., Trussell, S., Qu, Y., Gerringer, F., Stanczak, S., Venezia, T., … Trussell, R. (2018). A four-year simulation of soil aquifer treatment using columns filled with San Gabriel Valley sand. *Water Research*, *144*(626), 26–35. https://doi.org/10.1016/j.watres.2018.07.012

U.S. Environmental Protection Agency (EPA) (2017). *Potable Reuse Compendium*. Retrieved from https://www.epa.gov/sites/production/files/2018-01/documents/potablereusecompendium_3.pdf

Walshe, G. E., Pang, L., Flury, M., Close, M. E., & Flintoft, M. (2010). Effects of pH, ionic strength, dissolved organic matter, and flow rate on the co-transport of MS2 bacteriophages with kaolinite in gravel aquifer media. *Water Research*, *44*(4), 1255–1269. https://doi.org/10.1016/j.watres.2009.11.034

Yao, K. M., Habibian, M. T., & O’Melia, C. R. (1971). Water and Waste Water Filtration: Concepts and Applications. *Environmental Science and Technology*, *5*(11), 1105–1112. https://doi.org/10.1021/es60058a005

4. MANUSCRIPT 2: FATE AND TRANSPORT OF NITROGEN SPECIES, ORGANIC CARBON, DISINFECTION BY-PRODUCTS, AND EMERGING CONTAMINANTS IN A SOIL COLUMN EXPERIMENT

ABSTRACT

Managed Aquifer Recharge (MAR) is a method of indirect potable reuse which can provide additional environmental barriers to contaminants present in water through a process of natural attenuation termed as Soil Aquifer Treatment (SAT). Evaluation of SAT is critical in assessing MAR as a means to provide a sustainable source of drinking water. Soil column study is one of the ways to evaluate SAT at a meaningful scale. Experiments with soil columns were conducted at a pilot facility in Hampton Road Sanitation District (HRSD)'s York River Treatment Plant with the view to determine the effectiveness of MAR in the removal of different contaminants of concern. Four soil columns were constructed using sediment from the Potomac Aquifer System. The major objectives for the soil column study were the evaluation of the fate and transport of pathogens, nitrogen species, emerging pollutants and organic matter during SAT at two different travel times of 3.2 days and 30-days. The study also aimed to conduct a comparative analysis of the formation and subsequent removal of disinfection by products in the columns as a result of disinfection by free chlorine or monochloramine. Sampling and analysis of the influent and effluent for an experimental time of 4 months helped to develop an understanding of the different reactions taking place potentially causing attenuation of the contaminants of interest. Nitrogen transformation occurred in the columns with all nitrate completely reduced in the columns with 30 day of retention time indicating denitrification. However, an upward trend of ammonia in the monochloraminated column hinted at the

possibility of dissimilatory nitrate reduction to ammonia (DNRA). The influent bromate concentration ranged from 6 to 32 μg/L. Bromate was completely reduced in the 30-day columns; good removal was seen in the 3-day column effluents as well with only 3 sample points measured above the method reporting limit. TOC removal occurred in all four columns and observed removal was in the range of 25-35%. Among the analyzed contaminants of emerging concern, sucralose, 1,4-dioxane, acesulfame-K, iohexol, tris-(2 chloroisopropyl) phosphate (TCPP), sulfadiazine and 4-nonylphenol were detected at levels greater than 100 ng/L at least once in the column influent or effluent. Acesulfame-K and iohexal were consistently detected at levels greater than 1000 ng/L in the feed and were partially removed at 58 – 89% and 68 – 86% respectively. Partial removal of 1,4-dioxane was apparent in the 30-day columns. No conclusive removal trends were apparent for TCPP, 4-nonylphenol and sucralose. Compounds like carbamazepine and primidone, reported to be persistent in previous MAR studies were either not detected or detected at very low levels primarily due to removal by the upstream treatment processes of ozonation and biofiltration.

4.1 Introduction

Indirect potable reuse is a sustainable solution to the problem of increasing water demands of the present and more so the future. Water treatment processes including reverse osmosis, ultraviolet advanced oxidation processes (UV/AOP) have been adopted in conjunction with indirect potable water reuse applications often in combination. Managed aquifer recharge (MAR) is a method of indirect potable reuse in which water from various sources including reclaimed water is used for groundwater replenishment. Aquifer recharge provides a way of natural storage and an additional environmental barrier for some contaminants that persist in the water after undergoing advanced treatment. Natural attenuation of organics, contaminants and pathogens as water percolates through aquifer material during MAR is termed Soil Aquifer Treatment (SAT). (Bouwer and Rice, 1984; Idelovitch and Michail, 1984; Trussell et al. 2018)

As MAR is gaining more attention, increasing number of studies have evaluated the effectiveness of SAT in potable reuse applications. The scale ranges from lab scale soil column experiments to field studies at aquifer recharge sites. These studies primarily focus on figuring out the fate and transport of various pollutants during MAR process; determination of the reactions that occur in the aquifer and mechanisms that contribute to attenuation of these pollutants; and understanding the conditions in which the attenuation takes place. Trussell et al. (2018) investigated removal of organic carbon and emerging contaminants in four soil columns with different retention times ranging from 5 to 180 days and observed removal of N-nitrosodimethylamine (NDMA) and organic matter in all columns. Similarly, Patterson et al. (2009) also looked at nine emerging contaminants through soil columns at a comparable scale and modeled their breakthroughs. .On the other hand, Scheurer et al. (2009), Drewes et al. (2002) conducted field studies to look at pharmaceuticals and trace organics removal through SAT.

Wang et al. (2018) looked at bromate reduction in lab scale column and found that it was reduced in nitrate reducing conditions. Organic matter removal and transformation has been studied with soil columns by Zhao et al. (2007) and in the field by Quanrud (2002). Several others have focused on the role of specific conditions like the composition of organic substrate in the attenuation of trace organics (Alidina et al. 2014) and the temperature and redox on organics and nutrients removal (Abel et al. 2012). The compounds investigated are usually contaminants of interest, regulated or unregulated, due to their potential harmful effects to human health.

Nitrogen species including ammonia, nitrite, nitrate and Total Kjeldahl Nitrogen (TKN) contribute to the nutrient loading to water sources. Furthermore, National Primary Drinking Water Regulations imposes MCL of 10 mg-N/L for nitrate and 1 mg-N/L for nitrite in drinking water. Elevated nitrate is known to cause methemoglobinemia, also commonly called blue baby syndrome in infants (Bouchard et al. 1992). Nitrite can also cause damage to cells and may be carcinogenic at high concentrations. Most utilities monitor and regulate their Total Nitrogen (TN) level which encompasses regulation of all the nitrogen species. The transformation of nitrogen species at MAR sites has been an area of interest for a few studies (Miller et al. 2006). The vertical gradient of temperature, dissolved oxygen concentration, and substrate availability in the aquifer provides a spectrum of conditions conducive for both oxidizing and reducing microorganisms at different depths (Misra et al. 1974).

Organic matter in reuse systems can be characterized as natural organic matter (NOM) already present in drinking water, synthetic organic compounds and soluble microbial products (Drewes et al. 1999). Total organic carbon (TOC) and dissolved organic carbon (DOC) are used as parameters to measure organics in water. Investigation of organics removal by SAT of wastewater effluent has shown removal of TOC ranging from 50 to 90% (Quanrud et al. 2003, Amy et al. 1993, and Wilson et al. 1995). The concern related to TOC concentration is that organic matter can be precursors for disinfection byproducts. Additionally, the California regulations for surface spreading has a stringent requirement that TOC of wastewater origin does not exceed 0.5 mg/L in potable reuse applications (Trussell et al. 2018).

Recharge water is typically chemically disinfected with chlorine or possibly monochloramine to avoid biofouling in recharge wells and to potentially achieve additional disinfection. Organics present in the water react with disinfectants which lead to formation of disinfection by products which are potential risks to human health. Total trihalomethanes (TTHM) and haloacetic acids (HAA5) are disinfection by products that suspected to be carcinogenic and are regulated at MCLs of 80 μg/L and 60 μg/L, respectively. While they can be formed in the recharge water, DBPs have also been observed to be bio-transformed during aquifer recharge (Thomas et al. 2000). HAAs are more readily degraded in the aerobic zones while anaerobic conditions favor THM degradation which is a relatively slower process. (Quanrud et al. 2016)

Bromate is also considered carcinogenic and is a disinfection by product of ozonation. Bromide in the water is quickly oxidized to bromate in the presence of ozone. Ozonation has been commonly used in conjunction with biofiltration in the upstream treatment process of aquifer recharge in order to provide benefits of disinfection and assimilable organic carbon (AOC) formation and subsequent removal in the biologically active filters (van der Kooij et al. 1989). Bromate levels exceeding its 10 μg/L MCL can be formed and is not easily removed through adsorption or aerobic biodegradation in the biofilters. Wang et al. (2018a) reported effective removal of bromate by denitrifying bacteria in anoxic conditions in a lab scale study of MAR. Furthermore, bromate was also observed to be reduced (abiotic reduction) by ferrous iron

(+II) in MAR systems (Wang et al. 2018b). Chairez et al. (2010) reported bromate reduction by biogenic sulfide in batch bioassays which implies it can potentially be removed by sulfide present in the aquifer.

These natural and synthetic compounds can be categorized into pharmaceutical and personal care products, pesticides, herbicides, flame retardants, hormones, food additives, and surfactants. Not all CECs are easily biodegraded and remain persistent in the water systems. They have already been detected at very low levels in various water sources. MCLs for emerging contaminants do not exist although they are classified into candidate contaminant lists (CCL) and reviewed for regulatory requirements as more information is gathered about their impact. There are also advisory limits enforced by states like California for a few of these compounds, including NDMA and 1,4-dioxane. Several studies have focused on CECs and their possible attenuation in the subsurface. Banzhaf et al. (2012) studied sorption and biodegradation of carbamazepine, sulfamethoxazole and diclofenac. Strauss et al. (2011) and Fan et al. (2011) observed removal mechanisms for sulfamethoxazole and its metabolites. Other CECs investigated in soil column experiments are bisphenol-A, 17 β-estradiol, 17 α –ethynyl estradiol (Patterson et al, 2010), primidone, atenolol, meprobamate (Burke, et al., 2013), perfluoroalkyl acids (PFAAs) (McKenzie et al., 2016). Given increasing degradation of compounds as retention time increases, SAT presents a promising prospect to degrade the emerging pollutants in the environment since groundwater flow is relatively slow and retention time in aquifers is typically measured in months to years or even decades.

Soil columns enable the evaluation of SAT at a manageable scale which then provides a basis for implementation on a full scale. This column study was the first phase of Hampton Road Sanitation District (HRSD) Sustainable Water Initiative for Tomorrow (SWIFT) project for replenishment of the Potomac Aquifer System (PAS). Soil columns were assembled at the HRSD York River Treatment Plant pilot facility to simulate two different travel times in duplicate. Free chlorine and monochloramine were used to disinfect the feed water for comparison of DBP formation and removal across the columns. The experiments focused on evaluating the fate and transport of different solutes including nitrogen species, organic matter, disinfection by products and emerging pollutants in the soil columns with the view to determine the effectiveness of SAT in indirect potable reuse application. Although there have been several soil column experiments conducted to meet similar objectives, there are few that have been conducted at a scale comparable to this study. This study also assesses the extent of additional removal of aforementioned solutes that can be achieved through SAT after an advanced treatment process train of flocculation-sedimentation, ozonation, bio-filtration, adsorption in granular activated carbon and UV disinfection.

4.2 Materials and Methods

4.2.1 Column Design

The experimental set up consisted of four soil columns with the purpose of simulating two travel times relevant to the SWIFT project. Two columns were constructed to represent the estimated travel time required for recharge water to reach a monitoring well located at a radial distance of 15 m (50 ft.) from a 1.0 MGD recharge well at the SWIFT demonstration facility. The soil columns were designed to simulate a travel time of 3.2 days; henceforth referred to as 3-day columns. The goal was to optimize column dimensions and the feed flow rate for soil column operation by considering aspects such as minimum ratio of column height to diameter; volume of feed required per day and volume required for sampling. Using an estimated effective porosity of 0.35 and a design influent flow rate of 13 mL/min, the column diameter of 0.305 m (1 ft.) and media height of 2.3 m (7.5 ft.) were selected for the 3-day columns. Column height to diameter ratio was selected based on design considerations recommended to avoid preferential pathways and radial dispersion (Gibert et al., 2014). The 3-day columns were 2.4 m (8.0 ft.) in height and filled with aquifer sediment, primarily sand, to 2.3 m.

Two additional columns were constructed to represent 30-days travel time (henceforth referred to as 30-day columns). The diameter of the 30-day columns was also 0.305 m (1 ft.). The 30-day columns were 4.0 m (13 ft.) in height and filled with aquifer sediment to 3.7 m (12 ft.). The column properties for all four columns have been summarized in Table 13.

Table 13: Column dimensions and flow rate

Column ID	Travel Time (days)	Flow rate (mL/min)	Total height (m)	Depth of sand (m)	Diameter (m)
1 (30-day)	30	2.2	4.0	3.7	0.305
2 (30-day)					
3 (3-day)	3.2	13	2.4	2.3	0.305
4 (3-day)					

The columns were filled with aquifer sediment extracted from permeable material derived from the PAS. Sediment samples were washed thoroughly in a cement mixer and then sieved through a 4 mm screen to remove clay and larger debris. The washed and sieved sand was sent to ECS Mid-Atlantic, LLC (Williamsburg, VA) to conduct sieve analysis on three sets of sand samples. The uniformity coefficient calculated from the grain size distribution data was approximately 5 for all three samples. The sieve analysis data has been included in the Appendix (Figure 28). The columns were gradually filled with washed sediment followed by SWIFT finished water to saturate the sand. The columns had a layer of underdrain plate which were full beaded IMS caps made by Xylem Inc. (NY, USA). Plates were attached to the bottom of columns to ensure uniform distribution of water across the diameter and to provide a physical blocking system to avoid possible loss of sand. Masterflex ® L/S ® digital peristaltic pumps were used to have a pressurized up-flow in the columns. The type of tubing used for the experiment was polytetrafluoroethylene (PTFE) semi-clear tubing (6.35 mm OD, 3.175 mm ID) by Teflon ®; for the peristaltic pumps Masterflex ® L/S ® Tygon tubing EW-06509-14 and Masterflex ® L/S ® Tygon tubing EW-06509-13 were used for 3-day and 30-day columns respectively. All the columns were covered with 6 mil black polyethylene plastic wrap to avoid photolytic reactions due to light penetration.

The soil column experiments were essentially conducted in two phases. The first phase consisted of tracer tests to determine the columns' properties and pathogen challenge tests to evaluate pathogen removal. The experimental method followed has been described in detail in Manuscript I. The effective porosity, dispersivity and the travel times determined in the first phase of the study have been tabulated in Table 12.

Table 14: Dispersivity, effective porosity values and travel time of the soil columns estimated by the model

	30-day (#1)	**30-day (#2)**	**3-day (#3)**	**3-day (#4)**
Dispersivity (ft.)	0.41	0.27	0.42	0.15
Eff. Porosity	0.35	0.35	0.35	0.38
Travel time (days)	29.6	30.2	3.1	3.4

The SWIFT finished water provided influent to the columns. SWIFT finished water undergoes several treatment processes including flocculation/sedimentation, ozonation, biofiltration, and UV- disinfection. The influent going into the SWIFT Pilot was the denitrified effluent from HRSD York River Treatment Plant. The flocculation/sedimentation process removed about 20% of the TOC. The following process of ozonation was aimed at converting the remaining TOC to more assimilable organic carbon (AOC). Bromate, a regulated carcinogen is a by-product of ozonation that was formed in the process. The biomass established in the BAC degraded a portion of the AOC. Granular Activated Carbon (GAC) then provided adsorption sites for some of the organic carbon and other contaminants. The bed volume and the empty bed contact time of the BAC and GAC have been listed in Table13. The removal of a few Trace Organic Contaminants (TrOC) was observed across the BAC and GAC columns. This is an important implication for the composition of the influent that was feeding the columns, which was a highly treated effluent with mostly recalcitrant contaminants.

Table 15: Properties of the BAC and GAC

	Media Depth (ft)	EBCT (min)	Bed Volume (ft3)
BAC	5	10	0.98
GAC	6	20	1.18

4.2.2 Experimental Set-up

All four columns used in the previous study were used for the second phase of study. The objectives of the second phase were to evaluate the removal of other compounds such as CECs, nitrogen species and organic carbon and to compare two disinfectants: free chlorine and monochloramine with regards to DBP formation and their removal in the columns. After the completion of the pathogen challenge tests, the column set up was slightly changed to introduce chemical disinfection to the process. Each disinfectant was mixed into the continuous feed of one short and one long column with 3.2 days and 30-days travel time respectively.

For the influent, two 76-L (20-gallon) containers were filled every day with SWIFT finished water. High precision peristaltic pumps were used to pump the influent out of each container at a rate of 50 mL/min. Since the influent containers were kept refrigerated, electric heat tracing was used to keep water temperature constant at 20°C right before the introduction of disinfectant to the feed line. Free chlorine and monochloramine were the two types of disinfectant used for comparison in this study. The disinfectant stocks were prepared in amber bottles to delay the rate of photolytic decay. Free chlorine stock was made by diluting sodium hypochlorite with deionized water. Monochloramine was prepared by mixing sodium hypochlorite and ammonium sulfate in water treated by reverse osmosis. The doses of hypochlorite and ammonium sulfate were adjusted to obtain about 3.5 parts of total chlorine to 1 part of total ammonia. This preformed mono-chloramine was batched and diluted to prepare the mono-chloramine stock for the soil columns.

Table 16: Disinfectant concentration and volume

	Concentration (mg/L)	**Volume (L)**
Chlorine/Monochloramine	110	3

The free chlorine and mono-chloramine were pumped into the influent line with the help of peristaltic pumps (Figure 13). The targeted residual at the point of column feed was 1 mg/L for both disinfectants. The total contact time was six minutes which represented the time required for recharge water to reach the aquifer from the point of disinfection at the SWIFT demonstration facility. The influent was split into three sections: one line fed a 3-day column, one fed a 30-day column and the remaining one was used as an influent sampling line. The lengths of the tubing for each section were determined so as to provide the six minute contact time after the point of disinfectant mixing. The sampling line went into a collapsible container which was placed inside a refrigerator for preservation. This set-up allowed for sampling of influent without disrupting flow into the columns.

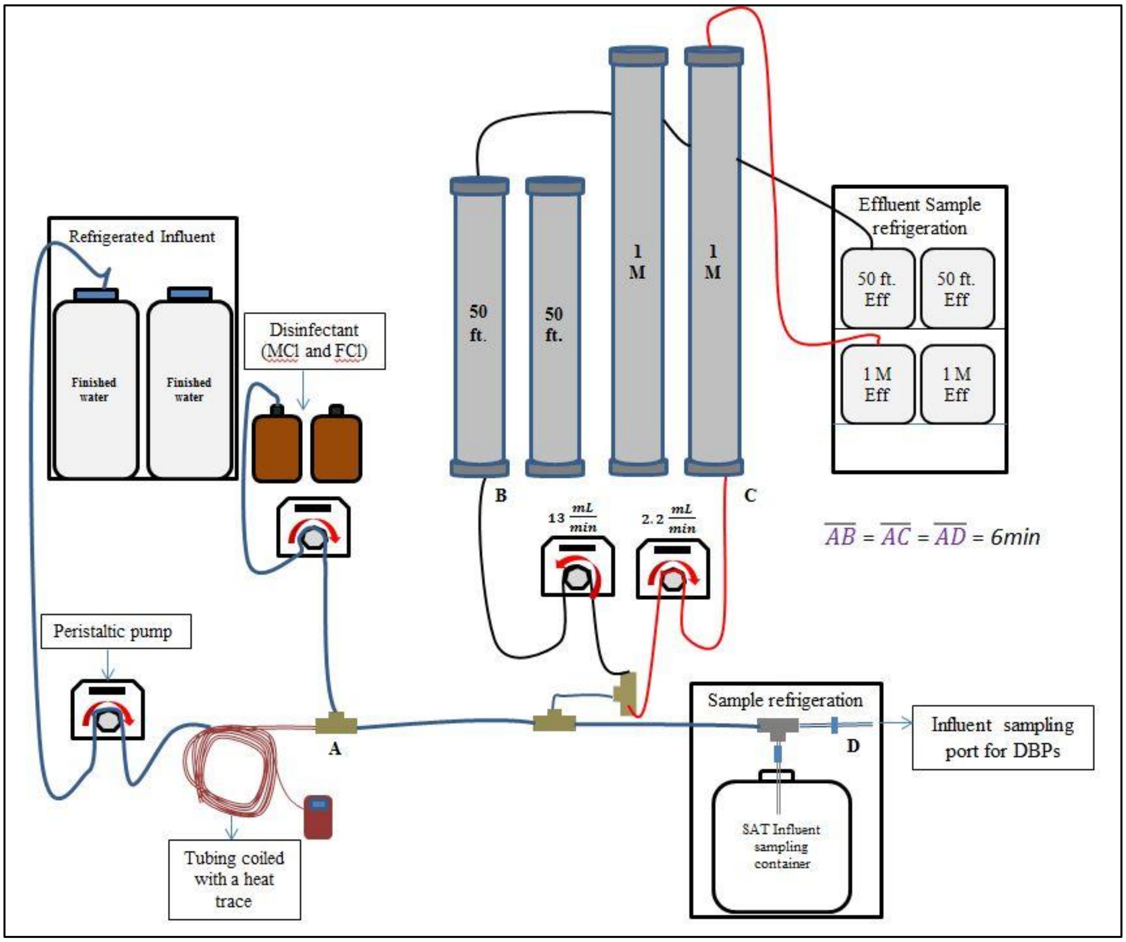


Figure 12: Soil Column set up for the second experimental phase with disinfected influent

4.2.3 Sampling and analysis

The influent and effluent were sampled for nitrogen species: ammonia, nitrate, nitrite, and Total Kjeldahl Nitrogen (TKN); phosphorus: total phosphorus and orthophosphate; organic carbon: Total organic carbon (TOC) and dissolved organic carbon (DOC); bromate; total trihalomethanes (TTHMs); and haloacetic acids (HAA5). Samples were analyzed by HRSD's

CEL lab. The analysis methods and sampling frequency have been listed in Table 15. For the 3-day columns, the influent and the effluent samples were scheduled to be taken approximately a travel time apart so that they could be compared.

Table 17: Analysis methods and sampling frequency for samples sent to CEL

Parameter	Analysis Method	Sampling Frequency		
		Inf. (Cl/MCl)	Eff (3-day)	Eff (30-day)
Ammonia/NO_x	EPA 350.1 as Lachat 10-107-06-1-C	3x/week for 3 months	3x/week for 3 months	1x/week for 4 months
NO_2	EPA 353.2 as Lachat 10-107-04-1-C			
NO_3	Calculated			
TKN	EPA 351.2 as Lachat 10-107-06-2-I			
Orthophosphate	EPA 365.1 as Lachat 10-115-01-1-A			
Total Phosphorus	EPA 365.1 as Lachat 10-115-01-1-F			
DOC	SM 5310 B-2011			
TOC	SM 5310 B-2011			
TTHM	EPA 624			
HAA5	EPA 552.2			

Influent and effluent samples were also taken for contaminants of emerging concern (CECs). Samples were sent to Eurofins Eaton Analytical in California for analysis. The compounds tested included flame retardants, hormones, pharmaceutical compounds, pesticides among others. The compounds analyzed, the frequency of sampling and the analysis method used have been listed in Table 16. There were 6 sampling events for the monochloraminated and the chlorinated influent. The 3-day effluents were also sampled 6 times while the 30-day effluents were sampled 5 times; these samples were co-ordinated to be taken 3-days and 30-days after the influent sampling events when possible.

Table 18: Analysis methods and sampling frequency for CECs

Compounds	Analysis method	Frequency		
		Inf (Cl/MCl)	Eff (3-day)	Eff (30-day)
NDMA	EPA Method 521	2x/month for 3 months	2x/month for 3 months	1x/month
1,4 – Dioxane	EPA Method 522			
Hormones (Natural/synthetic)[a]	EPA Method 529			
Perfluorinated compounds[b]	EPA Method 537			
Perchlorate	EPA Method 331			
Additional CECs[c]	Solid Phase Extraction (SPE) negative and positive mode			

a,b – A detailed list of the compounds has been included in the Appendix

c – Additional CECs is a broad category that has pharmaceuticals, personal care products, herbicides, pesticides, flame retardants and surfactants. A detailed list of the compounds analyzed is included in the Appendix

The influent to the columns was also analyzed to verify the residual of the disinfectant in the water. This check for chlorine and mono-chloramine was conducted in the SWIFT Pilot lab with the help of HACH Portable Parallel Analyzers (PPA). The range of acceptable chlorine or monochloramine residual was considered to be 1.0 ± 0.5 mg/L. Additional parameters that were analyzed included turbidity, pH and UV transmittance. HACH TL2300 Turbidimeter was used for turbidity analysis. pH was measured using Thermo Scientific's pH Benchtop meter and probe. Thermo Scientific Genesys 10S UV-Vis Spectrophotometer was used for measuring UV transmittance/absorbance;

Dissolved oxygen (DO) concentration of the influent water was measured once per day using HACH's hand held DO probe and HQ40D multi-meter. The effluent DO concentration of the four columns were continuously measured by the DO probes on top of the columns and logged onto the PLC.

4.3 Results and Discussion

4.3.1 TOC and DOC

The average TOC in the feed water was 4 mg/L. DOC comprised of a major fraction (~98%) of this TOC. The TOC in the feed water was expected to be recalcitrant as the water had undergone processes of floc-sedimentation, ozonation and biofiltration where a large fraction of the readily biodegradable carbon would be expected to be removed. An average of 35% TOC removal was observed across both 3-day columns. Contrary to expectation, higher removal was not achieved with a longer retention time in the 30-day columns, with removal at 25%. Since the longer 30-day columns have more adsorption sites compared to the 3-day columns, less removal through the 30-day columns implied that adsorption was not the dominant mechanism for TOC removal. The 30-day columns were not sampled as frequently as the 3-day columns and the lesser data points could have skewed the calculated values of percent removal. Nevertheless, the 30-day effluent TOC concentrations were comparable to the 3-day column effluents, on average approximately 0.5 mg/L higher. Additionally, it was observed that a biofilm would quickly grow on the inner walls of the 30-day effluent tubing possibly due to the effluent water flowing at a slow rate through the long tubing. Although the tubing was changed as soon as growth was observed, it is likely that on few occasions fouling from the tubing with biological growth could have acted as a source of additional TOC.

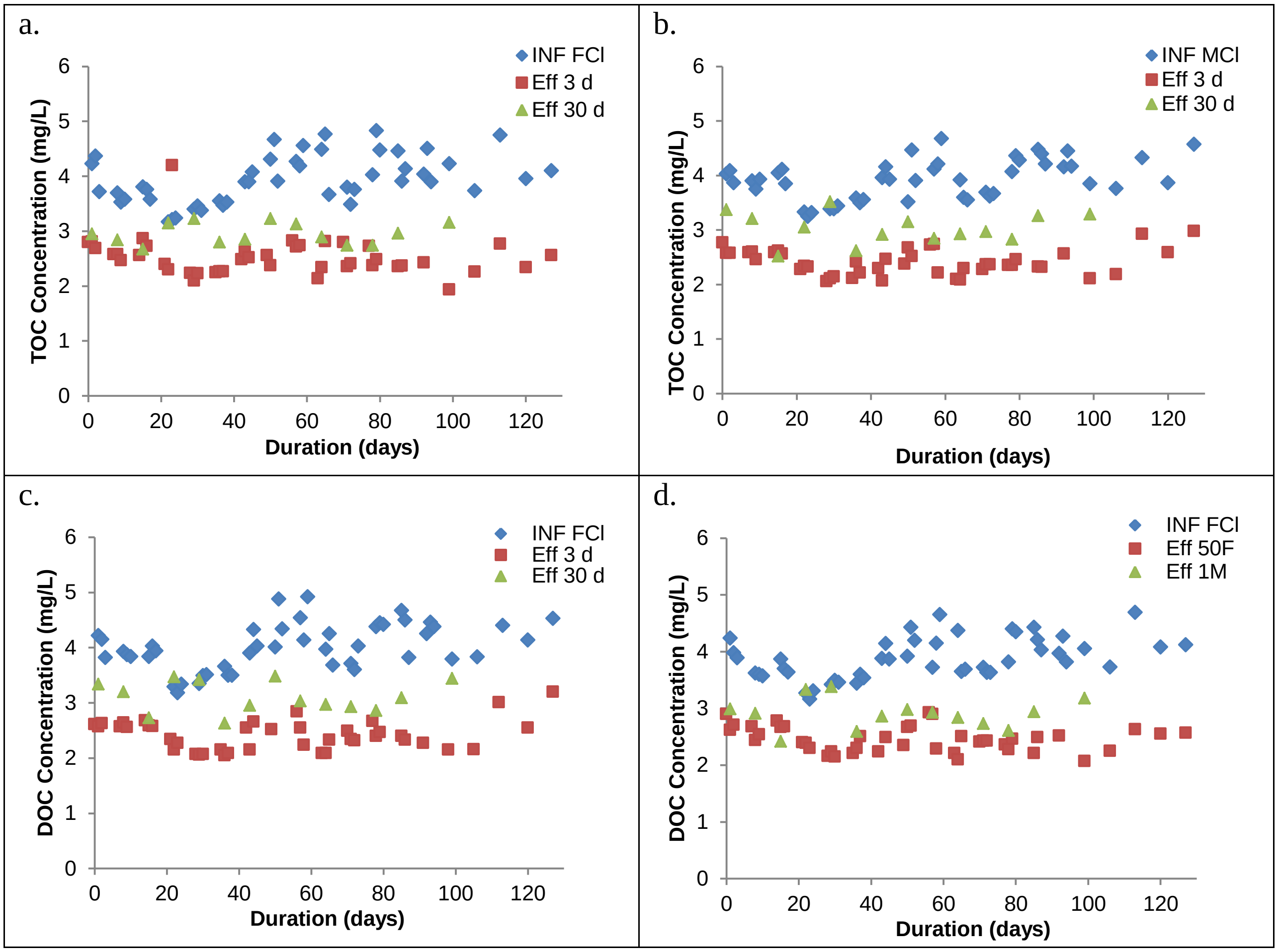


Figure 13: TOC values of column influent and effluents for 3-day and 30-day free-chlorinated columns (a, c) and mono-chloraminated columns (b, d) and DOC plots for chlorinated columns; (second row) TOC and DOC plots for mono-chloraminated columns

4.3.2 Dissolved Oxygen

The transport and attenuation of solutes and contaminants in the soil columns were significantly affected by redox conditions in the columns. The average DO concentration going into the columns was 15 mg/L as O_2. All of the oxygen was consumed at the end of all four columns. An average of 15 mg/L was present in the column feed throughout the experiment; oxygen levels at the end of all four columns reached zero. Nitrate was still present in the 3-day column effluent while it was completely reduced at the end of the 30-day columns. So, stratified zones with oxic and anoxic conditions appear to have existed across the length of the 3-day columns; and oxic, anoxic and anaerobic conditions appear to have existed across the length of the 30-day columns.

a.

b.

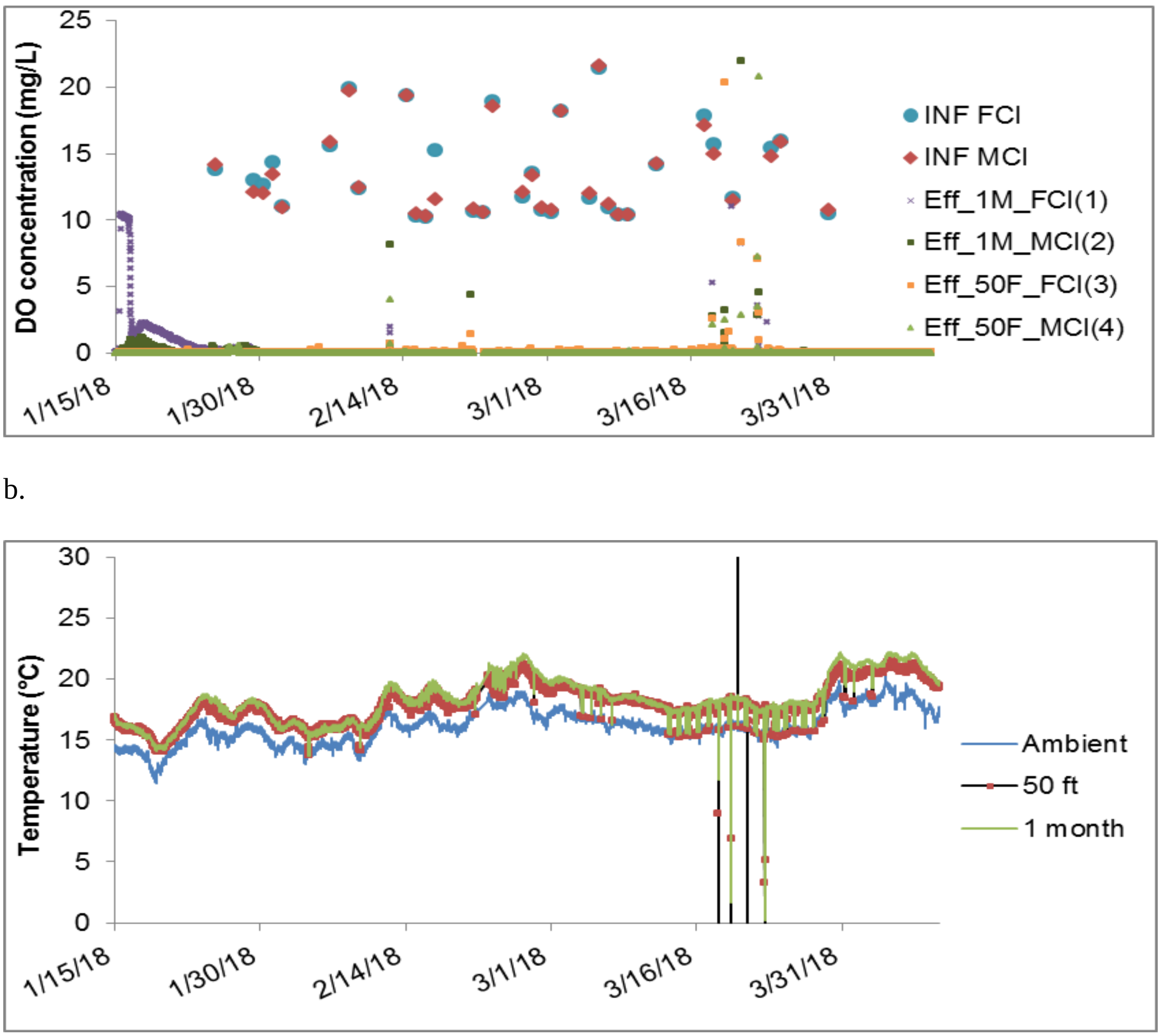


Figure 14: a. Discrete measurements of dissolved oxygen concentration in the column influent (frequency 1x/day) and continuous measurements of column effluents during the experimental run time. b. Continuous measurements of ambient temperature and temperature values of the 3-day and 30-day columns.

The events of high DO in the effluent, as seen in Figure 15 a, occurred in the initial experimental stage when the set-up had to be changed in order to start disinfecting the column feed as described in Section 4.2.2. No water was moving through the columns during this time. Additionally, a few data points above zero at the tail end of the experiment corresponds with the period of fluctuating temperature measurements which pointed to an instrumentation error in the probes.

4.3.2 Nitrogen Species and Bromate

The nitrogen species that were analyzed in the column influent and effluent were nitrite, NOx, ammonia and TKN. The majority of the fraction of NOx in the influent was comprised of nitrate; nitrite concentration was conssitenly under the measuring range of 0.01 mg/L (see Figure 15 b, c). The nitrite concentration before the mixing of chlorine or monochloramine was negligible since the biofilters in the upstream process performed complete nitrification of the ammonia present in the pilot influent. Therefore, no increase in chlorine demand was observed in the soil column feed. Effluent nitrite in the 3-day column with chlorinated feed was mostly above detection limit and therefore consistently higher than the influent nitrite, although the highest measured concentration was only 0.13 mg/L. Nitrite concentration gradually decreased and reached a steay state of 0.02 mg/L after 40 days of experimental time. This could be a result of partial denitrification which might be favored due to the non-readily biodegradable TOC in the influent, insufficient for complete denitrification. However, this phenomenon only occured in the initial stages which could be an indication of the microorganisms taking time to get acclimated after free chlorine disinfection. Apart from TOC, reduced iron can also act as an electron donor in the reduction of nitrate to nitrite (Carlson et al. 2018). The column feed had non-detect levels of iron. Additionally, the sand used to construct the columns was washed thoroughly and exposed to atmosphere. The iron content present was expected to have oxidized after this process. However, low levels of bound ferrous could still have remained in the media, the oxidation of the bound ferrous and the reduction of nitrate could explain the formation of nitrite in the initial days of the experiment. In the monochloraminated 3-day columns, ammonia was consistently removed to non-detect levels with nitrite levels also mostly under the measuring range (see Figure 16 a., b). Nitrate in the effluent was equal to and at times slightly higher than the influent concentration which suggested complete nitrification of influent ammonia to nitrate (see Figure 16 c.).

The data for 30-day chlorinated column indicate a short phase where nitrate reduction and an increase in nitrite concentration occurred (see Figure 15 b., c). After this phase, the nitrate was reduced to non-detect levels while the ammonia level was steady at 0.5 mg/L in the effluent. Considering the fact that there was no ammonia in the feed of the free chlorinated columns, ammonia had to be formed or released from the column media. One possible mechanism that could cause this is dissimilatory nitrate reduction to ammonia (DNRA). DNRA is favored in a cabon rich environment with a low nitrate (electron acceptor) concentration (Teidje, 1988). There was about 4 mg/L TOC going into the columns which empirically is roughly equivalent to 10 mg/L of COD. Given that complete consumption of TOC was not seen in the 30-day columns, it would be inaccurate to assume a carbon rich environment in the columns. However Tiedje (1998) also found that continual anoxic conditions select some DNRA microbes that are obligate anaerobes over denitrifiers. After complete DO consumption, anoxic conditions would persist in the columns and DNRA could be favored. The monochloraminated 30-day column, had consistent nitrate removal but the effluent ammonia levels showed a steady increase (see Figure 15 a,c). Assuming DNRA was taking place in this column as well, a fraction of the ammonia seen in the monochloraminated 30-day column effluent could have formed from this mechanism. However, DNRA cannot fully explain the remaining ammonia levels causing a steady rise in the effluent. An average of 0.33 mg/L of total ammonia was added to the influent of the monochloraminated column through monochloramine addition. Since ammonium has been reported to sorb onto clay particles (Bouwer 1996; Fox et al. 2000; Hafer 2000), the remaining ammonia causing an upward trend could be a result of desorption of previously sorbed ammonia.

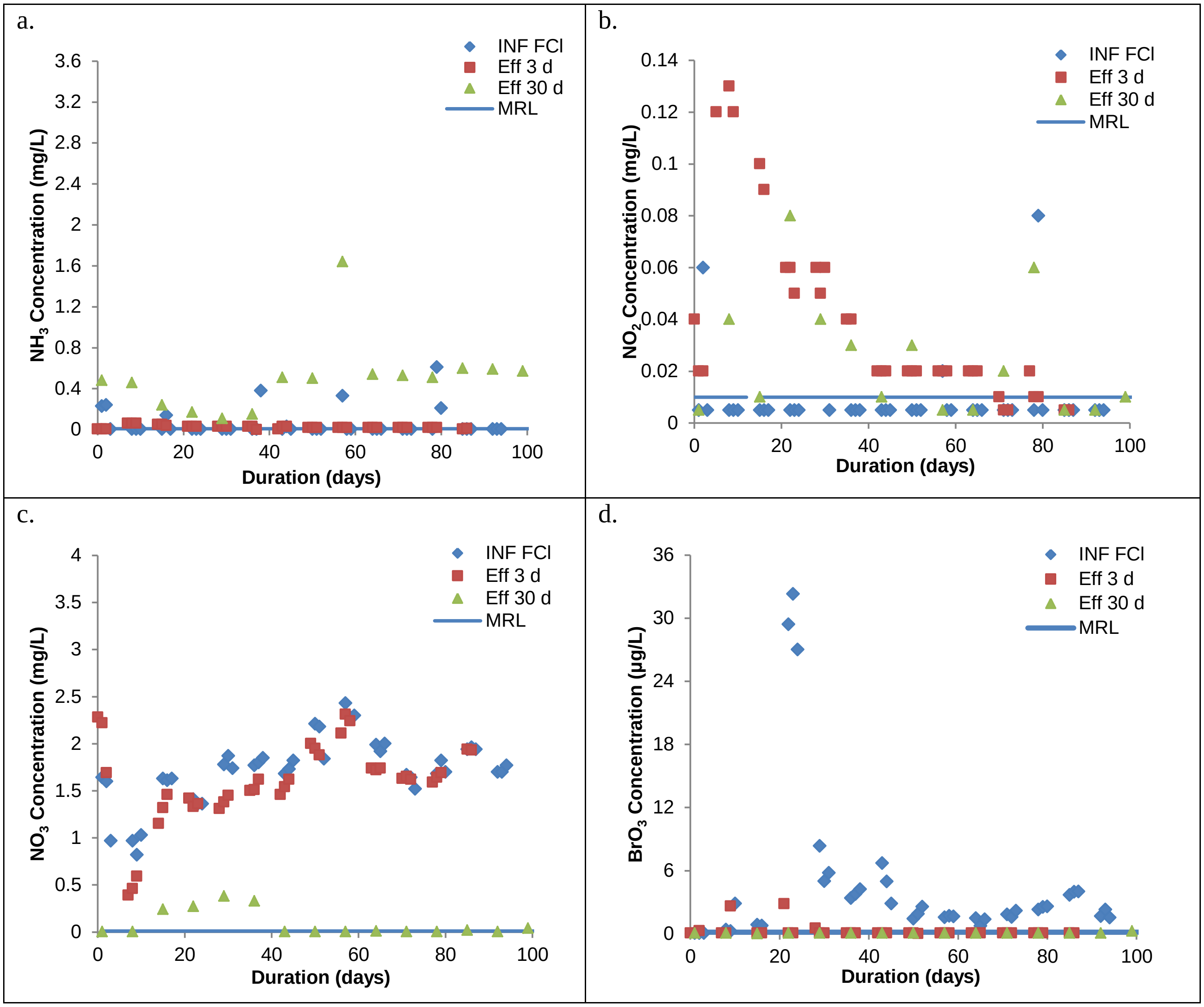


Figure 15: Influent and effluent levels of ammonia (a), nitrite (b), nitrate (c) and bromate (d) in the 3-day and 30-day free chlorinated columns over experimental run time. Effluent values were corrected for travel time.

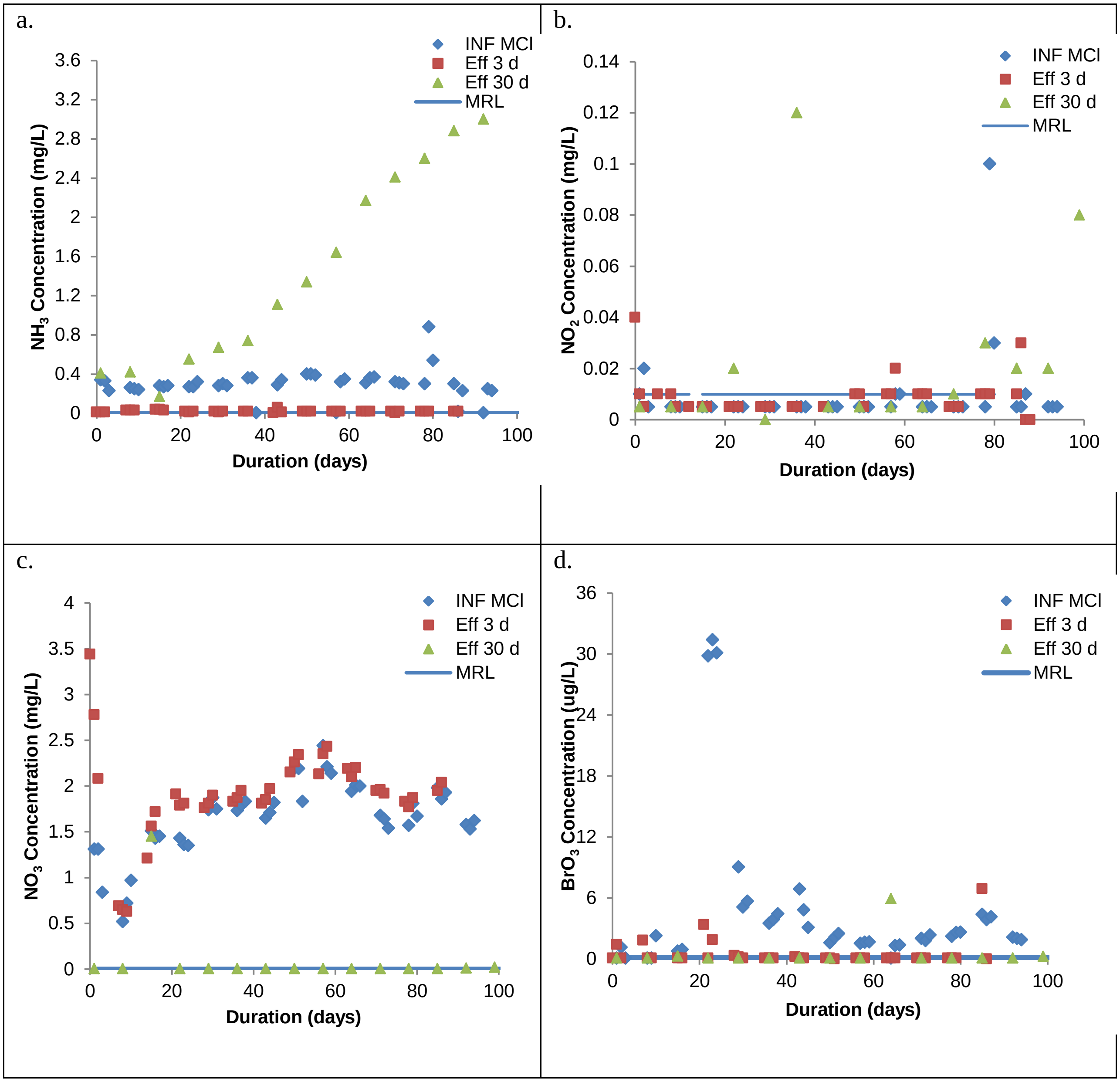


Figure 16: Influent and effluent levels of ammonia (a), nitrite (b), nitrate (c) and bromate (d) in the 3-day and 30-day mono-chloraminated columns over experimental run time.

Bromate reduction occurred in both 3-day and 30-day columns. There was no notable difference between chlorinated and monochloraminated columns in terms of influent or effluent trends. Bromate reduction was expected to be closely tied to nitrate reduction in the columns.

Wang et al. (2018) in their study concluded that denitrifying bacteria were able to reduce bromate in nitrate reducing anoxic zones of soil columns. Similar results were obtained by Hijnen et al. (1999) in an experiment that evaluated bromate removal in denitrifying fixed-bed bioreactor. All four columns reached nitrate reducing conditions as the dissolved oxygen concentration in the effluent were consistently zero or close to it. It would be safe to conclude that the 30-day columns had extended zones that were conducive for nitrate reduction. Bromate was completely removed in the 30-day columns in this study along with nitrate. In the shorter columns, partial bromate removal was observed initially which was followed by complete removal of bromate. The average influent concentration was 7 μg/L. Although this value was not notably high, it was representative of the bromate concentration in the aquifer recharge water at the demonstration facility. There were a few influent spikes in the range of 30 μg/L and the corrrespnding low effluent values suggested attenuation. Similar to nitrate, bromate could also act as an electron acceptor for the oxidation of sulfide and ferrous. A continuous monitoring of iron or sulfide levels in the column effluent was not conducted and therefore it would be difficult to determine the mechanistic pathway of bromate reduction. However, the reduction pathway by ferrous as discussed for nitrate would be applicable for bromate as well.

4.3.3 Phosphorus

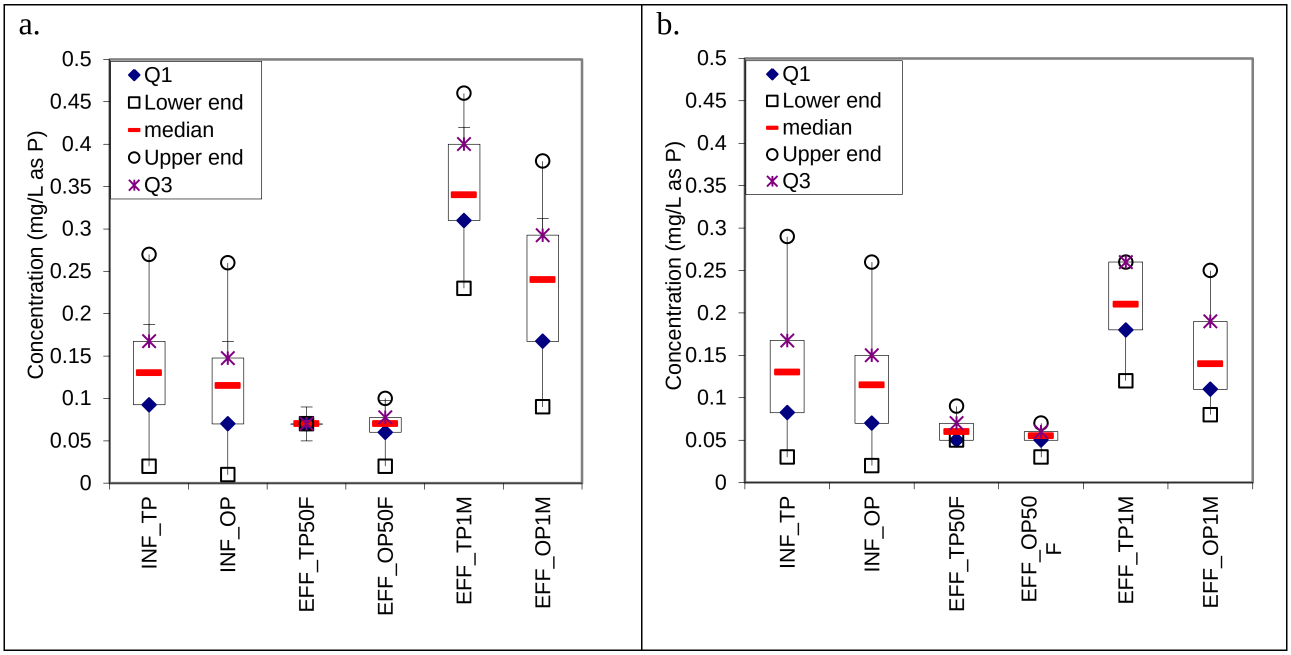


Figure 17: Box and whisker plots of Total Phosphorus (TP) and orthophosphate (OP) values in the influent and effluent of 3-day and 30-day free chlorinated columns (a); 3-day and 30-day mono-chloraminated columns (b) measured during the experimental run time

The categories of Total phosphorus (TP) comprise of orthophosphate and long chain polyphosphates. Both total phosphorus and orthophosphate was higher in the effluent of 30-day columns than the influent. TP in the influent and effluent mostly comprised of orthophosphate. There could be two possible explanations for this. The first alternative woud be the decay of biomass that could have released organophosphates, a fraction of the organhosphates could then be mineralized to orthophosphate. The second alternative could be the leaching of phosphate present in the sand media complexed or precipitated with metals such as calcium, magnesium and iron. In anaerbobic conditions phosphates tend to get released due to reduction of ferric compounds bound with phosphates (Schoumans, 2015). The average difference between the influent and the effluent TP levels in the monochloraminated columns was 0.05 mg P/day and 0.7 mg P/day for the chlorinated columns. the amount of P being released in the chlorinated column was notable which suggests chlorination might facilitate the leaching of phosphate. However, the reasons as to why that happens is unclear and not many have studied this impact of chlorination on phosphorus in sandy soil.

4.3.5 TTHM and HAA5

Total trihalomethanes (TTHMs) were formed in the influent feed mixed with free chlorine as disinfectant. The influent TTHM concentration remained relatively constant at an average of 8 μg/L. A spike in the concentration was observed for a couple of weeks from 57th – 66th experimental day which corresponded with the event of chlorinated backwashing of the biofilters. For this purpose, free chlorine was added to the backwash tank. The column feed was prepared by disinfecting the overflow of this backwash tank with UV. Since, this was the only time period when concentration of influent disinfected by monochloramine was above the detection limit, the cause for the spike was attributed to the reaction of free chlorine residual in the overflow water

In the case of the 3-day column disinfected with chlorine, there is more formation of trihalomethanes by the end of the travel time evident from the effluent concentrations which are consistently higher compared to the influent concentrations. The concentration of chlorine in the influent was in the range of 0.5-1.5 mg/L; the effluent concentration was under the measuring range indicating the complete removal of chlorine across the column. The retention time in the 3-day columns provided extended contact time for chlorine to react with the THM precurors still present in the feed water. However, TTHMs were completely removed across the 30-day column. According to mechanistic studies, the reduction of disinfection by products occurs in anaerobic conditions (Quanrud et al., 2016). McQuarrie et al. (2003) also demonstrated removal of TTHM across soil columns which increased from 8% to 40% as the column residence time increased from 14 days to 34 days. Given that the DO concentration in the effluent of both 3-day columns were consistently zero but nitrate was still present, anoxic conditions were reached by 3.2 days of retention time. Considering all factors uniform between the 3-day and the 30-day column, the 30-day retention time in the 30-day column would have an extended anaerobic zone where more removal of THM could occur.

Compounds that comprised majority of the TTHM concentration were brominated compounds such as bromoform and monochlorodibromomethane. Bromide reacts with hypochlorite to form HOBr which in turn reacts with the natural organic matter to form brominated DBPs. HOBr and OBr^- are more reactive than HOCl and OCl^- which could explain the higher concentration of brominated DBPs.

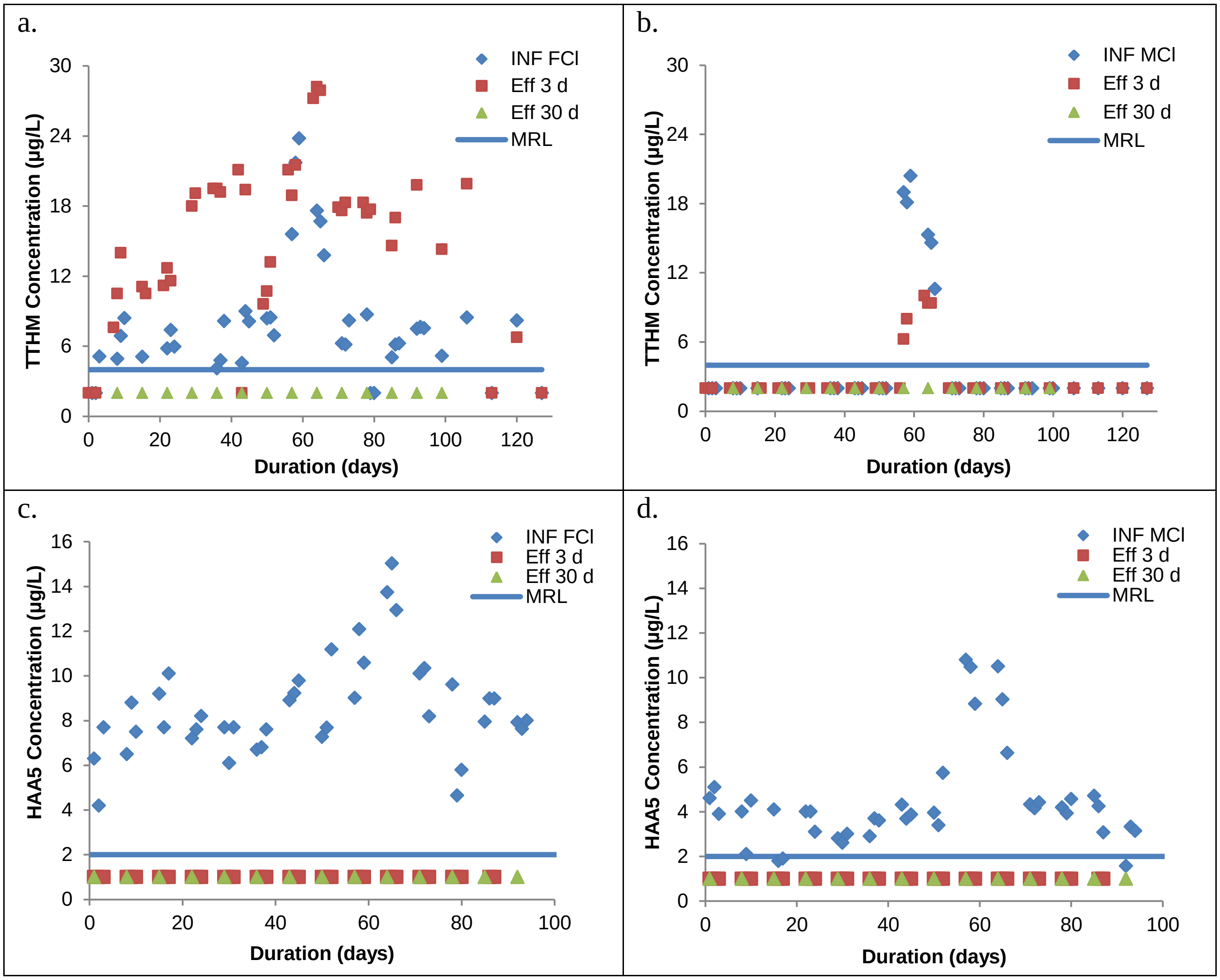


Figure 18: TTHM and HAA5 plots for chlorinated columns (a, c); monochloraminated columns (b, d)

Haloacetic acids (HAA5) were produced in the influent disinfected by both chlorine and monochloramine. The concentration in the chlorinated influent was on an average 50% higher compared to the monochloraminated influent. Similar to THM formation in the columns, HAA formation is also due to the reaction of disinfectant residual with NOMs. However, the formed HAAs, if any, were completely removed in both the 3-day and the 30-day columns. Oxic conditions favor HAA reduction. The feed had saturated levels of dissolved oxygen concentration; so the bottom of both 3-day and 30-day columns would have oxic zones till the point of complete dissolved oxygen consumption. HAAs are also more readily biodegraded compared to THMs (Quanrud et al. 2016). A difference was noted between THM and HAA formation by monochloramine. There were no detected influent values of THM in the monochloraminated influent except the ones measured in the weeks of chlorinated backwashes. The same spike in influent concentration of HAA was observed during the same time period. Unlike TTHM, HAA5 were detected in the influent disinfected with monochloramine. The method reporting limit for TTHM is higher (4 μg/L) compared to HAA5 (2 μg/L). Although this could have contributed to more HAA5 detects, there were still significant number of data points that were above 4 μg/L. There have not been studies that suggest that HAAs are formed more readily by monochloramine compared to TTHM. Dibromoacetic acid constituted majority of the HAA5 concentration. Neither chlorine nor monochloramine formed monochloroacetic acid. Monobromoacetic acid was only formed by chlorine. Chlorination formed brominated compounds at higher concentrations compared to monochloramination. Di and trihalogenated acetic acids formed at higher concentrations compared to monohalogenated acetic acids in general.

4.4.6 Contaminants of Emerging Concern

The column influent and effluent were sampled for a range of emerging contaminants. These included pharmaceutical compounds, personal care products, pesticides, herbicides and flame retardants among others. Emerging contaminants were not sampled continuously. The schedule and frequency of sampling has been described in Section 4.2.3. Out of 107 compounds analyzed, the majority were not detected in the column influent or effluent. The 73 compounds listed in Table 17 were never detected. Some of these compounds were removed by the preliminary processes of ozonation-biofiltration while some compounds like PFOA and PFOS were never above detection in the denitrified effluent feeding the pilot.

Table 19: Contaminants that were always below the detection limit in the soil column influent and effluent along with their method reporting limits

Compounds	MRL	Compounds	MRL
1,7-Dimethylxanthine	10 ng/L	Ketoprofen	5 ng/L
4-tert-Octylphenol	50 ng/L	Lincomycin	10 ng/L
Albuterol	5 ng/L	Lopressor	20 ng/L
Amoxicillin (semi-quantitative)	80 ng/L	Metazachlor	5 ng/L
Andorostenedione	5 ng/L	Methylparaben	20 ng/L
Atenolol	5 ng/L	Naproxen	10 ng/L
Atrazine	5 ng/L	Nifedipine (semi quantitative)	20 ng/L
Bendroflumethiazide	5 ng/L	Norethisterone	5 ng/L
Bezafibrate	5 ng/L	OUST (Sulfameturon,methyl)	5 ng/L
Bromacil	5 ng/L	Pentoxifylline	5 ng/L
Butylparaben	5 ng/L	Perchlorate	0.5 µg/L
Carbadox	5 ng/L	Perfluoro octanesulfonic acid - PFOS	0.04 µg/L
Carbamazepine	5 ng/L	Perfluoro-1-butanesulfonic acid -PFBS	0.09 µg/L
Chloramphenicol	10 ng/L	Perfluoro-1-hexanesulfonic acid - PFHX	0.03 µg/L
Chlorotoluron	5 ng/L	Perfluoroheptanoic acid - PFHpA	0.01 µg/L
Cimetidine (semi quantitative)	5 ng/L	Perfluoro-n-nonanoic acid - PFNA	0.02 µg/L
Clofibric Acid	5 ng/L	Perfluorooctanoic acid - PFOA	0.02 µg/L
Cyanazine	5 ng/L	Phenazone	5 ng/L
DACT	50 ng/L	Progesterone	5 ng/L
DEA	5 ng/L	Propazine	5 ng/L
DEET	10 ng/L	Simazine	5 ng/L
Dehydronifedipine	5 ng/L	Sulfachloropyridazine	5 ng/L
DIA	5 ng/L	Sulfadimethoxine	5 ng/L
Diazepam	5 ng/L	Sulfamerazine	5 ng/L
Diclofenac	5 ng/L	Sulfamethazine	5 ng/L
Dilantin	20 ng/L	Sulfamethizole	5 ng/L
Diltiazem	5 ng/L	Sulfamethoxazole	5 ng/L
Diuron	5 ng/L	Sulfathiazole	20 ng/L
Equilin	0.004 µg/L	TDCPP	100 ng/L
Estriol	0.001 µg/L	Testosterone	0.0001 µg/L
Ethylparaben	20 ng/L	Theophylline	20 ng/L
Flumeqine	10 ng/L	Thiabendazole	5 ng/L
Fluoxetine	10 ng/L	Triclocarban	5 ng/L
Gemfibrozil	5 ng/L	Triclosan	5 ng/L
Isobutylparaben	5 ng/L	Trimethoprim	5 ng/L
Isoproturon	100 ng/L	Warfarin	5 ng/L

Out of the CECs analyzed, 17 CECs were non-regulatory performance indicator compounds chosen for HRSD's SWIFT project to provide information about the performance of the treatment processes. These included public health indicators that are unregulated compounds but are of interest from a public health standpoint and performance efficacy indicators that are compounds which are fairly persistent but may not be harmful to human health. Of the 17 indicator compounds, 8 were not detected in either the column influent or the column effluent, including DEET, perchlorate, PFOA, PFOS, phenytoin, atenolol, carbamazepine, and triclosan. 1,4-dioxane and sucralose regularly showed up in both the influent and effluent at significant levels. The remaining compounds were detected intermittently. None of the compounds were measured above the notification limits or health advisory level.

Table 20: Summary of the indicator compounds

Performance Indicators	Detected range of Concentration	Notification and health advisory limits
Public Health Indicators		
1,4-dioxane	<0.07 - 0.38 μg/L	1 μg/L (CA Notification Limit)
17-β-estradiol	<0.0004 - 0.00051 μg/L	TBD
DEET	<10 ng/L	200,000 ng/L (MN Health Guidance Value)
Ethinyl estradiol	<5.0 – 9.6 ng/L	TBD
Tris(2-carboxyethyl)phosphine (TCEP)	<10 – 25 ng/L	5,000 ng/L (MN Health Guidance Value)
NDMA	<2.0 – 4.0 ng/L	10 ng/L (CA Notification Limit)
Perchlorate	<0.5 μg/L	6 μg/L (CA Notification Limit)
Perfluorooctanoic Acid (PFOA) and Perfluorooctanesulfonic Acid (PFOS)	<0.04 μg/L	0.07 μg/L (USEPA Health Advisory)
Treatment Efficacy Indicators		
Cotinine	<10 – 36 ng/L	1 μg/L
Primidone	<20 – 34 ng/L	10 μg/L
Phenytoin (Dilantin)	< 20 ng/L	2 μg/L
Meprobamate	<5 – 23 ng/L	200 μg/L
Atenolol	<5 ng/L	4 μg/L
Carbemazepine	<5 ng/L	10 μg/L
Estrone	≤25 ng/L	320 μg/L
Sucralose	<100 – 120000 ng/L	150,000 μg/L
Triclosan	<10 ng/L	2,100 μg/L

There were a few compounds that were detected at significant levels in the influent and effluent. The threshold of 100 ng/L was used to determine a significant level of detection. As mentioned earlier, 1,4-dioxane and sucralose were the indicator compounds that fell under this category. Both 1,4-dioxane and sucralose were regularly detected in both the influent and the effluent. 1,4-dioxane was partially removed in the 30-day columns on a consistent basis whereas there was no decipherable trend in the 3-day columns since effluent values were intermittently detected at levels above, below and equal to the influent values. This is in contrast with results by Steffan (2007), who saw no anaerobic biodegradation of 1,4-dioxane in microcosm experiments, even with extended retention time. On the contrary, retention time seemed to have a positiveeffect on 1,4-dioxane attenuation in this study. Similarly, the artificial sweetener, sucralose seemed to be attenuated to some extent in all four columns in this study. Sucralose has been reported to be generally persistent in SAT studies with very slow to no removal in aerobic or anaerobic conditions (Scheurer, 2009). But Labre et al . (1993, 1994) saw the mineralization of sucralose in loam by microbial activity, although the microbes responsible were not identified. Similar mechanism could explain the partial removal of sucralose in the columns. There were few instances of effluent concentrations spiking. While desorption could have explained the observed spike, sorption is not considered an effective removal mechanism for sucralose as observed by Sho et al. (2011). Therefore, the sudden instances of high sucralose levels in the effluent was considered to be a result of high sucralose spikes in the influent that was not captured during influent sampling.

Table 21: Observed number of detections and concentration range of emerging contaminants detected at >100 ng/L at least once in the column influent or effluent

Compounds	No. of detections			Concentration range (ng/L)	Summary of observed removal trends
	Influent	3-day Effluent	30-day Effluent		
Total no. of samples collected	**12**	**12**	**10**		
1,4-dioxane	12	12	9	<70 – 380	No clear trend in 3-day columns Partial removal in 30-day columns
Sucralose	12	10	10	<100 – 120000	No clear trend
Acesulfame-K	11	6	10	<20 – 11000	Partial removal in all four columns
Iohexal	12	11	10	<40 – 9100	
4-nonylphenol	7	6	8	<100 – 10000	No clear trend
TCPP	5	4	3	<100 – 1000	
Sulfadiazine	3	0	2	<5 – 610	Potential removal in all four columns

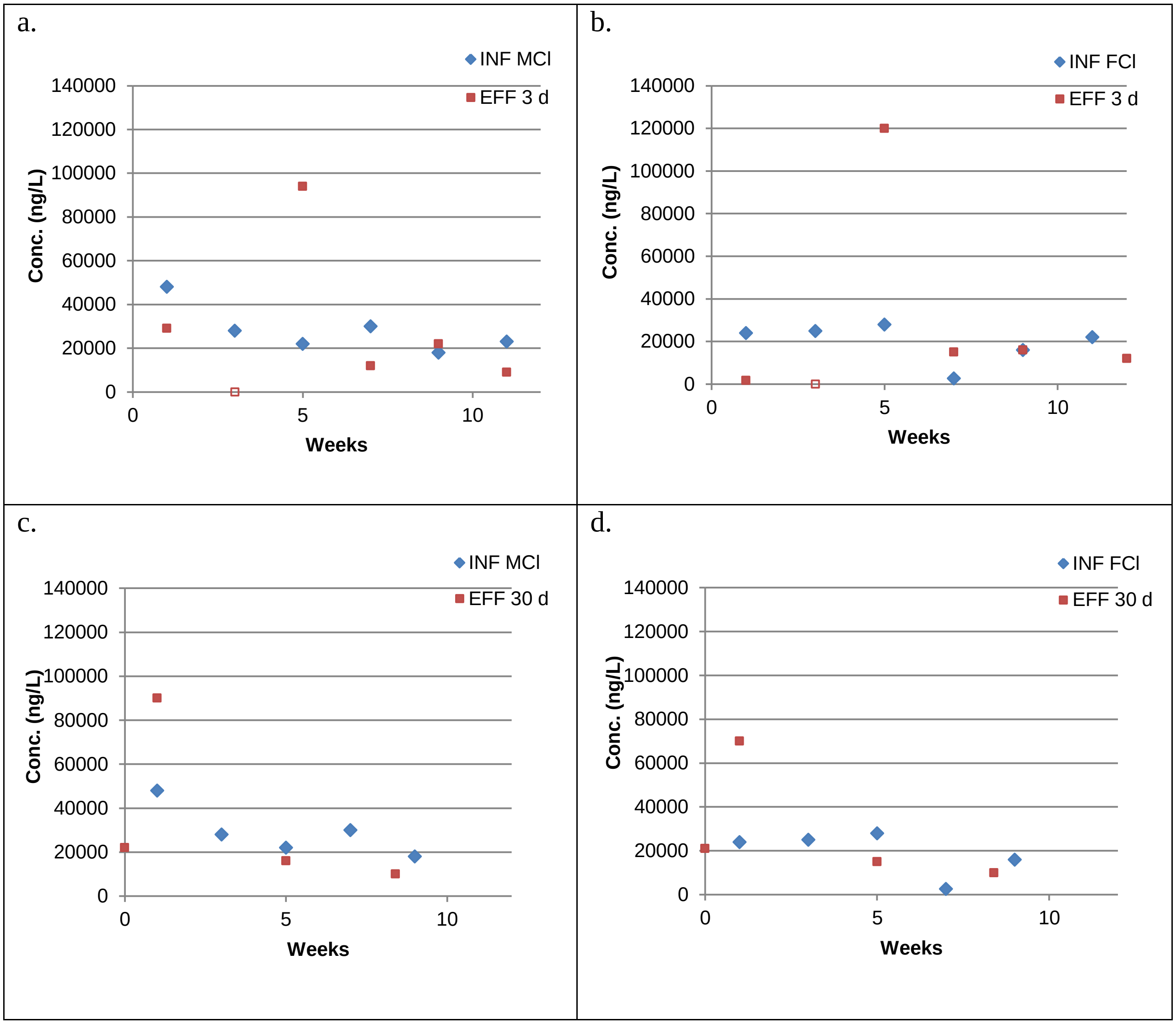


Figure 19: Influent and Effluent values for sucralose in 3-day columns (a, b) and 30-day columns (c, d). Effluent values were corrected for time. Data points with no fill represent values below the MRL.

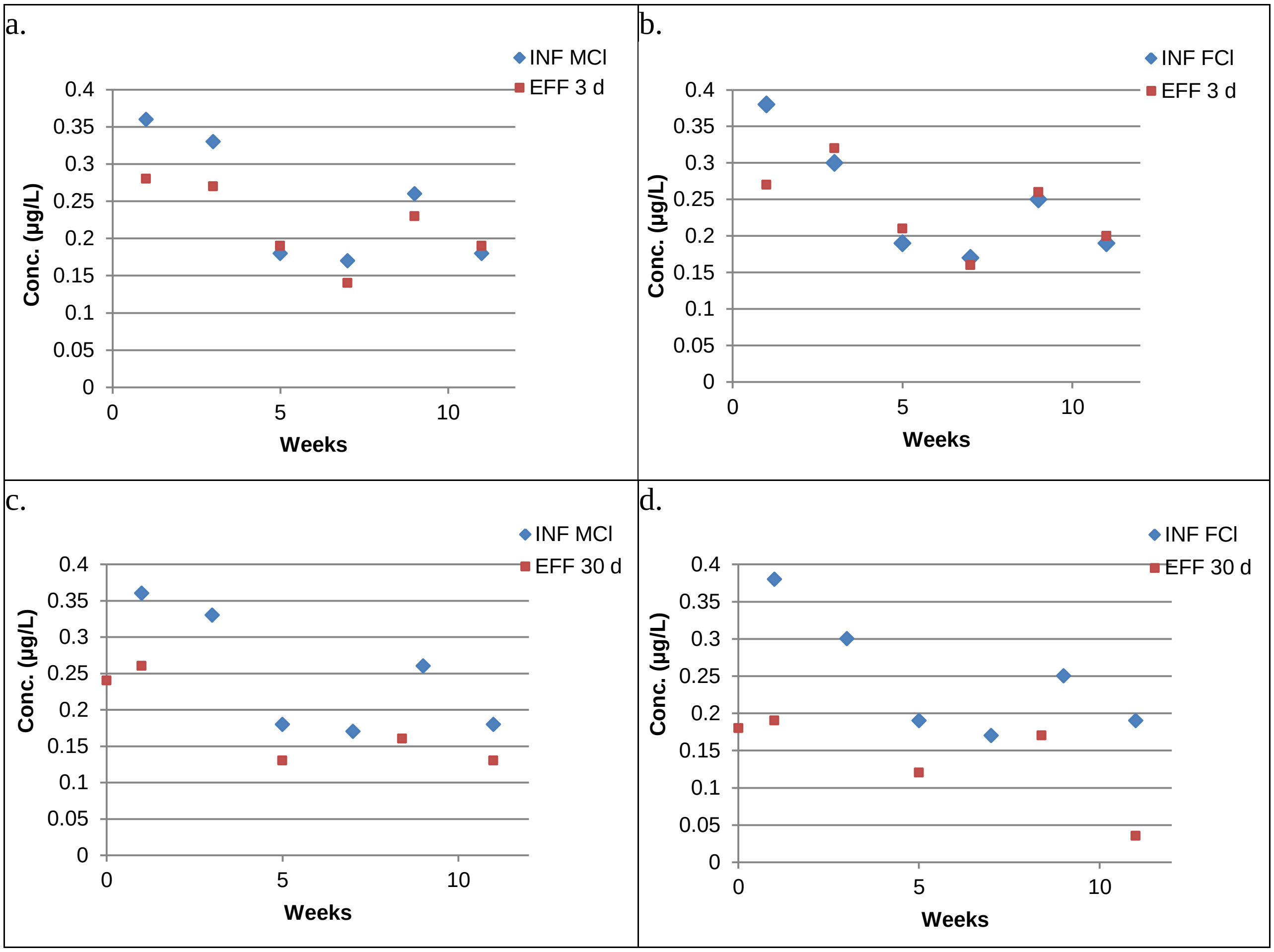


Figure 20: Influent and effluent values for 1,4 – dioxane in 3-day columns (a, b) and 30-day columns (c, d). Effluent values were corrected for time. Data points with no fill represent values below the MRL.

Acesulfame-K is another artificial sweetener that was regularly measured at significant levels (>100 ng/L) in the influent. The comparison of influent and effluent concentrations indicated attenuation across all four columns. Acesulfame-K had a more consistent removal trend compared to sucralose. The average percent removal for acesulfame-K was 89% and 58% in the 3-day columns and 30-day columns respectively. Non-detects were considered as half of the method reporting limit and for data sets with effluent values greater than the influent, percent removal was considered to be zero. This is in contrast with the findings of Scheurer (2009) where acesulfame-K was observed to be persistent in SAT, although it has to be noted that Scheurer's study was conducted with wastewater as the feed. The difference in feed water composition could be expexted to affect the removal.

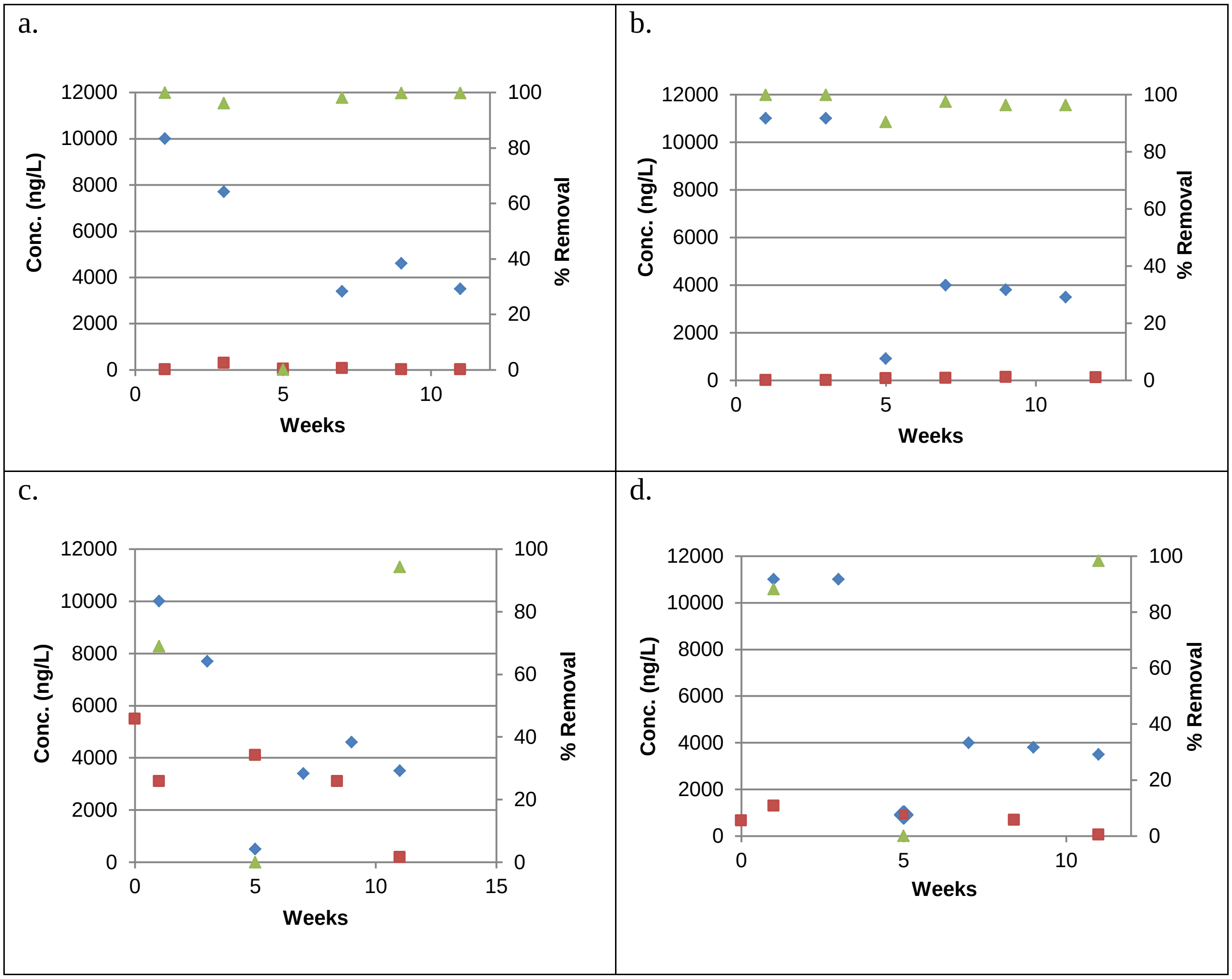


Figure 21: Influent (blue diamonds) and effluent values (red squares) of acesulfame-K plotted (left axis) over experimental time for 3-day mono-chloraminated column (a), 3-day free chlorinated column (b), 30-day column mono-chloraminated column (c) and 30-day free chlorinated column. Effluent values were corrected for time and removals for each data set calculated and plotted on the right axis. The percent removal for data sets with effluent greater than the influent were considered zero.

Iohexal was another compound that was regularly detected and partially removed in all four columns. The average percent removal for iohexal was 68% for the 3-day columns and 86% for the 30-day columns. There have been a few studies conducted on the fate of this X-ray contrast agent in MAR systems that attempt to describe its attenuation mechanism. Fast degradation of the compound in suboxic conditions was observed (Stuyfzand et al. 2007) and a very low half life of <1 day in aerobic conditions (Patterson et al. 2011) but no degradation in anaerobic conditions (Patterson et al. 2010, 2011). However in this study, additional removal was seen in the 30-day columns compared to the 3-day columns. This could imply that more attenuation occurred in the extended anoxic/anaerobic zones of the 30-day columns since data shows that DO levels had already reached zero at the end of the 3-day columns and assuming that the pattern of DO consumption was the same across all columns.

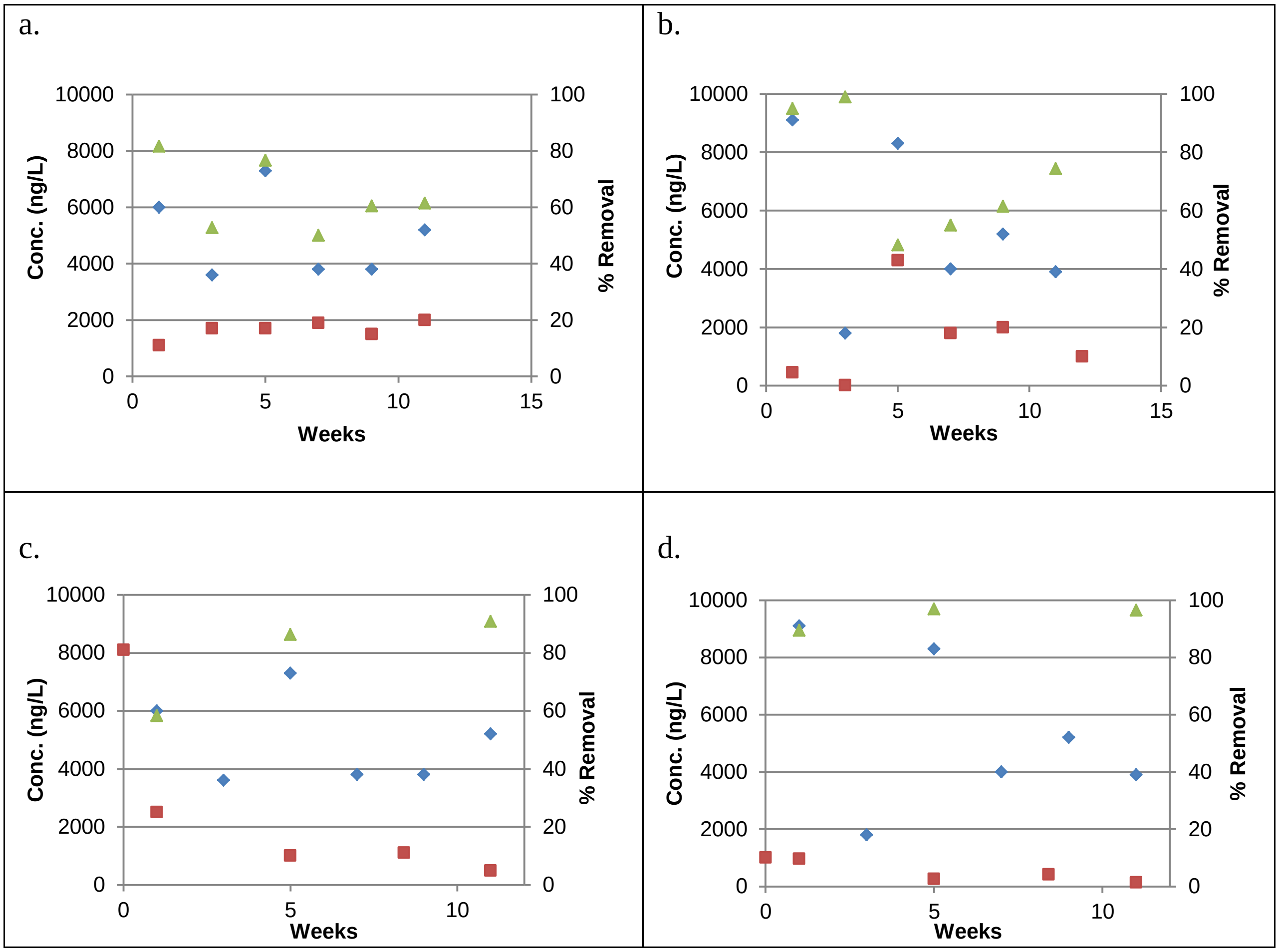


Figure 22: Influent (blue diamonds) and effluent values (red squares) of iohexal plotted (left axis) over experimental time for 3-day mono-chloraminated column (a), 3-day free chlorinated column (b), 30-day column mono-chloraminated column (c) and 30-day free chlorinated column. Effluent values were corrected for time and removals for each data set calculated and plotted on the right axis. The percent removal for data sets with effluent greater than the influent were considered zero.

Sulfadiazine was detected a few times in the range of 100-610 ng/L in the influent; degradation and/or adsorption in all four columns is a possibility since the only two effluent values detected out of the 30-day columns were also low in magnitude. 4-nonylphenol and TCPP were also detected at high concentrations but there was no decipherable trend in the influent or effluent of either of the four columns.

Table 22: Observed number of detections and concentration ranges of emerging contaminants in the column influent and effluent

Compounds	No. of detects			Concentration range (ng/L)			Summary of detections observed and possible trends
	Inf.	3-day Eff	30-day Eff	Inf.	3-day Eff.	30-day Eff.	
Total no. of samples	**12**	**12**	**10**				
Butalbital	1	0	0	<5 – 5.4	<5	<5	Detected in Influent
Primidone	2	0	0	≤20 - 21	<20	<20	
Propylparaben	1	0	0	<5 – 6.2	<5	<5	
Estrone	1	0	0	≤25	<25	<25	
BPA	1	0	8	<10 - 60	<10	<10 - 58	Detected in Influent Effluent - 30-day Possibility of removal in 3-day columns
17-α-Ethinyl Estradiol	3	0	1	<5 – 9.6	<5	<5 – 6.2	
NDMA	3	0	1	<2 – 4.6	<2	≤2	
Ibuprofen	2	0	1	<10 – 25	<10	≤10	
Oxolinic Acid	1	0	1	<10 - 15	<10	<10 - 24	
Chloridazon	2	1	0	<5 – 16	<5 – 56	<5	Detected in Influent Effluent - 3-day Possibility of removal in 30-day columns
Linuron	2	1	0	<5 – 8.9	<5 – 11	<5	
TCEP	10	5	0	<5 - 25	<5 - 21	<5	
17-β-Estradiol	0	0	1	<0.4	<0.4	<0.4 – 0.51	Detected in Effluent – 30-day Inconclusive
4-androstene-3,17-dione	0	0	1	<0.3	<0.3	<0.3 – 0.48	
Quinoline	0	0	4	<5	<5	<5 – 6.9	
Triclosan	0	0	2	<10	<10 – 16	<10	Detected in Effluent – 3-day Inconclusive
2,4-D	0	1	0	<5	<5 - 21	<5	
Iopromide	0	1	0	<5	<5 – 7.9	<5	
Ketorolac	0	2	0	<5	<5 - 64	<5	
Meclofenamic Acid	0	2	0	<5	<5 – 7.2	<5	
Theobromine	0	4	2	<10	<10 - 32	<10 - 71	Dectected in Effluent – 3-day Effluent – 30-day Inconclusive
Lidocaine	0	3	2	<5	<5 – 7.4	<5 - 25	
Caffeine	0	2	6	<5	<5 – 51	<5 - 28	
Erithromycin	1	2	2	<10 – 12	<10 - 15	<10 - 13	No clear trend
Meprobamate	9	10	7	<5 – 18	<5 - 24	<5 - 16	
Acetaminophen	10	8	5	<5 - 31	<5 - 34	<5 - 16	No clear trend in 3-day columns Possible partial removal in 30-day

Butalbital, primidone, propylparaben and estrone were detected at most in two sampling events in the influent. Although the effluent values were non-detects, their removal through the columns cannot be considered definitive since the influent values were only few ng/L higher than their respective method reporting limits. It is uncertain if complete removal would still occur had the influent concentrations been consistently higher. Drewes et al. (2002) found primidone to persist even after six years of sub-surface recharge; similar observations were made by Alidina et al. (2014) and Hass et al. (2012). Therefore, persistence of primidone could be expected in the soil columns had the concentration in the influent been higher.

17-α-Ethinyl Estradiol, NDMA, ibuprofen and oxolinic acid were detected at low levels in the influent. 3-day column effluents were consistently non-detects while some 30-day column effluent values were above the MRL. Although one might infer from this data, that longer retention time was not benificial for the attenuation of these compounds, the low levels and the infrequency of detection do not allow for a definitive conclusion. Bisphenol-A (BPA), however, had an interesting trend; it was never detected in the 3-day columns but was observed at 30 – 60 ng/L in both 30-day column effluents. This could be be an indication of either desorption of previously sorbed BPA or contamination of sample and/or instrument.

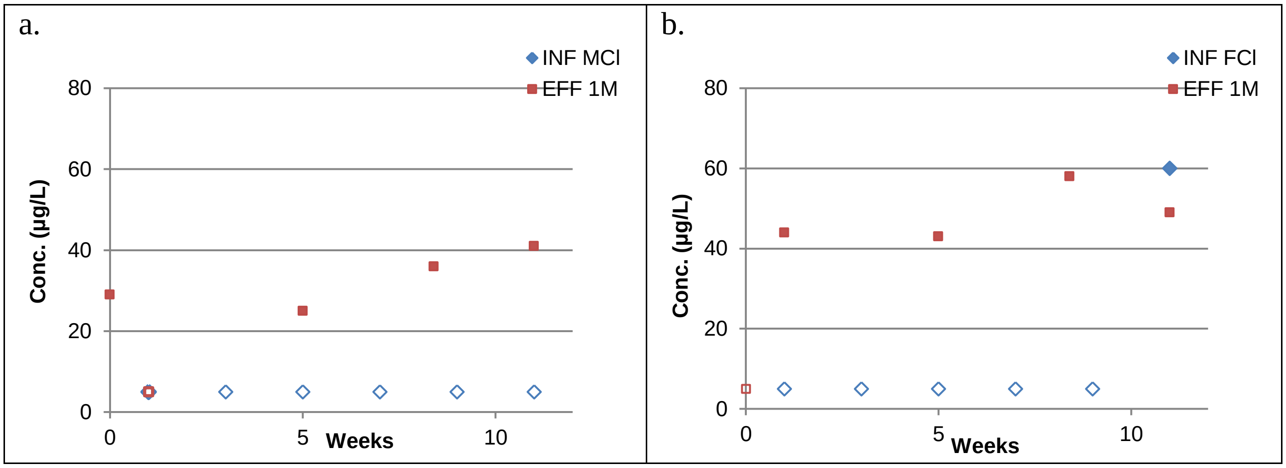


Figure 23: Influent and effluent values of Bisphenol-A (BPA) - 30-dayin mono-chloraminated 30-day column (a.) and in free chlorinated 30-day column (b.). Effluent values were corrected for travel time. Data points with no fill were below the MRL.

TCEP, which is a flame retardant similar to TCPP, was regularly detected at around two times the method reporting limit (10 ng/L). Effluents from the 3-day columns were occasionally detected at levels close to the influent values. However, all the 30-day column effluents were non-detects which indicated removal. This could imply that longer retention time could potentially be beneficial for TCEP attenuation which agreed with the findings of Laws et al. (2011) where removal of both TCEP and TCPP increased from <20% to approximately 50% and 80% respectively as investigated travel time increased from 3-days to 60 days.Acetaminophen had similar effluent trend in the 30-day columns. The effluent values were consistently lower than the influent, so partial removal was possible. However, acetaminophen did not have a clear trend in the 3-day columns.

The compounds 17-β-Estradiol, 4-androstene-3,17-dione, quinoline, triclosan, and 2,4-D were only detected in the column effluents of either the 3-day or the 30-day columns. These were mostly one time detects and no conclusion regarding attenuation could be drawn from the data observed.

Theobromine, caffeine, and lidocaine were detected only in the effluent of all four columns. The trend for lidocaine was similar to that of BPA; especially in the 30-day chlorinated column, where desorption or formation through transformation seemed to be occurring.

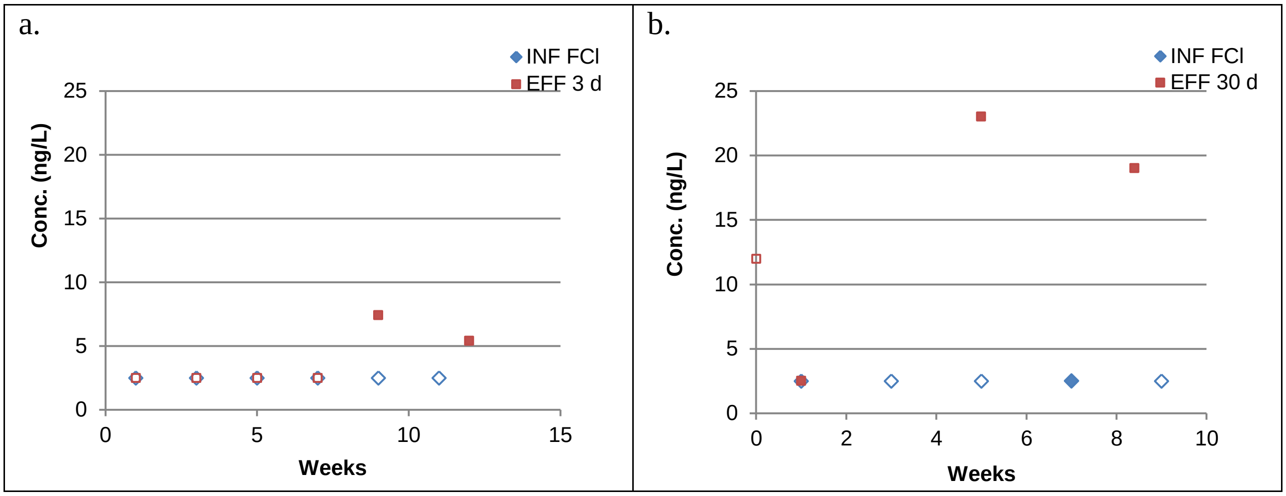


Figure 24: Influent and effluent values of Lidocaine in chlorinated 3-day columns (a.) and 30-day columns (b). Effluent values were corrected for travel time. Data points with no fill were below MRL.

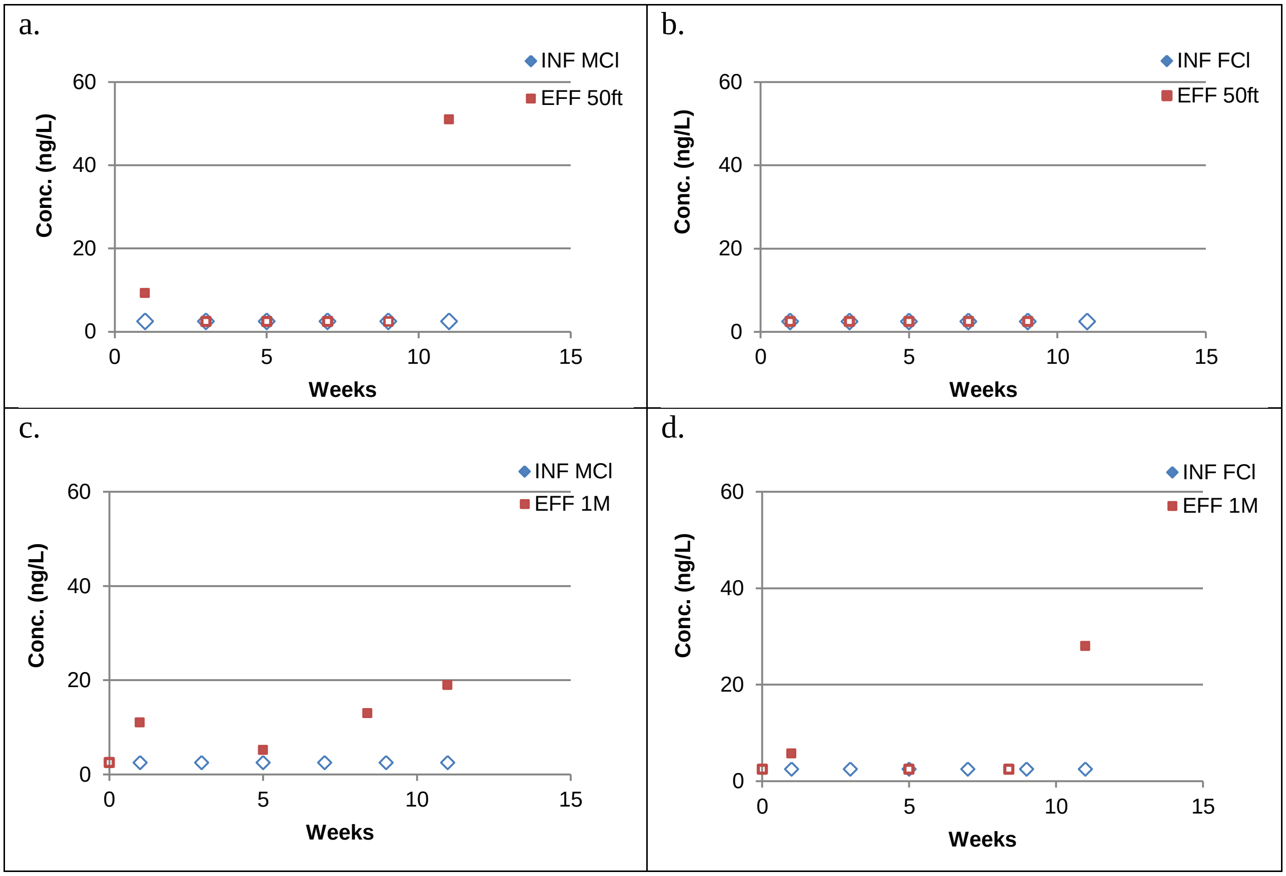


Figure 25: Influent and effluent values of caffeine in monochloraminated columns 3-day (a) and 30-day (c) 3-day free chlorinated column (b), 30-day monochloraminated column (c) and (d)

Theobromine and caffeine are both stimulants found in food and drinks.Caffeine was detected a total of six times in the 30-day column effluents and twice in the 3-day column effluents. One possible explanation would be the desorption of caffeine previously sorbed onto the column media. But caffeine is considered readily degradable (D'Alessio et al. 2018; Alidina et al. 2014) andit is implausible for it to have persisted after even 3-days of retention time. It is possible that the detects were results of sample contamination since caffeine sampling and analysis is sensitive and the concentration is at the scale of ng/L. As with caffeine, there was no clear trend for theobromine; there were intermittent detects and non-detects in the column effluent (see Figure 26). Although, theobromine is a metabolite of caffeine, non detect levels of caffeine in the influent suggested that the theobromine detections were unlikely to have resulted from caffeine degradation in the columns. Similar to the case of caffeine, this could have been caused by sample contamination.

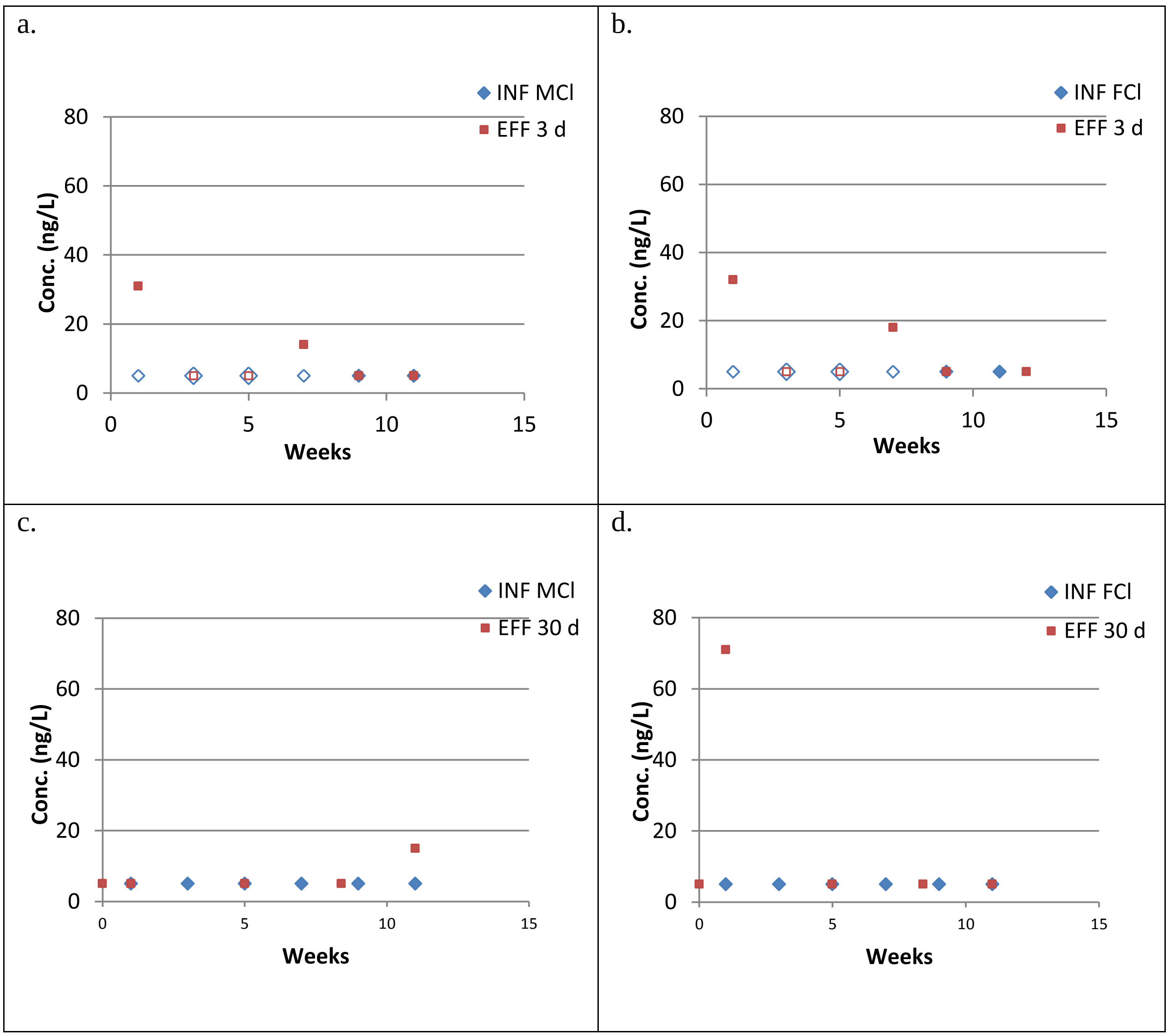


Figure 26: Influent and effluent values of thobromine in 3-day columns (a, b) and 30-day columns (c, d). Effluent values were corrected for travel time. Data points with no fill were below the MRL of 10 ng/L

The remaining compounds that were detected but did not fit the bracket of the categories discussed above were erythromycin and meprobamate. Erithromycin was only detected once in the influent and twice in both 3-day and 30-day columns but at concentrations not higher than 12 ng/L. Meprobamate was regularly detected at levels not higher than 25 ng/L. There was no conclusive trend apparent in the plots for its removal.

4.4 Conclusion

The results of this column study help understand the fate and transport mechanisms of various regulated and non-regulated compounds and contaminants of concern that are pertinent to potable water reuse applications. The study elucidates that SAT is a good treatment step to follow the processes of ozonation, biofiltration and UV since it can provide additional removal of contaminants. Nitrate and bromate was completely reduced in the 30-day columns; good removal of bromate and was seen in the 3-day column effluents as well. 25 – 35% of TOC removal occurred in all four columns. The comparative study between two disinfectants confirmed that monochloramine was a safer disinfectant to use since it formed lower levels of disinfection by products (DBPs) compared to free chlorine. Nonetheless, the conventionally measured DBPs got completely removed after a month of travel time regardless of the disinfectant used. Among the CECs analyzed, acesulfame-K and iohexal were consistently detected at levels greater than 1000 ng/L in the feed and were partially removed at 58 – 89% and 68 – 86% respectively. Clear removal trends were not observed for most CECs which pointed to the need for additional research and study to better understand the fate and transport of these contaminants during MAR. It was evident that redox conditions varied at different column depths which significantly affected the attenuation mechanisms of compounds. Although multiple port sampling at different column depths is hard to achieve in a column without creating preferential pathways, it would have provided a more comprehensive picture of different conditions and reactions occurring along the column depth. Filling this knowledge gap was realized as pivotal to increasing understanding of the attenuation mechanisms of solutes during MAR. Nonetheless, this study adds to the growing body of literature that discusses SAT in MAR systems as a promising alternative for indirect potable reuse.

4.5 References

Alidina, M., Li, D., Ouf, M., & Drewes, J. E. (2014). Role of primary substrate composition and concentration on attenuation of trace organic chemicals in managed aquifer recharge systems. *Journal of environmental management*, *144*, 58-66.

Banzhaf, S., & Hebig, K. H. (2016). Use of column experiments to investigate the fate of organic micropollutants - A review. *Hydrology and Earth System Sciences*, *20*(9), 3719–3737. https://doi.org/10.5194/hess-20-3719-2016

Banzhaf, S., Nödler, K., Licha, T., Krein, A., & Scheytt, T. (2012). Redox-sensitivity and mobility of selected pharmaceutical compounds in a low flow column experiment. *Science of the Total Environment*, *438*, 113–121. https://doi.org/10.1016/j.scitotenv.2012.08.041

Bertelkamp, C., Reungoat, J., Cornelissen, E. R., Singhal, N., Reynisson, J., Cabo, A. J., … Verliefde, A. R. D. (2014). Sorption and biodegradation of organic micropollutants during river bank filtration: A laboratory column study. *Water Research*, *52*, 231–241. https://doi.org/10.1016/j.watres.2013.10.068

Bolong, N., Ismail, A. F., Salim, M. R., & Matsuura, T. (2009). A review of the effects of emerging contaminants in wastewater and options for their removal. *Desalination*, *239*(1–3), 229–246. https://doi.org/10.1016/j.desal.2008.03.020

Bond, T., Goslan, E. H., Parsons, S. A., & Jefferson, B. (2012). A critical review of trihalomethane and haloacetic acid formation from natural organic matter surrogates. *Environmental Technology Reviews*, *1*(1), 93–113. https://doi.org/10.1080/09593330.2012.705895

Bouchard, D.C., Williams, M. K., & Surampalli, R. Y. (1992). Nitrate contamination of groundwater: sources and potential health effects. *Journal-American Water Works Association*, 84(9), 85-90.

Bouwer, H., & Rice, R. C. (1948). Renovation of Wastewater at the 23rd Avenue Rapid Infiltration Project Renovation Avenue of wastewater rapid infiltration at the project. *Water Pollution Control Federation*, *56*(1), 76–83.

Burke, V., Treumann, S., Duennbier, U., Greskowiak, J., & Massmann, G. (2013). Sorption behavior of 20 wastewater originated micropollutants in groundwater - Column experiments with pharmaceutical residues and industrial agents. *Journal of Contaminant Hydrology*, *154*, 29–41. https://doi.org/10.1016/j.jconhyd.2013.08.001

Carlson, H. K., Clark, I. C., Blazewicz, S. J., Iavarone, A. T., & Coates, J. D. (2013). Fe(II) oxidation is an innate capability of nitrate-reducing bacteria that involves abiotic and biotic reactions. *Journal of Bacteriology*, *195*(14), 3260–3268. https://doi.org/10.1128/JB.00058-13

Chairez, M., Luna-Velasco, A., Field, J. A., Ju, X., & Sierra-Alvarez, R. (2010). Reduction of bromate by biogenic sulfide produced during microbial sulfur disproportionation. *Biodegradation*, *21*(2), 235–244. https://doi.org/10.1007/s10532-009-9296-5

D'Alessio, M., Onanong, S., Snow, D. D., & Ray, C. (2018). Occurrence and removal of pharmaceutical compounds and steroids at four wastewater treatment plants in Hawai'i and their environmental fate. *Science of the Total Environment*, *631–632*, 1360–1370. https://doi.org/10.1016/j.scitotenv.2018.03.100

Demirel, S., Uyanık, İ., Yurtsever, A., Çelikten, H., & Uçar, D. (2014). Simultaneous Bromate and Nitrate Reduction in Water Using Sulfur-Utilizing Autotrophic and Mixotrophic Denitrification Processes in a Fixed Bed Column Reactor. *CLEAN–Soil, Air, Water*, *42*(9), 1185-1189.

Drewes, J. E., & Fox, P. (1999). Fate of natural organic matter (NOM) during groundwater recharge using reclaimed water. *Water Science and Technology*, 40(9), 241-248.

Drewes, J. E., Fox, P., & Jekel, M. (2001). Occurrence of iodinated X-ray contrast media in domestic effluents and their fate during indirect potable reuse. *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering*, *36*(9), 1633–1645. https://doi.org/10.1081/ESE-100106248

Drewes, J. E., Heberer, T., & Reddersen, K. (2002). Fate of pharmaceuticals during indirect potable reuse. In *Water Science and Technology* (Vol. 46, pp. 73–80). https://doi.org/10.2166/wst.2002.0058

Estrella, M. R., Brusseau, M. L., Maier, R. S., Pepper,', I. L., Wierenga, P. J., & Miller, R. M. (1993). *Biodegradation, Sorption, and Transport of 2,4-Dichlorophenoxyacetic Acid in Saturated and Unsaturated Soils*. *APPLIED AND ENVIRONMENTAL MICROBIOLOGY* (Vol. 59). Retrieved from http://aem.asm.org/

EPA (2017). Potable Reuse Compendium. Retrieved from: https://www.epa.gov/sites/production/files/201801/documents/potablereusecompendium_3

Fan, Z., Casey, F. X. M., Hakk, H., Larsen, G. L., & Khan, E. (2011). Sorption, fate, and mobility of sulfonamides in soils. *Water, Air, and Soil Pollution*, *218*(1–4), 49–61. https://doi.org/10.1007/s11270-010-0623-6

Greenstein, K. E., Lew, J., Dickenson, E. R. V., & Wert, E. C. (2018). Investigation of biotransformation, sorption, and desorption of multiple chemical contaminants in pilot-scale drinking water biofilters. *Chemosphere*, *200*, 248–256. https://doi.org/10.1016/j.chemosphere.2018.02.107

Gunnison, D., Zappi, M. E., Teeter, C., Pennington, J. C., & Bajpai, R. (2000). Attenuation mechanisms of N-nitrosodimethylamine at an operating intercept and treat groundwater remediation system. *Journal of Hazardous Materials*, *73*(2), 179–197. https://doi.org/10.1016/S0304-3894(99)00175-2

Hijnen, W. A. M., Jong, R., & Van Der Kooij, D. (1999). Bromate removal in a denitrifying bioreactor used in water treatment. *Water Research*, *33*(4), 1049–1053. https://doi.org/10.1016/S0043-1354(98)00306-6

Hijnen, W. A. M., Voogt, R., Veenendaal, H. R., Van der Jagt, H., & Van der Kooij, D. (1995). Bromate reduction by denitrifying bacteria. *Applied and Environmental Microbiology*, *61*(1), 239–244.

Hiscock, K. M., Lloyd, J. W., & Lerner, D. N. (1991). Review of natural and artificial denitrification of groundwater. *Water Research*, *25*(9), 1099–1111. https://doi.org/10.1016/0043-1354(91)90203-3

Idelovitch, E., & Michail, M. (1984). Soil-aquifer treatment: a new approach to an old method of wastewater reuse. *Journal (Water Pollution Control Federation)*, 936-943.

Kim, H. C., Lee, W. M., Lee, S., Choi, J., & Maeng, S. K. (2017). Characterization of organic precursors in DBP formation and AOC in urban surface water and their fate during managed aquifer recharge. *Water Research*, *123*, 75–85. https://doi.org/10.1016/j.watres.2017.06.038

Kim, W.-S., & Cunningham, J. A. (2014). Biodegradation of Bisphenol-A and 17β-Estradiol Under Alternating Aerobic/Anoxic Conditions. *Environmental Engineering Science*, *31*(5), 232–242. https://doi.org/10.1103/PhysRevD.15.1137

Laws, B. V., Dickenson, E. R. V., Johnson, T. A., Snyder, S. A., & Drewes, J. E. (2011). Attenuation of contaminants of emerging concern during surface-spreading aquifer recharge. *Science of the Total Environment*, *409*(6), 1087–1094. https://doi.org/10.1016/j.scitotenv.2010.11.021

Li, D., Alidina, M., & Drewes, J. E. (2014). Role of primary substrate composition on microbial community structure and function and trace organic chemical attenuation in managed aquifer recharge systems. *Applied Microbiology and Biotechnology*, *98*(12), 5747–5756. https://doi.org/10.1007/s00253-014-5677-8

McQuarrie, J. P., & Carlson, K. (2003). Secondary Benefits of Aquifer Storage and Recovery: Disinfection By-Product Control. *Journal of Environmental Engineering*, *129*(5), 412. https://doi.org/Article

Misra, C., Nielsen, D. R., & Biggar, J. W. (1974). Nitrogen Transformations in Soil During Leaching: III. Nitrae Reduction in Soil Columns 1. *Soil Science Society of America Journal*, *38*(2), 300-304.

Nalinakumari, B., Cha, W., & Fox, P. (2010). Effects of Primary Substrate Concentration on NDMA Transport during Simulated Aquifer Recharge. *Journal of Environmental Engineering*, *136*(4), 363–370. https://doi.org/10.1061/(ASCE)EE.1943-7870.0000168

Nham, H. T. T., Greskowiak, J., Nödler, K., Rahman, M. A., Spachos, T., Rusteberg, B., … Licha, T. (2015). Modeling the transport behavior of 16 emerging organic contaminants during soil aquifer treatment. *Science of the Total Environment*, *514*, 450–458. https://doi.org/10.1016/j.scitotenv.2015.01.096

Park, S., & Lee, W. (2018). Removal of selected pharmaceuticals and personal care products in reclaimed water during simulated managed aquifer recharge. *Science of the Total Environment*, *640–641*, 671–677. https://doi.org/10.1016/j.scitotenv.2018.05.221

Patterson, B. M., Shackleton, M., Furness, A. J., Pearce, J., Descourvieres, C., Linge, K. L., … Spadek, T. (2010). Fate of nine recycled water trace organic contaminants and metal(loid)s during managed aquifer recharge into a anaerobic aquifer: Column studies. *Water Research*, *44*(5), 1471–1481. https://doi.org/10.1016/j.watres.2009.10.044

Pereira, V. J., Linden, K. G., & Weinberg, H. S. (2007). Evaluation of UV irradiation for photolytic and oxidative degradation of pharmaceutical compounds in water. *Water Research*, *41*(19), 4413–4423. https://doi.org/10.1016/j.watres.2007.05.056

Petit, C., & Bandosz, T. J. (2010). Enhanced adsorption of ammonia on metal-organic framework/graphite oxide composites: Analysis of surface interactions. *Advanced Functional Materials*, *20*(1), 111–118. https://doi.org/10.1002/adfm.200900880

Quanrud, D. M., Hafer, J., Karpiscak, M. M., Zhang, J., Lansey, K. E., & Arnold, R. G. (2003). Fate of organics during soil-aquifer treatment: Sustainability of removals in the field. *Water Research*, *37*(14), 3401–3411. https://doi.org/10.1016/S0043-1354(02)00489-X

Quanrud, D. M., Hafer, J., Karpiscak, M. M., Zhang, J., Lansey, K. E., & Arnold, R. G. (2003). Fate of organics during soil-aquifer treatment: Sustainability of removals in the field. *Water Research*, *37*(14), 3401–3411. https://doi.org/10.1016/S0043-1354(02)00489-X

Sauvé, S., & Desrosiers, M. (2014). A review of what is an emerging contaminant. *Chemistry Central Journal*, *8*(1), 15.

Schaefer, C. E., Andaya, C., Urtiaga, A., McKenzie, E. R., & Higgins, C. P. (2015). Electrochemical treatment of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) in groundwater impacted by aqueous film forming foams (AFFFs). *Journal of Hazardous Materials*, *295*, 170–175. https://doi.org/10.1016/j.jhazmat.2015.04.024

Scheurer, M., Brauch, H. J., & Lange, F. T. (2009). Analysis and occurrence of seven artificial sweeteners in German waste water and surface water and in soil aquifer treatment (SAT). *Analytical and Bioanalytical Chemistry*, *394*(6), 1585–1594. https://doi.org/10.1007/s00216-009-2881-y

Scheytt, T. J., Mersmann, P., & Heberer, T. (2006). Mobility of pharmaceuticals carbamazepine, diclofenac, ibuprofen, and propyphenazone in miscible-displacement experiments. *Journal of Contaminant Hydrology*, *83*(1–2), 53–69. https://doi.org/10.1016/j.jconhyd.2005.11.002

Scheytt, T., Mersmann, P., Leidig, M., Pekdeger, A., & Heberer, T. (2004). Transport of pharmaceutically active compounds in saturated laboratory columns. *Ground Water*, *42*(5), 767–773. https://doi.org/10.1111/j.1745-6584.2004.tb02730.x

Scheytt, T., Mersmann, P., Lindstädt, R., & Heberer, T. (2005). Determination of sorption coefficients of pharmaceutically active substances carbamazepine, diclofenac, and ibuprofen, in sandy sediments. *Chemosphere*, *60*(2), 245–253. https://doi.org/10.1016/j.chemosphere.2004.12.042

Soh, L., Connors, K. A., Brooks, B. W., & Zimmerman, J. (2011). Fate of sucralose through environmental and water treatment processes and impact on plant indicator species. *Environmental Science and Technology*, *45*(4), 1363–1369. https://doi.org/10.1021/es102719d

Ståhl, M. (2000). The influence of organic carbon on nitrogen transformations in five wetland soils. *Soil Science Society of America Journal*, *64*(3), 1129-1136.

Steffan, R. J. (2007). *Biodegradation of 1, 4-dioxane*. SHAW ENVIRONMENTAL INC LAWRENCEVILLE NJ.

Stevenson, F. J., Nommik, H., & Vahtras, K. (1982). Retention and Fixation of Ammonium and Ammonia in Soils. https://doi.org/10.2134/agronmonogr22.c4

Strauss, C., Harter, T., & Radke, M. (2011). Effects of pH and Manure on Transport of Sulfonamide Antibiotics in Soil. *Journal of Environment Quality*, *40*(5), 1652. https://doi.org/10.2134/jeq2010.0535

Suzuki, R., Kameda, I., Takabe, Y., Nishimura, F., & Itoh, S. (2015). *Removal of Dissolved Organic Matter and Disinfection By-products Formation Potential in the Upper Layer during Soil Aquifer Treatment*. *Journal of Water and Environment Technology* (Vol. 13).

Tiedje, J. M. (1988). Ecology of denitrification and dissimilatory nitrate reduction to ammonium. *Environmental Microbiology of Anaerobes*, 179–244. https://doi.org/10.1016/j.jacc.2011.09.010

Trussell, B., Trussell, S., Qu, Y., Gerringer, F., Stanczak, S., Venezia, T., … Trussell, R. (2018). A four-year simulation of soil aquifer treatment using columns filled with San Gabriel Valley sand. *Water Research*, *144*(626), 26–35. https://doi.org/10.1016/j.watres.2018.07.012

Wang, F., Salgado, V., van der Hoek, J. P., & van Halem, D. (2018). Bromate reduction by iron(II) during managed aquifer recharge: A laboratory-scale study. *Water (Switzerland)*, *10*(4). https://doi.org/10.3390/w10040370

Wang, F., van Halem, D., Ding, L., Bai, Y., Lekkerkerker-Teunissen, K., & van der Hoek, J. P. (2018). Effective removal of bromate in nitrate-reducing anoxic zones during managed aquifer recharge for drinking water treatment: Laboratory-scale simulations. *Water Research*, *130*, 88–97. https://doi.org/10.1016/j.watres.2017.11.052

5. ENGINEERING SIGNIFICANCE

Potable reuse is the sustainable solution to the problems of strenuos water demands the world faces and will be facing in the years to come. MAR as a method of indirect potable reuse, therefore, is a process of extreme significance. Apart from providing a sustainable drinking water source, MAR also addresses the problem of land subsidence which is an issue particularly in the coastal areas. Potable reuse applications, in the past, were focussed on the use of membrane based treatment such as reverse osmosis or UV/AOP to treat wastewater effluent with the view to produce water compliant with drinking water standards. SAT at the tail end of an advanced treatment process of ozonation-biofiltration-granulated activated carbon and UV disinfection also proved to be a promising method of providing additional barriers to pathogens and contaminants present in the water, as seen in this study. This treatment train option might be a good alternative for facilities that want to opt for a more passive method of achieving additional removal of contaminants for the purposes of potable reuse. Effective pathogen removals displayed in soil column studies such as this, also means that the burden of achieving disinfection credits does not have to be put on some upstream processes like ozonation, UV andd chemical disinfection. The ability to lower ozone and/or UV dose affects the design decisions and operation of recharge facilities.

REFERENCES

Abel, C. D. T., Sharma, S. K., Malolo, Y. N., Maeng, S. K., Kennedy, M. D., & Amy, G. L. (2012). Attenuation of bulk organic matter, nutrients (N and P), and pathogen indicators during soil passage: Effect of temperature and redox conditions in simulated soil aquifer treatment (SAT). *Water, Air, and Soil Pollution*, *223*(8), 5205–5220. https://doi.org/10.1007/s11270-012-1272-8

Alidina, M., Li, D., Ouf, M., & Drewes, J. E. (2014). Role of primary substrate composition and concentration on attenuation of trace organic chemicals in managed aquifer recharge systems. *Journal of environmental management*, *144*, 58-66.

Anders, R., & Chrysikopoulos, C. V. (2006). Evaluation of factors controlling the time-dependent inactivation rate coefficients of bacteriophage MS2 and PRD1. *Environmental sciencw & technology*, *40*(10), 3237-3242.

Anders, R., & Chrysikopoulos, C. V. (2009). Transport of viruses through saturated and unsaturated columns packed with sand. *Transport in Porous Media, 76(1),* 121-138.

Banzhaf, S., & Hebig, K. H. (2016). Use of column experiments to investigate the fate of organic micropollutants - A review. *Hydrology and Earth System Sciences*, *20*(9), 3719–3737. https://doi.org/10.5194/hess-20-3719-2016

Banzhaf, S., Nödler, K., Licha, T., Krein, A., & Scheytt, T. (2012). Redox-sensitivity and mobility of selected pharmaceutical compounds in a low flow column experiment. *Science of the Total Environment*, *438*, 113–121. https://doi.org/10.1016/j.scitotenv.2012.08.041

Bertelkamp, C., Reungoat, J., Cornelissen, E. R., Singhal, N., Reynisson, J., Cabo, A. J., … Verliefde, A. R. D. (2014). Sorption and biodegradation of organic micropollutants during river bank filtration: A laboratory column study. *Water Research*, *52*, 231–241. https://doi.org/10.1016/j.watres.2013.10.068

Bitton, G., & Harvey, R. W. (1992). Transport of pathogens through soils and aquifers. *Environmental microbiology*, *19*, 103-123.

Blaustein, R. A., Pachepsky, Y., Hill, R. L., Shelton, D. R., & Whelan, G. (2013). Escherichia coli survival in waters: Temperature dependence. *Water Research*, *47*(2), 569–578. https://doi.org/10.1016/j.watres.2012.10.027

Bolong, N., Ismail, A. F., Salim, M. R., & Matsuura, T. (2009). A review of the effects of emerging contaminants in wastewater and options for their removal. *Desalination*, *239*(1–3), 229–246. https://doi.org/10.1016/j.desal.2008.03.020

Bond, T., Goslan, E. H., Parsons, S. A., & Jefferson, B. (2012). A critical review of trihalomethane and haloacetic acid formation from natural organic matter surrogates. *Environmental Technology Reviews*, *1*(1), 93–113. https://doi.org/10.1080/09593330.2012.705895

Boon, P. L., Moriarty, D. J. W., & Saffigna, P. G. (1986). Nitrate metabolism in sediments from seagrass (Zostera capricorni) beds of Moreton Bay, Australia. *Marine Biology*, *91*(2), 269-275.

Bouchard, D.C., Williams, M. K., & Surampalli, R. Y. (1992). Nitrate contamination of groundwater: sources and potential health effects. *Journal-American Water Works Association*, 84(9), 85-90.

Bouwer, H., & Rice, R. C. (1948). Renovation of Wastewater at the 23rd Avenue Rapid Infiltration Project Renovation Avenue of wastewater rapid infiltration at the project. *Water Pollution Control Federation*, *56*(1), 76–83.

Burke, V., Treumann, S., Duennbier, U., Greskowiak, J., & Massmann, G. (2013). Sorption behavior of 20 wastewater originated micropollutants in groundwater - Column experiments with pharmaceutical residues and industrial agents. *Journal of Contaminant Hydrology*, *154*, 29–41. https://doi.org/10.1016/j.jconhyd.2013.08.001

California Department of Health (CDPH) (2014). Retrieved from https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/documents/lawbook/RWregulations_20140618.pdf

Carlson, H. K., Clark, I. C., Blazewicz, S. J., Iavarone, A. T., & Coates, J. D. (2013). Fe(II) oxidation is an innate capability of nitrate-reducing bacteria that involves abiotic and biotic reactions. *Journal of Bacteriology*, *195*(14), 3260–3268. https://doi.org/10.1128/JB.00058-13

Carpenter, C., Fayer, R., Trout, J., & Beach, M. J. (1999). Chlorine disinfection of recreational water for Cryptosporidium parvum. *Emerging infectious diseases*, *5*(4), 579.

Chairez, M., Luna-Velasco, A., Field, J. A., Ju, X., & Sierra-Alvarez, R. (2010). Reduction of bromate by biogenic sulfide produced during microbial sulfur disproportionation. *Biodegradation*, *21*(2), 235–244. https://doi.org/10.1007/s10532-009-9296-5

Chrysikopoulos, C. V., & Aravantinou, A. F. (2012). Virus inactivation in the presence of quartz sand under static and dynamic batch conditions at different temperatures. *Journal of Hazardous Materials*, *233–234*, 148–157. https://doi.org/10.1016/j.jhazmat.2012.07.002

Chrysikopoulos, C. V., & Sim, Y. (1996). One-dimensional virus transport in homogeneous porous media with time-dependent distribution coefficient. *Journal of Hydrology*, *185*(1-4), 199-219.

Chrysikopoulos, C. V., & Vogler, E. T. (2004). Estimation of time dependent virus inactivation rates by geostatistical and resampling techniques: Application to virus transport in porous media. *Stochastic Environmental Research and Risk Assessment*, *18*(2), 67–78. https://doi.org/10.1007/s00477-003-0130-z

Cordy, G. E., Duran, N. L., Bouwer, H., Rice, R. C., Furlong, E. T., Zaugg, S. D., ... & Kolpin, D. W. (2004). Do pharmaceuticals, pathogens, and other organic waste water compounds persist when waste water is used for recharge?. *Groundwater Monitoring & Remediation*, *24*(2), 58-69.2004 Do pharmaceuticals, pathogens and other compounds persist when they pass through soil columns. (n.d.).

D'Alessio, M., Onanong, S., Snow, D. D., & Ray, C. (2018). Occurrence and removal of pharmaceutical compounds and steroids at four wastewater treatment plants in Hawai'i and their environmental fate. *Science of the Total Environment*, *631–632*, 1360–1370. https://doi.org/10.1016/j.scitotenv.2018.03.100

Dehwah, A. H. A., & Missimer, T. M. (2017). Seabed gallery intakes: Investigation of the water pretreatment effectiveness of the active layer using a long-term column experiment. *Water Research*, *121*, 95–108. https://doi.org/10.1016/j.watres.2017.05.014

Demirel, S., Uyanık, İ., Yurtsever, A., Çelikten, H., & Uçar, D. (2014). Simultaneous Bromate and Nitrate Reduction in Water Using Sulfur‐Utilizing Autotrophic and Mixotrophic Denitrification Processes in a Fixed Bed Column Reactor. *CLEAN–Soil, Air, Water*, *42*(9), 1185-1189.

Drewes, J. E., & Fox, P. (1999). Fate of natural organic matter (NOM) during groundwater recharge using reclaimed water. *Water Science and Technology*, 40(9), 241-248.

Drewes, J. E., Fox, P., & Jekel, M. (2001). Occurrence of iodinated X-ray contrast media in domestic effluents and their fate during indirect potable reuse. *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering*, *36*(9), 1633–1645. https://doi.org/10.1081/ESE-100106248

Drewes, J. E., Heberer, T., & Reddersen, K. (2002). Fate of pharmaceuticals during indirect potable reuse. In *Water Science and Technology* (Vol. 46, pp. 73–80). https://doi.org/10.2166/wst.2002.0058

Estrella, M. R., Brusseau, M. L., Maier, R. S., Pepper,', I. L., Wierenga, P. J., & Miller, R. M. (1993). *Biodegradation, Sorption, and Transport of 2,4-Dichlorophenoxyacetic Acid in Saturated and Unsaturated Soils*. *APPLIED AND ENVIRONMENTAL MICROBIOLOGY* (Vol. 59). Retrieved from http://aem.asm.org/

Fan, Z., Casey, F. X. M., Hakk, H., Larsen, G. L., & Khan, E. (2011). Sorption, fate, and mobility of sulfonamides in soils. *Water, Air, and Soil Pollution*, *218*(1–4), 49–61. https://doi.org/10.1007/s11270-010-0623-6

Fand, R. M., & Thinakaran, R. (1990). The Influence of the Wall on Flow Through Pipes Packed With Spheres. *Journal of Fluids Engineering*, *112*(1), 84. https://doi.org/10.1115/1.2909373

Gibert, O., Hernández Amphos, M., Vilanova, E., Cornellà, O., Wefer-Roehl, A., & Kübeck, C. (2012). *Guidelining protocol for soil-column experiments assessing fate and transport of trace organics Title: Guidelining protocol for soil-column experiments assessing fate and transport of trace organics*. Work Package: 12 Deliverable number: Partner responsible: CETaqua Deliverable author(s): Quality assurance. Retrieved from www.demeau-fp7.eu

Greenstein, K. E., Lew, J., Dickenson, E. R. V., & Wert, E. C. (2018). Investigation of biotransformation, sorption, and desorption of multiple chemical contaminants in pilot-scale drinking water biofilters. *Chemosphere*, *200*, 248–256. https://doi.org/10.1016/j.chemosphere.2018.02.107

Gunnison, D., Zappi, M. E., Teeter, C., Pennington, J. C., & Bajpai, R. (2000). Attenuation mechanisms of N-nitrosodimethylamine at an operating intercept and treat groundwater remediation system. *Journal of Hazardous Materials*, *73*(2), 179–197. https://doi.org/10.1016/S0304-3894(99)00175-2

Hebig, K. H., Nödler, K., Licha, T., & Scheytt, T. J. (2014). Impact of materials used in lab and field experiments on the recovery of organic micropollutants. *Science of the Total Environment*, *473–474*, 125–131. https://doi.org/10.1016/j.scitotenv.2013.12.004

Hijnen, W. A. M., Brouwer-Hanzens, A. J., Charles, K. J., & Medema, G. (2006). Erratum: Transport of MS2 phage, Escherichia coli, Clostridium perfringens, Cryptosporidium parvum, and Giardia intestinalis in a gravel and a sandy soil (Environmental Science and Technology (2005) 39 (7860-7868)). *Environmental Science and Technology*. https://doi.org/10.1021/es0580237

Hijnen, W. A. M., Jong, R., & Van Der Kooij, D. (1999). Bromate removal in a denitrifying bioreactor used in water treatment. *Water Research*, *33*(4), 1049–1053. https://doi.org/10.1016/S0043-1354(98)00306-6

Hijnen, W. A. M., Voogt, R., Veenendaal, H. R., Van der Jagt, H., & Van der Kooij, D. (1995). Bromate reduction by denitrifying bacteria. *Applied and Environmental Microbiology*, *61*(1), 239–244.

Hiscock, K. M., Lloyd, J. W., & Lerner, D. N. (1991). Review of natural and artificial denitrification of groundwater. *Water Research*, *25*(9), 1099–1111. https://doi.org/10.1016/0043-1354(91)90203-3

Hozalski, R. M. (2003). Evaluation of Microspheres as Surrogates for Cryptosporidium parvum Oocysts in Filtration Experiments, *37*(5), 1037–1042. https://doi.org/10.1021/es025521w

Idelovitch, E., & Michail, M. (1984). Soil-aquifer treatment: a new approach to an old method of wastewater reuse. *Journal (Water Pollution Control Federation)*, 936-943.

Kaspar, H. F., Tiedje, J. M., & Firestone, R. B. (1981). Denitrification and dissimilatory nitrate reduction to ammonium in digested sludge. *Canadian Journal of Microbiology*, *27*(9), 878–885. https://doi.org/10.1139/m81-139

Kim, H. C., Lee, W. M., Lee, S., Choi, J., & Maeng, S. K. (2017). Characterization of organic precursors in DBP formation and AOC in urban surface water and their fate during managed aquifer recharge. *Water Research*, *123*, 75–85. https://doi.org/10.1016/j.watres.2017.06.038

Kim, W.-S., & Cunningham, J. A. (2014). Biodegradation of Bisphenol-A and 17β-Estradiol Under Alternating Aerobic/Anoxic Conditions. *Environmental Engineering Science*, *31*(5), 232–242. https://doi.org/10.1103/PhysRevD.15.1137

Klitzke, S., Schroeder, J., Selinka, H. C., Szewzyk, R., & Chorus, I. (2015). Attenuation and colloidal mobilization of bacteriophages in natural sediments under anoxic as compared to oxic conditions. *Science of the Total Environment*, *518–519*, 130–138. https://doi.org/10.1016/j.scitotenv.2015.02.031

Labare, M. P., & Alexander, M. (1994). Microbial cometabolism of sucralose, a chlorinated disaccharide, in environmental samples. *Applied Microbiology and Biotechnology*, *42*(1), 173–178. https://doi.org/10.1007/BF00170242

Laws, B. V., Dickenson, E. R. V., Johnson, T. A., Snyder, S. A., & Drewes, J. E. (2011). Attenuation of contaminants of emerging concern during surface-spreading aquifer recharge. *Science of the Total Environment*, *409*(6), 1087–1094. https://doi.org/10.1016/j.scitotenv.2010.11.021

Layton, A. C., Gregory, B. W., Seward, J. R., Schultz, T. W., & Sayler, G. S. (2000). Mineralization of steroidal hormones by biosolids in wastewater treatment systems in Tennessee U.S.A. *Environmental Science and Technology*, *34*(18), 3925–3931. https://doi.org/10.1021/es9914487

Lewis, J., & Sjöstrom, J. (2010). Optimizing the experimental design of soil columns in saturated and unsaturated transport experiments. *Journal of Contaminant Hydrology*. https://doi.org/10.1016/j.jconhyd.2010.04.001

Li, D., Alidina, M., & Drewes, J. E. (2014). Role of primary substrate composition on microbial community structure and function and trace organic chemical attenuation in managed aquifer recharge systems. *Applied Microbiology and Biotechnology*, *98*(12), 5747–5756. https://doi.org/10.1007/s00253-014-5677-8

Mayotte, J. M., Hölting, L., & Bishop, K. (2017). Reduced removal of bacteriophage MS2 in during basin infiltration managed aquifer recharge as basin sand is exposed to infiltration water. *Hydrological Processes*, *31*(9), 1690–1701. https://doi.org/10.1002/hyp.11137

McCaulou, D. R., Bales, R. C., & Arnold, R. G. (1995). Effect of Temperature-Controlled Motility on Transport of Bacteria and Microspheres Through Saturated Sediment. *Water Resources Research*, *31*(2), 271–280. https://doi.org/10.1029/94WR02569

McKenzie, E. R., Siegrist, R. L., McCray, J. E., & Higgins, C. P. (2015). Effects of chemical oxidants on perfluoroalkyl acid transport in one-dimensional porous media columns. *Environmental Science and Technology*, *49*(3), 1681–1689. https://doi.org/10.1021/es503676p

McQuarrie, J. P., & Carlson, K. (2003). Secondary Benefits of Aquifer Storage and Recovery: Disinfection By-Product Control. *Journal of Environmental Engineering*, *129*(5), 412. https://doi.org/Article

Miller, J. H., Ela, W. P., Lansey, K. E., Chipello, P. L., & Arnold, R. G. (2009). Nitrogen Transformations during Soil–Aquifer Treatment of Wastewater Effluent—Oxygen Effects in Field Studies. *Journal of Environmental Engineering*, *132*(October), 1298–1306. https://doi.org/10.1061/(ASCE)0733-9372(2006)132:10(1298)

Misra, C., Nielsen, D. R., & Biggar, J. W. (1974). Nitrogen Transformations in Soil During Leaching: III. Nitrae Reduction in Soil Columns 1. *Soil Science Society of America Journal*, *38*(2), 300-304.

Murphy, E. M., & Ginn, T. R. (2000). Modeling microbial processes in porous media. *Hydrogeology Journal*, *8*(1), 142–158. https://doi.org/10.1007/s100409900043

Nalinakumari, B., Cha, W., & Fox, P. (2010). Effects of Primary Substrate Concentration on NDMA Transport during Simulated Aquifer Recharge. *Journal of Environmental Engineering*, *136*(4), 363–370. https://doi.org/10.1061/(ASCE)EE.1943-7870.0000168

Nham, H. T. T., Greskowiak, J., Nödler, K., Rahman, M. A., Spachos, T., Rusteberg, B., … Licha, T. (2015). Modeling the transport behavior of 16 emerging organic contaminants during soil aquifer treatment. *Science of the Total Environment*, *514*, 450–458. https://doi.org/10.1016/j.scitotenv.2015.01.096

Nommik, H., & Vahtras, K. (1982). Retention and fixation of ammonium and ammonia in soils. *Nitrogen in agricultural soils*, (nitrogeninagrics), 123-171.

Pang, L. (2009). Microbial Removal Rates in Subsurface Media Estimated From Published Studies of Field Experiments and Large Intact Soil Cores. *Journal of Environment Quality*, *38*(4), 1531. https://doi.org/10.2134/jeq2008.0379

Pang, L., Close, M., Goltz, M., Noonan, M., & Sinton, L. (2005). Filtration and transport of Bacillus subtilis spores and the F-RNA phage MS2 in a coarse alluvial gravel aquifer: Implications in the estimation of setback distances. *Journal of Contaminant Hydrology*, *77*(3), 165–194. https://doi.org/10.1016/j.jconhyd.2004.12.006

Park, S., & Lee, W. (2018). Removal of selected pharmaceuticals and personal care products in reclaimed water during simulated managed aquifer recharge. *Science of the Total Environment*, *640–641*, 671–677. https://doi.org/10.1016/j.scitotenv.2018.05.221

Patterson, B. M., Shackleton, M., Furness, A. J., Pearce, J., Descourvieres, C., Linge, K. L., … Spadek, T. (2010). Fate of nine recycled water trace organic contaminants and metal(loid)s during managed aquifer recharge into a anaerobic aquifer: Column studies. *Water Research*, *44*(5), 1471–1481. https://doi.org/10.1016/j.watres.2009.10.044

Peng, X., Murphy, T., & Holden, N. M. (2008). Evaluation of the effect of temperature on the die-off rate for Cryptosporidium parvum oocysts in water, soils, and feces. *Applied and Environmental Microbiology*. https://doi.org/10.1128/AEM.01442-08

Pereira, V. J., Linden, K. G., & Weinberg, H. S. (2007). Evaluation of UV irradiation for photolytic and oxidative degradation of pharmaceutical compounds in water. *Water Research*, *41*(19), 4413–4423. https://doi.org/10.1016/j.watres.2007.05.056

Petit, C., & Bandosz, T. J. (2010). Enhanced adsorption of ammonia on metal-organic framework/graphite oxide composites: Analysis of surface interactions. *Advanced Functional Materials*, *20*(1), 111–118. https://doi.org/10.1002/adfm.200900880

Pham, M., Mintz, E. A., & Nguyen, T. H. (2009). Deposition kinetics of bacteriophage MS2 to natural organic matter: Role of divalent cations. *Journal of Colloid and Interface Science*, *338*(1), 1–9. https://doi.org/10.1016/j.jcis.2009.06.025

Pourmoghadas, H., & Kinman, R. N. (2013). Relationship between nine haloacetic acids with total organic halogens in different experimental conditions. *Iranian Journal of Environmental Health Science and Engineering*, *10*(26), 1. https://doi.org/10.1186/1735-2746-10-26

Quanrud, D. M., Arnold, R. G., Wilson, L. G., Gordon, H. J., Graham, D. W., & Amy, G. L. (1996). Fate of organics during column studies of soil aquifer treatment. *Journal of Environmental Engineering*, *122*(4), 314-321.

Quanrud, D. M., Hafer, J., Karpiscak, M. M., Zhang, J., Lansey, K. E., & Arnold, R. G. (2003). Fate of organics during soil-aquifer treatment: Sustainability of removals in the field. *Water Research*, *37*(14), 3401–3411. https://doi.org/10.1016/S0043-1354(02)00489-X

Runkel, R. L. (1996). Solution of the advection-dispersion equation: continuous load of finite duration. *Journal of Environmental Engineering*, *122*(9), 830-832.

Santamaría, J., Quinonez-Diaz, M. D. J., Lemond, L., Arnold, R. G., Quanrud, D., Gerba, C., & Brusseau, M. L. (2011). Transport of Cryptosporidium parvum oocysts in sandy soil: Impact of length scale. *Journal of Environmental Monitoring*, *13*(12), 3481–3484. https://doi.org/10.1039/c1em10390c

Sasidharan, S., Torkzaban, S., Bradford, S. A., Kookana, R., Page, D., & Cook, P. G. (2016). Transport and retention of bacteria and viruses in biochar-amended sand. *Science of the Total Environment*, *548–549*, 100–109. https://doi.org/10.1016/j.scitotenv.2015.12.126

Sauvé, S., & Desrosiers, M. (2014). A review of what is an emerging contaminant. *Chemistry Central Journal*, *8*(1), 15.

Schaefer, C. E., Andaya, C., Urtiaga, A., McKenzie, E. R., & Higgins, C. P. (2015). Electrochemical treatment of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) in groundwater impacted by aqueous film forming foams (AFFFs). *Journal of Hazardous Materials*, *295*, 170–175. https://doi.org/10.1016/j.jhazmat.2015.04.024

Scheurer, M., Brauch, H. J., & Lange, F. T. (2009). Analysis and occurrence of seven artificial sweeteners in German waste water and surface water and in soil aquifer treatment (SAT). *Analytical and Bioanalytical Chemistry*, *394*(6), 1585–1594. https://doi.org/10.1007/s00216-009-2881-y

Scheytt, T. J., Mersmann, P., & Heberer, T. (2006). Mobility of pharmaceuticals carbamazepine, diclofenac, ibuprofen, and propyphenazone in miscible-displacement experiments. *Journal of Contaminant Hydrology*, *83*(1–2), 53–69. https://doi.org/10.1016/j.jconhyd.2005.11.002

Scheytt, T., Mersmann, P., Leidig, M., Pekdeger, A., & Heberer, T. (2004). Transport of pharmaceutically active compounds in saturated laboratory columns. *Ground Water*, *42*(5), 767–773. https://doi.org/10.1111/j.1745-6584.2004.tb02730.x

Scheytt, T., Mersmann, P., Lindstädt, R., & Heberer, T. (2005). Determination of sorption coefficients of pharmaceutically active substances carbamazepine, diclofenac, and ibuprofen, in sandy sediments. *Chemosphere*, *60*(2), 245–253. https://doi.org/10.1016/j.chemosphere.2004.12.042

Schijven, J. F., De Bruin, H. A. M., Hassanizadeh, S. M., & De Roda Husman, A. M. (2003). Bacteriophages and clostridium spores as indicator organisms for removal of pathogens by passage through saturated dune sand. *Water Research*, *37*(9), 2186–2194. https://doi.org/10.1016/S0043-1354(02)00627-9

Schijven, J. F., Hassanizadeh, S. M., & De Bruin, R. H. A. M. (2002). Two-site kinetic modeling of bacteriophages transport through columns of saturated dune sand. *Journal of Contaminant Hydrology*, *57*(3–4), 259–279. https://doi.org/10.1016/S0169-7722(01)00215-7

Schwartz, F. W. (1977). Macroscopic dispersion in porous media: The controlling factors. *Water Resources Research*, *13*(4), 743–752. https://doi.org/10.1029/WR013i004p00743

Sirivithayapakorn, S., & Keller, A. (2003). Transport of colloids in saturated porous media: A pore-scale observation of the size exclusion effect and colloid acceleration. *Water Resources Research*, *39*(4).

Soh, L., Connors, K. A., Brooks, B. W., & Zimmerman, J. (2011). Fate of sucralose through environmental and water treatment processes and impact on plant indicator species. *Environmental Science and Technology*, *45*(4), 1363–1369. https://doi.org/10.1021/es102719d

Ståhl, M. (2000). The influence of organic carbon on nitrogen transformations in five wetland soils. *Soil Science Society of America Journal*, *64*(3), 1129-1136.

Steffan, R. J. (2007). *Biodegradation of 1, 4-dioxane*. SHAW ENVIRONMENTAL INC LAWRENCEVILLE NJ.

Stevik, T. K., Aa, K., Ausland, G., & Hanssen, J. F. (2004). Retention and removal of pathogenic bacteria in wastewater percolating through porous media: A review. *Water Research*. https://doi.org/10.1016/j.watres.2003.12.024

Stevik, T. K., Aa, K., Ausland, G., & Hanssen, J. F. (2004). Retention and removal of pathogenic bacteria in wastewater percolating through porous media: A review. *Water Research*. https://doi.org/10.1016/j.watres.2003.12.024

Strauss, C., Harter, T., & Radke, M. (2011). Effects of pH and Manure on Transport of Sulfonamide Antibiotics in Soil. *Journal of Environment Quality*, *40*(5), 1652. https://doi.org/10.2134/jeq2010.0535

Suzuki, R., Kameda, I., Takabe, Y., Nishimura, F., & Itoh, S. (2015). *Removal of Dissolved Organic Matter and Disinfection By-products Formation Potential in the Upper Layer during Soil Aquifer Treatment*. *Journal of Water and Environment Technology* (Vol. 13).

Syngouna, V. I., & Chrysikopoulos, C. V. (2011). Transport of biocolloids in water saturated columns packed with sand: Effect of grain size and pore water velocity. *Journal of Contaminant Hydrology*, *126*, 301–314. https://doi.org/10.1016/j.jconhyd.2011.09.007

Thomas, J. M., McKay, W. A., Cole, E., Landmeyer, J. E., & Bradley, P. M. (2000). The fate of haloacetic acids and trihalomethanes in an aquifer storage and recovery program, Las Vegas, Nevada. *Groundwater*, *38*(4), 605-614.

Tiedje, J. M. (1988). Ecology of denitrification and dissimilatory nitrate reduction to ammonium. *Environmental Microbiology of Anaerobes*, 179–244. https://doi.org/10.1016/j.jacc.2011.09.010

Trussell, B., Trussell, S., Qu, Y., Gerringer, F., Stanczak, S., Venezia, T., … Trussell, R. (2018). A four-year simulation of soil aquifer treatment using columns filled with San Gabriel Valley sand. *Water Research*, *144*(626), 26–35. https://doi.org/10.1016/j.watres.2018.07.012

U.S. Environmental Protection Agency (EPA) (2017). *Potable Reuse Compendium*. Retrieved from https://www.epa.gov/sites/production/files/2018-01/documents/potablereusecompendium_3.pdf

van Der Kooij, D., Hijnen, W. A. M., & Kruithof, J. C. (1989). The Effects of Ozonation, Biological Filtration and Distribution on the Concentration of Easily Assimilable Organic Carbon (AOC) in Drinking Water. *Ozone: Science & Engineering*, *11*(3), 297–311. https://doi.org/10.1080/01919518908552443

Walshe, G. E., Pang, L., Flury, M., Close, M. E., & Flintoft, M. (2010). Effects of pH, ionic strength, dissolved organic matter, and flow rate on the co-transport of MS2 bacteriophages with kaolinite in gravel aquifer media. *Water Research*, *44*(4), 1255–1269. https://doi.org/10.1016/j.watres.2009.11.034

Wang, F., Salgado, V., van der Hoek, J. P., & van Halem, D. (2018). Bromate reduction by iron(II) during managed aquifer recharge: A laboratory-scale study. *Water (Switzerland)*, *10*(4). https://doi.org/10.3390/w10040370

Wang, F., van Halem, D., Ding, L., Bai, Y., Lekkerkerker-Teunissen, K., & van der Hoek, J. P. (2018). Effective removal of bromate in nitrate-reducing anoxic zones during managed aquifer recharge for drinking water treatment: Laboratory-scale simulations. *Water Research*, *130*, 88–97. https://doi.org/10.1016/j.watres.2017.11.052

Xiao, F., Simcik, M. F., Halbach, T. R., & Gulliver, J. S. (2015). Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in soils and groundwater of a U.S. metropolitan area: Migration and implications for human exposure. *Water Research*, *72*, 64–74. https://doi.org/10.1016/j.watres.2014.09.052

Yao, K. M., Habibian, M. T., & O'Melia, C. R. (1971). Water and Waste Water Filtration: Concepts and Applications. *Environmental Science and Technology*, *5*(11), 1105–1112. https://doi.org/10.1021/es60058a005

Yoo, H. H., Miller, J. H., Lansey, K., & Reinhard, M. (2006). EDTA, NTA, alkylphenol ethoxylate and DOC attenuation during soil aquifer treatment RID A-1006-2008. *Journal of Environmental Engineering-Asce*, *132*(6), 674–682. https://doi.org/10.1061/(ASCE)0733-9372(2006)132:6(674)

Zhao, Q., Xue, S., You, S., & Wang, L. (2007). Removal and transformation of organic matter during soil-aquifer treatment. *Journal of Zhejiang University-SCIENCE A*, *8*(5), 712–718. https://doi.org/10.1631/jzus.2007.A0712

APPENDIX

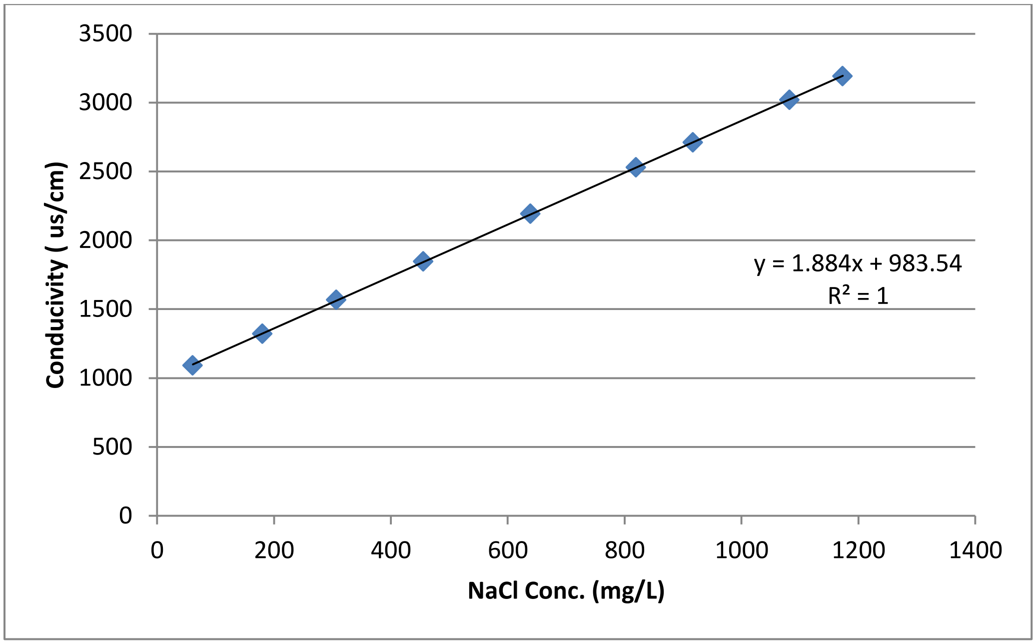
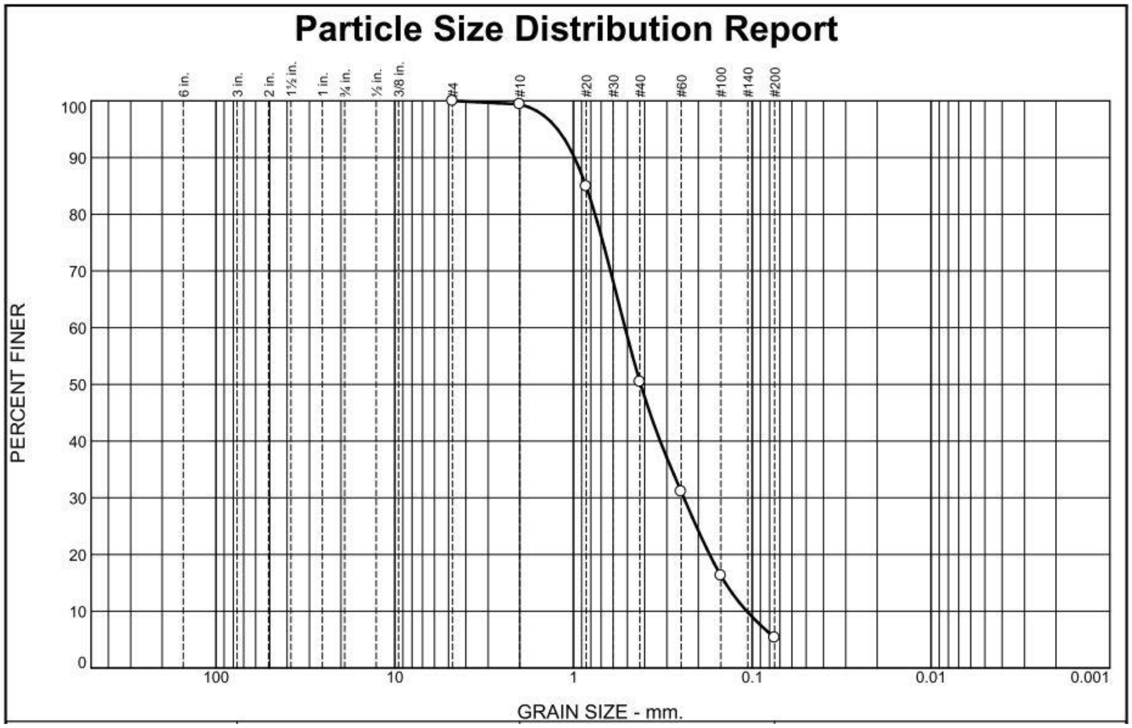


Figure 27: Change in conductivity values as a result of changing Sodium chloride concentration in water



% +3"	% Gravel	% Sand		% Fines	
		Coarse	Fine	Silt	Clay
0.0	0.8	48.8	44.7	5.7	

SIEVE SIZE	PERCENT FINER	SPEC.* PERCENT	PASS? (X=NO)
#4	100.0		
#10	99.2		
#20	82.6		
#40	50.4		
#60	31.2		
#100	16.7		
#200	5.7		

* (no specification provided)

Material Description

(SP-SM) FINE TO MEDIUM POORLY-GRADED SAND, with Silt, Light-Grey

Atterberg Limits

PL= NP LL= NP PI= NP

Coefficients

D_{90}= 1.0720 D_{85}= 0.9085 D_{60}= 0.5216
D_{50}= 0.4211 D_{30}= 0.2410 D_{15}= 0.1389
D_{10}= 0.1041 C_u= 5.01 C_c= 1.07

Classification

USCS= SP-SM AASHTO= A-1-b

Remarks

Figure 28: Particle size distribution for the washed and sieved sand used for column construction

Table 23: List of emerging pollutants and their categories

Compound	Type
N-Nitroso dimethylamine (NDMA)	DBP
TCEP	Flame retardant
TCPP	Flame retardant
TDCPP	Flame retardant
1,7-Dimethylxanthine	Food derivative
Caffeine	Food derivative
Theobromine	Food derivative
Ethylparaben	Food derivative
Sucralose	Artificial Sweetener
Acesulfame-K	Artificial Sweetener
Bromacil	Herbicide
Chloridazon	Herbicide
Chlorotoluron	Herbicide
DACT	Herbicide
Diuron	Herbicide
Isoproturon	Herbicide
Linuron	Herbicide
OUST (Sulfameturon,methyl)	Herbicide
Propazine	Herbicide
Simazine	Herbicide
Andorostenedione	Hormone
Progesterone	Hormone
Testosterone	Hormone
Estradiol	Hormone
Estriol	Hormone
Estrone	Hormone
Ethinyl Estradiol - 17 alpha	Hormone
17 alpha-ethynylestradiol	Hormone
17-beta-Estradiol	Hormone
4-androstene-3,17-dione	Hormone
Equilin	Hormone
Estriol	Hormone
Estrone	Hormone
Testosterone	Hormone
1,4-dioxane	Industrial by-product
BPA	Industrial by-product
Butylparaben	Personal Care Product
Isobutylparaben	Personal Care Product
Methylparaben	Personal Care Product
Propylparaben	Personal Care Product
Triclocarban	Personal Care Product
Atrazine	Pesticide
Cyanazine	Pesticide
DEA	Pesticide

DEET	Pesticide
DIA	Pesticide
Metazachlor	Pesticide
2,4-D	Pesticide
Acetaminophen	Pharmaceutical
Albuterol	Pharmaceutical
Amoxicillin (semi-quantitative)	Pharmaceutical
Atenolol	Pharmaceutical
Bezafibrate	Pharmaceutical
Carbadox	Pharmaceutical
Carbamazepine	Pharmaceutical
Carisoprodol	Pharmaceutical
Cimetidine (semi quantitative)	Pharmaceutical
Cotinine	Pharmaceutical
Dehydronifedipine	Pharmaceutical
Diazepam	Pharmaceutical
Dilantin	Pharmaceutical
Diltiazem	Pharmaceutical
Erythromycin	Pharmaceutical
Flumeqine	Pharmaceutical
Fluoxetine	Pharmaceutical
Ketoprofen	Pharmaceutical
Ketorolac	Pharmaceutical
Lidocaine	Pharmaceutical
Lincomycin	Pharmaceutical
Lopressor	Pharmaceutical
Meclofenamic Acid	Pharmaceutical
Meprobamate	Pharmaceutical
Nifedipine (semi quantitative)	Pharmaceutical
Norethisterone	Pharmaceutical
Oxolinic acid	Pharmaceutical
Pentoxifylline	Pharmaceutical
Phenazone	Pharmaceutical
Primidone	Pharmaceutical
Quinoline	Pharmaceutical
Sulfachloropyridazine	Pharmaceutical
Sulfadiazine	Pharmaceutical
Sulfadimethoxine	Pharmaceutical
Sulfamerazine	Pharmaceutical
Sulfamethazine	Pharmaceutical
Sulfamethizole	Pharmaceutical
Sulfamethoxazole	Pharmaceutical
Sulfathiazole	Pharmaceutical
Theophylline (semi-quantitative)	Pharmaceutical
Thiabendazole	Pharmaceutical
Trimethoprim	Pharmaceutical
Bendroflumethiazide	Pharmaceutical
Butalbital	Pharmaceutical
Chloramphenicol	Pharmaceutical

Clofibric Acid	Pharmaceutical
Diclofenac	Pharmaceutical
Gemfibrozil	Pharmaceutical
Ibuprofen	Pharmaceutical
Naproxen	Pharmaceutical
Triclosan	Pharmaceutical
Warfarin	Pharmaceutical
Perchlorate	Propellant/Fertilizer
Iohexal	X-ray contrasting agent
Iopromide	X-ray contrasting agent
4-nonylphenol - semi quantitative	Surfactant
4-tert-Octylphenol	Surfactant
Perfluoro octanesulfonic acid - PFOS	Surfactant
Perfluoro-1-butanesulfonic acid -PFBS	Surfactant
Perfluoro-1-hexanesulfonic acid - PFHX	Surfactant
Perfluoroheptanoic acid - PFHpA	Surfactant
Perfluoro-n-nonanoic acid -PFNA	Surfactant
Perfluorooctanoic acid - PFOA	Surfactant