Evaluation of Contaminant Removal Through Soil Aquifer Treatment by a Lab Scale Soil Column Experiment Including a Trace Contaminant Spike Test

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ABSTRACT

Soil aquifer treatment (SAT), the removal of contaminants during percolation through soil, is a

strategy employed in managed aquifer recharge (MAR), one method of indirect potable water

reuse. As part of Hampton Roads Sanitation District's (HRSD) MAR project, The Sustainable

Water Initiative for Tomorrow (SWIFT), a soil column study was performed using four columns

filled with sand taken from the Potomac Aquifer System (PAS) as well as water from various

stages in SWIFT's 1MGD demonstration facility. Two pairs of two columns were operated in

series, simulating 3 days and 1 month of travel time through aerobic to anaerobic conditions.

During Phase 1 of testing, each pair of columns was fed from different stages in the SWIFT

treatment process. During Phase 2 of testing, one set of columns was spiked with a conservative

tracer bromide, and several contaminants of emerging concern (CECs). The contaminants

monitored during both phases included total organic carbon (TOC), nitrogen species, and the

disinfection byproducts bromate and NDMA. During Phase 2 of testing, CECs, iron, arsenic,

bromide, and sulfate were monitored in addition to those monitored during Phase 1. About 50%

of the TOC was removed within 3 days of travel time, with no additional removal observed in 1

month. Nitrate was conserved in the 3-day columns, but completely removed after 1 month,

indicating denitrification. Bromate and NDMA were reduced significantly in the 3-day columns

and mostly non-detect in the 1-month effluent. Many of the spiked CECs were reduced

significantly in the 3-day column indicating degradation. Three compounds exhibited some

retardation through both columns but were not degraded. A few compounds, notably

perfluorooctanoic acid (PFOA), showed no retardation or degradation.

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GENERAL AUDIENCE ABSTRACT

In order to continue to meet the water demands of the future, potable reuse is a necessary and effective solution. HRSD's SWIFT project aims to create a sustainable source of drinking water through advanced treatment of its wastewater effluent and subsequent recharge of the Potomac Aquifer in a process known as managed aquifer recharge (MAR). During MAR, chemical and biological contaminants are attenuated or removed through a process known as soil aquifer treatment (SAT). HRSD installed pilot-scale soil columns at their 1MGD SWIFT demonstration facility to evaluate the potential removal of contaminants. During the study, removal of contaminants, both regulated and unregulated, was observed. This study demonstrated that SAT provides an effective environmental barrier against many contaminants and helped to inform the level of treatment necessary to protect public health during MAR potable reuse projects.

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INTRODUCTION

Managed Aquifer Recharge

Because of health concerns around the consumption of reclaimed wastewater, direct potable reuse, i.e. recycling of wastewater directly into the potable water system without dilution or additional environmental barriers, is not yet a widely accepted strategy. Managed aquifer recharge (MAR) is one strategy of introducing an environmental barrier into the water reuse cycle. MAR projects involve either surface spreading (Fox et al., 2001; Zhou et al., 2009; Schmidt et al., 2012; Laws et al., 2011; Valhondo et al., 2015) or direct injection into an aquifer in order to replenish the supply of groundwater. The quality of the water varies greatly from project to project, ranging from raw wastewater, to treated wastewater, and advanced treated wastewater. Often, MAR is used to store treated drinking water in areas that have seasonally variable sources of fresh water. This practice is referred to as aquifer storage and recovery (ASR).

For water reuse, the US EPA recommends filtration and disinfection of treated wastewater for surface spreading operations but an additional advanced oxidation step for direct injection. In California, conventional filtration and disinfection are required for surface spreading, whereas reverse osmosis (RO) and advanced oxidation are required as pretreatment prior to direct injection (DDW, 2015). This additional required treatment is attributed to the utilization of the vadose zone during surface spreading which is where the bulk of pathogen and organic contaminant removal occurs (National Research Council, 1998). Because the vadose zone provides additional treatment at little cost, wastewater reuse projects utilizing direct injection, e.g. Orange County Water District's Groundwater Replenishment System, have been relatively rare and have utilized RO in their treatment process (US EPA, 2017).

So far little research has focused on the removal of contaminants by soil aquifer treatment in saturated conditions that would otherwise be well removed by RO, e.g. pharmaceuticals and perfluorinated compounds. Additionally, some nutrients that are removed by RO could contribute to the growth of a microbiological community capable of degrading trace compounds.

SWIFT Project Overview

The Sustainable Water Initiative for Tomorrow (SWIFT) project is an indirect potable water reuse project with the goal of replenishing the Potomac Aquifer System (PAS). Hampton Roads Sanitation District (HRSD) plans to build advanced water treatment systems at five of its existing wastewater treatment plants. The advanced water treatment plants will treat wastewater to potable standards before injecting the treated effluent into the Potomac Aquifer. Injection into the aquifer, as opposed to direct potable reuse, provides multiple benefits. The Potomac Aquifer is a confined system that does not receive large amounts of natural recharge. Over time, withdrawal rates have greatly outstripped recharge rates, decreasing the overall pressure in the aquifer. This decreased pressure not only makes withdrawal from the aquifer more difficult, but also allows for saltwater intrusion as the aquifer is adjacent to the Atlantic Ocean. Additionally, decreasing pressure in the aquifer exacerbates the effects of land subsidence, a growing concern in the Tidewater region of Virginia. Recharge into the aquifer from the SWIFT project could help to relieve the stress put on the Potomac Aquifer by overpumping. While the planned SWIFT recharge capacity of 100MGD may not fully match the current withdrawal capacity in the region, the pressure created from injection into the aquifer could still have a substantial effect (CH2M, 2016).

Another additional benefit of indirect potable reuse through MAR is the additional treatment gained through soil aquifer treatment (SAT). SAT is the process of contaminant attenuation,

retardation, and removal during transport through soil. Contaminants may be removed via straining (turbidity and pathogens), adsorption to soil and minerals (organics and metals), or chemical and biological degradation (organics, disinfection byproducts, and nutrients).

Currently, HRSD recharges water into the PAS at a 1 million gallon per day (MGD) capacity demonstration facility at its Nansemond Wastewater Treatment Plant (WWTP) in Suffolk, VA. The 1MGD advanced treatment facility uses Nansemond Treatment Plant's secondary clarifier effluent as its influent water source. The advanced treatment train consists of coagulation, flocculation, and sedimentation followed by ozonation and biofiltration. After biofiltration, the water is treated by granular activated carbon (GAC) filters and ultraviolet (UV) disinfection before recharge via an injection well. A low dose of monochloramine (NH_2Cl) is added to the SWIFT water to protect the recharge well from biofouling and the pH is adjusted to prevent corrosion of the well and metals mobilization in the aquifer. The process flow diagram for the SWIFT demonstration facility is shown in Figure 1.

SWIFT RESEARCH CENTER PROCESS FLOW DIAGRAM
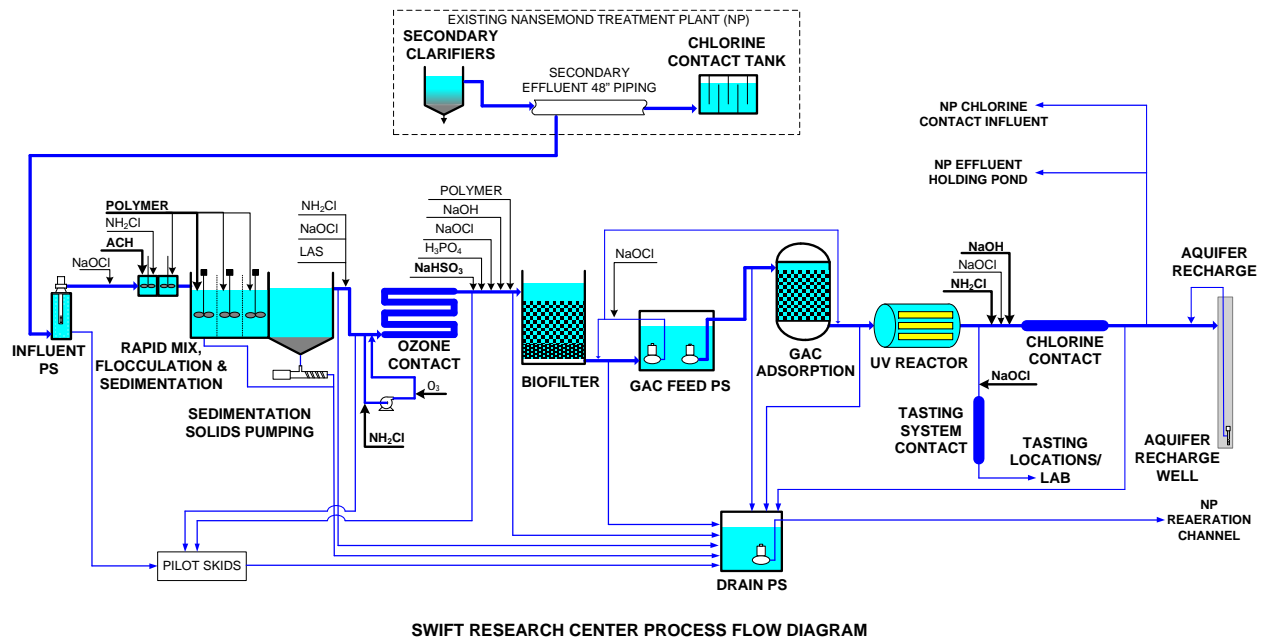
Figure 1: Process flow diagram for the 1MGD SWIFT demonstration facility at HRSD's Nansemond Treatment plant site. Chemical addition points in bold were in use during the testing period, non-bolded chemicals are potential addition points not in use

The SWIFT program follows all primary maximum contaminant limits (PMCLs) set by the Safe Drinking Water Act (SDWA). In addition to these limits, the SWIFT program has set limits on total nitrogen (TN) and total organic carbon (TOC) and has set action limits for 18 non-regulatory performance indicators (see Tables 1 and 2). Of the 18 compounds, some have public health concerns associated with their presence, e.g. n-nitrosodimethylamine (NDMA), 1,4-dioxane. Other indicator compounds are representative of the effectiveness of treatment but are not suspected to have adverse health effects at realistic environmental concentrations, e.g. sucralose.

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Table 1: SWIFT Program TOC and TN Limits

	Daily Maximum	Monthly Average
TOC	6mg/L	4mg/L
TN	8mg/L-N	5mg/L-N

Table 2: List of non-regulatory performance indicators chosen by the SWIFT program to evaluate removal of CECs

	Notification/Health Advisory Limits
Public Health	
1,4-Dioxane	1µg/L
17-β-Estradiol	TBD
DEET	200µg/L
Ethinyl Estradiol	TBD
TCEP	5µg/L
NDMA	10ng/L
Perchlorate	6µg/L
PFOA+PFOS	70ng/L (combined)
Treatment Effectiveness	
Cotinine	1µg/L
Primidone	10µg/L
Dilantin (Phenytoin)	2µg/L
Meprobamate	200µg/L
Atenolol	4µg/L
Carbamazepine	10µg/L
Estrone	320µg/L
Sucralose	150mg/L
Triclosan	2100µg/L

HRSD has installed four wells on the Nansemond Treatment Plant site to monitor the potential transport of contaminants. The first monitoring well is located 50ft from the recharge well and is able to sample from 11 discrete depth ranges corresponding to similarly screened depths in the recharge well. The other three wells are located 400, 450, and 500ft away from the recharge well. They sample from the three different major divisions of the Potomac Aquifer: the Upper

Potomac Aquifer (UPA), Middle Potomac Aquifer (MPA), and Lower Potomac Aquifer (LPA). Before start of operations, the estimated travel time to the 50ft well was an average of three days varying by screen. The estimated travel time to the further conventional wells was on the order of months to years. The estimated 3-day travel time to the 50ft well was used for the design of the pilot-scale soil columns at SWIFT Research Center.

SAT Project Objectives

Soil columns were initially installed at the SWIFT pilot facility at HRSD's York River Treatment Plant in 2017. The SWIFT pilot, including the soil columns, was moved to Nansemond Treatment Plant after the construction of the 1MGD SWIFT Demonstration Facility in 2018. Since that time, it has continued to operate using water from the 1MGD SWIFT facility, monitoring contaminant transport during SAT. While operating at York River, the columns were used to evaluate the transport and attenuation of chemical and biological contaminants including pathogens, TOC, nitrogen compounds, disinfection byproducts (DBPs), and contaminants of emerging concern (CECs). While the removal of bulk TOC and nitrogen compounds was well defined, the low influent concentration of DBPs and the variable influent concentration of CECs made evaluating their removal difficult. Many compounds of interest were never observed in the influent or observed very near detection limit, making the determination of their potential removal impossible (Pradhan, 2018).

The removal of the DBPs bromate and NDMA during SAT is of particular interest as the SWIFT treatment train takes specific steps to either remove or prevent the formation of these compounds. Monochloramine is added during ozonation to inhibit bromate formation. While effective, monochloramine may also inhibit the advanced oxidation of certain compounds during ozonation, e.g. 1,4-dioxane and meprobamate, via suppression of hydroxyl radicals (Pearce,

2018). Monochloramine addition also effectively lowers the amount of nitrogen permitted in the influent to a SWIFT plant as little to no nitrogen removal is expected prior to recharge. This potentially increases supplemental carbon addition requirements at the upstream wastewater plant. NDMA, another major DBP formed during ozonation, is well removed via direct photolysis with UV. However, controlling UV dose based on NDMA photolysis may require more energy than controlling dose based on disinfection, lowering the efficiency of the overall treatment process.

The main objective of this study was to evaluate the removal of relevant contaminants that were not observed or observed at very low concentrations in the soil column influent during normal operation of the pilot at York River Treatment Plant. These contaminants were not observed in the influent either due to absence from the York River Treatment Plant influent or due to the various conventional and advanced water treatment processes before injection into the soil columns. Additionally, this study evaluated the removal of DBPs at concentrations representing little to no controls on their formation and removal during advanced treatment. Evaluating the removal of these contaminants is important to future design of MAR reuse projects as contaminant concentration may vary drastically regionally, temporally, or with varying levels of treatment.

LIT REVIEW

Soil Column Studies

Soil column studies are used to predict solute transport and attenuation in an aquifer. The most commonly studied parameter during soil column studies is TOC (Sharma et al., 2008). However, removal of several classes of contaminants including trace organic compounds (Trussell et al.,

2018; Laws et al., 2011), nitrogen species (Fronczyk et al., 2016), and pathogens (Pradhan, 2018) is possible in the subsurface. In addition to contaminant removal, mobilization of contaminants (usually metals) is also possible and has also been studied using soil columns (Burton et al., 2011; Lim et al., 2007).

Column Materials and Packing

In soil column experiments all materials used should be inert, non-corrosive, and non-sorptive. Column material is usually stainless steel, glass, or a non-sorptive plastic e.g. polyvinylchloride (PVC). The column material should not allow for light penetration to avoid enhancing phototrophic microbial growth as well as photolytic decay of contaminants. Another consideration is the type of tubing used. Hebig et al, 2014 demonstrated that certain trace compounds adsorb over time to flexible plastic materials, e.g. Tygon and silicone tubing. Higher density plastics, e.g. Teflon, High Density Polyethylene (HDPE) were found to have much less sorptive capacity and are therefore generally preferred. Column dimensions are also a consideration during design. Columns with a large diameter to height ratio have issues with transversal dispersion. However, columns with a small diameter to height ratio allow for sideflow to become a significant portion of the total flow through the column (Banzhaf and Hebig, 2016). Lewis and Sjöstrom, 2010 recommended a 4:1 column height to diameter ratio to avoid both flow path issues.

Soil column studies use one of two packing methods for introduction of media into the column: monolithic (undisturbed) and packed (disturbed). Undisturbed columns utilize core samples of soil as their column media. These columns more closely represent the conditions in the immediate vicinity of the core sample but are harder to obtain and transport. They also allow for channeling or short circuiting, which makes interpretation of fate and transport data much more

difficult. Packing columns involves compacting the media during introduction into the column, usually with water. This method allows for much more homogenous column media but has been sometimes been shown to overestimate removal of contaminants (Lewis and Sjöstrom, 2010).

Column Operation

Soil column experiments are used to simulate both saturated and unsaturated (vadose) zones of aquifers. In order to simulate saturated conditions, soil columns are usually operated with the influent being pumped into the bottom of the columns. This ensures that no additional aeration takes place during the introduction of water into the column. When simulating a vadose zone, soil columns are fed from the top of the column, sometimes in batches (Linlin et al., 2011), to allow the water to percolate through an unsaturated zone providing additional aeration.

In order to simulate long travel times, either very slow flow rates or very long columns are required. Sharma et al., 2008 found that travel time, not distance has much more influence on removal of contaminants. In order to save space, instead of increasing column length, columns are sometimes run in series (Trussell, Abel et al., 2013; Wang et al., 2018 (2)). As sampling directly along a soil column can significantly affect flow (depending on column flow rates), running columns in series allows for unobtrusive intermediate sample points.

Fate and Transport of Solutes

The bulk of soil column studies are focused on the transport and attenuation of chemical solutes including TOC, nitrogen species, DBPs and DBP formation potential, trace contaminants, and metals. Some of these compounds, e.g. nitrate, arsenic, are regulated. Other compounds, e.g. NDMA are relevant as they are suspected to be harmful to human health and regulation is anticipated in the future. Some trace compounds, e.g. carbamazepine, are not suspected to be

harmful, but are surrogates for a certain class of compounds. The removal of indicator compounds is therefore indicative of a general attenuation of that class of compound (EPA, 2017).

Tracer Compounds

In order to evaluate the properties of soil column media, e.g. porosity, dispersivity, tracer tests are often employed. A tracer test involves adding a specific tracer compound to a system and measuring the change in that compound's concentration a certain distance away. Based on the change in concentration over time, a breakthrough curve (BTC) can be developed and the effects of advection and dispersion in the system can be determined. There are several factors to consider when choosing a conservative tracer compound. As the tracer is meant to track the flow of water, the compound should be highly mobile in water. This means the compound must be highly soluble in water and must not be influenced by sorption to the column media. The compound must also be non-reactive in the system into which it is introduced. For example, readily biodegradable compounds cannot be used in biologically active columns. The tracer should also not affect the transport of other compounds, especially when active monitoring of other compounds is concurrent with the tracer test. The compound is ideally easy to measure at relatively low concentrations so that a high influent concentration is not necessary to obtain a well resolved BTC. Due to these considerations, small, inorganic anions are the most common choice for tracer tests, e.g. Cl^- (McQuarrie and Carlson, 2003; Schmidt et al., 2012), Br^- (Hohn et al., 2006; Patterson et al., 2011; Trussell et al., 2018), and SO_4^{2-} (Fox et al., 2001).

Organic Carbon

A major goal of many MAR projects is the reduction of organic carbon (Sharma et al, 2008). While organic carbon itself is not regulated, DBPs formed by the reaction of organic carbon with chlorine are regulated. Therefore, although DBP formation potential is not perfectly correlated with TOC, it is generally desirable for drinking water sources to have low concentrations of organic carbon. TOC can also be an indicator of the presence of harder to quantify or identify trace organic compounds (TOrCs) sourced from wastewater. As with DBP formation potential, the correlation between TOC and TOrCs is not perfect, however, TOC can be used as one tool in characterizing the wastewater fraction of reuse water.

Since TOC is a bulk measurement of a large suite of compounds and does not fully describe the nature of the carbon in water, other methods of characterization are necessary. One such method is UVT-254, a measurement of the transmittance of ultraviolet light at a wavelength of 254nm. The 254nm wavelength is associated with a carbon-carbon double bond and therefore higher absorbance (lower transmittances) are associated with a higher organic carbon content. Specific UV absorbance (SUVA) is the UVT-254 measurement normalized for TOC concentration. SUVA can therefore be used to compare the character of organic carbon in two waters with different TOC concentrations (Zhang et al., 2015).

During soil aquifer treatment of recycled water, TOC generally decreases as travel time through soil increases. TOC removal during SAT can be attributed mainly to sorption (Mansell et al., 2004) and biodegradation/assimilation (Essandoh et al., 2011; Trussell et al., 2018;). Sorption to aquifer media is a major contributor to TOC reduction when the organic fraction of the soil is particularly high. This is sometimes the case in surface spreading, treatment wetlands, and riverbank filtration operations (Burke et al., 2013; Bertelkamp et al., 2012). When the organic

fraction of soil is low, as is common during direct injection operations (Patterson et al., 2011),

the majority of TOC removal can be attributed to biodegradation and biological assimilation.

Apart from travel time, the main factor affecting TOC reduction during soil aquifer treatment is

the redox conditions in the aquifer. More TOC degradation is generally observed in aerobic

conditions compared to anoxic/anaerobic in numerous studies (Abel et al., 2012; Bertelkamp et

al., 2016; Kahl et al., 2017; Lekkerkerker-Teunissen et al., 2012). This is due to the greater

energetic yield of the oxygen reduction reaction, compared to other potential electron acceptors:

nitrate, iron, sulfate, and organic carbon.

Another consideration affecting TOC removal during SAT is the fraction of TOC that is readily

biodegradable. In a column study simulating wastewater travelling in saturated conditions,

Essandoh et al., 2011 observed the majority of the DOC reduction in the first 100mm of the

column. This fraction of biodegradable carbon is highly dependent on the source of recharge

water, including the upstream treatment processes prior to recharge. For instance, ozonation may

convert recalcitrant carbon to more degradable or assimilable carbon through oxidation.

Nitrogen

Various nitrogen species including ammonia, nitrite, nitrate, and organic nitrogen are present in

wastewater. While wastewater utilities typically monitor their nitrogen from a TN perspective,

drinking water is regulated with respect to specific compounds. The Safe Drinking Water Act

regulates nitrate and nitrite to 10mg/L-N and 1mg/L-N, respectively. There are a number of

transformations nitrogen compounds can undergo in groundwater whether during MAR

operations or natural recharge. Reduced nitrogen species (TKN) can be assimilated into

microorganisms or, in the presence of oxygen, nitrified to the more oxidized species, nitrate.

Because oxygen is a strong electron acceptor, nitrification is most common in the vadose zone of surface spreading operations or in the immediate vicinity of a direct injection well if there is dissolved oxygen (DO) present in the finished water. Denitrification, the transformation from the oxidized nitrate to reduced nitrogen gas, also often occurs in the subsurface. In order for nitrate to be reduced, it requires the absence of oxygen and the presence of an electron donor in the form of organic carbon or reduced mineral species. As such, reduction occurs deeper in an unconfined aquifer or further away from an injection zone. Fronczyk et al., 2016 and Valhondo et al., 2015 observed robust denitrifying conditions established in soil with a high percentage of organic carbon available. Fronczyk et al. also observed a decrease in ammonia across a column with high organic content, which was attributed to sorption. No nitrate sorption was observed in any soil type.

Denitrification coupled to mineral oxidation has been reported on both the micro (Parmentier et al., 2014; Yang et al., 2018; Hayakawa et al., 2013) and macro scale (Roques et al., 2018; Herrmann et al., 2017; Pauwels et al., 2010; Smith et al., 2017; Craig et al., 2010). Reduced iron is the most commonly reported mineral species to serve as an electron donor. Reported reduced iron species include zero-valent iron (Fe^0), pyrite (FeS_2), siderite ($FeCO_3$), biotite, and dissolved Fe^{2+}. Andre, et al. 2011 observed nitrate reduction coupled to pyrite, but only after the addition of acetate to act as a carbon source. Sulfur oxidation coupled to nitrate reduction has also been reported. In Ju et al., 2006 elemental sulfur as well as sulfide produced from sulfur disproportionation were found to reduce nitrate. The sulfur was oxidized fully to sulfate in these studies.

Bromate

Bromate (BrO_3^-) is a disinfection byproduct formed during advanced oxidation of water
containing bromide. It is a suspected carcinogen and is regulated by the SDWA not to exceed a
concentration of 10μg/L in drinking water. Since advanced oxidation followed by MAR is a
relatively rare process, there are few studies that have investigated the removal of bromate
through SAT. Hubner et al., 2016 and Hijnen et al., 1995 observed no bromate removal in oxic
conditions, despite the fact that bromate reduction to bromide is more energetically favored than
both nitrate and oxygen reduction (Kirisits and Snoeyink, 1999). This implies that kinetics is a
large factor in determining which electron acceptor is used: oxygen or bromate. In most studies,
bromate removal occurred either at the same time or after nitrate reduction. Some studies suggest
that this co-occurrence is due to denitrifiers that are also capable of reducing bromate. This is
supported by Wang et al., 2018 (2), which observed very high bromate reduction in a
denitrifying reactor followed by a sharp decrease in reduction when the nitrate feed was
removed. Other studies have observed more rapid reduction of bromate when coupled with sulfur
(Demirel et al., 2014; Chairez et al., 2009) and iron (Fan et al., 2006; Wang et al., 2018 (1))
oxidation, as opposed to oxidation of organics. In these studies, nitrate hardly competed with
bromate for electron donors. However, these were batch and culture studies and bromate
reduction coupled to mineral oxidation has not yet been observed on a larger scale.

N-Nitrosodimethylamine

NDMA is a disinfection byproduct, not currently regulated by the SDWA. It is formed via
ozonation and monochloramination of water containing NDMA precursors. NDMA is a
suspected carcinogen, which has a health advisory limit in the low ng/L range varying on the
locality (EPA, 2017). It is highly soluble in water, having a low K_{ow} and Henry's Law constant.

Gunnison et al., 2000 observed very low sorption of NDMA to various types of soils, confirming its potential mobility during MAR. A number of studies (Gunnison et al., 2000; Weidhaas and Dupont, 2013; Zhou et al., 2009) have observed significant to complete biodegradation of NDMA under aerobic conditions. Others have noted that NDMA degrades in both anoxic and anaerobic conditions (Nalinakumari et al., 2010; Trussell et al., 2018; Drewes et al., 2006; Patterson et al., 2012). Generally, these studies observed faster degradation rates in aerobic conditions compared to anoxic and anaerobic. A long acclimation period (on the order of months) before significant NDMA degradation was observed for most of these studies. Nalinakumari et al. suggested that NDMA removal is enhanced by increased TOC concentrations and may be cometabolic, however was not able to identify a specific cometabolic substrate. Szecsody et al., 2008 found that NDMA degraded readily in most redox conditions, but most quickly in oxic conditions with the addition of propane. Weidhaas et al., 2013 observed increased NDMA removal with addition of methane as a cosubstrate.

1,4-Dioxane

1,4-dioxane is an organic compound common in legacy solvents and often found in WWTPs at concentrations above or near the EPA health advisory limit of 1µg/L. Because of its recalcitrant nature and high solubility in water, 1,4-dioxane is also a common groundwater pollutant, often seen in sites contaminated by chlorinated solvents, e.g. PCE (Karges et al., 2018). Advanced oxidation is the most effective and widespread strategy for 1,4-dioxane degradation, however, some biodegradation of 1,4-dioxane has been observed. Various studies (Parales et al., 1994; Barajas-Rodriguez and Freedman, 2018; Inoue et al., 2018) have isolated, through cultures or batch reactors, microorganisms capable of degrading 1,4-dioxane either cometabolically or as the sole carbon and energy source. While most studies observe inhibition of 1,4-dioxane degradation

in the absence of oxygen, Shen et al., 2007 observed enhanced biological degradation of 1,4-dioxane in batch reactors in anaerobic, Fe(III)-reducing conditions.

1,4-dioxane degradation via hydroxide (OH) radical reactions is well reported. As such, one method of 1,4-dioxane degradation is via Fenton-like reactions involving Fe (II) and an oxidant. Yan et al., 2018 used natural sediment as an iron source with the addition of oxidants (persulfate and hydrogen peroxide) to achieve in-situ 1,4-dioxane degradation. Zeng et al., 2018 observed similar 1,4-dioxane degradation from OH radicals produced from the oxidation of iron-containing clay minerals. In this study, oxygen was used to produce the necessary hydroxide radicals.

Degradation of 1,4-dioxane on a larger scale is slower and less commonly reported. Nishimura et al., 2014 conducted soil column studies on effluent from an A2O wastewater plant. Approximately 25% removal was observed in lab-scale column experiments. No additional removal was observed with increased hydraulic retention time (HRT) and negligible removal was observed on a separate, larger-scale reactor. Natural attenuation of 1,4-dioxane in groundwater was reported by Chiang et al., 2008. In this study, a half-life of 7 years best fit the observed decreases in concentration at the affected site.

Perfluorinated Alkyl Substances

Perfluorinated/polyfluorinated alkyl substances (PFAS) is a term representing a large suite of compounds characterized by a carbon-fluorine bond. PFAS compounds have a variety of uses in different industries. They are found in many water-resistant products, such as Teflon. PFAS is also a groundwater contaminant often found near airforce bases and other sites that use it in aqueous film forming fire-fighting foams (Guelfo et al., 2018). Due to the strength of the carbon-

fluorine bond, PFAS compounds are highly recalcitrant and are not degraded biologically or chemically in standard conditions. Sorption onto activated carbon and RO are the most effective current technologies for treating PFAS. The sorptive behavior of a given PFAS compound depends on its chemical structure, with longer chain compounds generally sorbing more than shorter, and sulfonic acids sorbing more than carboxylic acids. This general trend was observed by Hansen et al., 2010, who measured sorption of PFAS to GAC media. Siriwardena et al., 2019 observed a preferential sorption of perfluorooctanoic acid (PFOA) vs. perfluorooctanesulfonic acid (PFOS) to GAC. Hamid et al., 2018 observed more short chain perfluoroalkyl acids (PFAAs) compared to longer chain in a review of fate of PFASs in landfill leachate, implying that shorter chain PFAS are more mobile, while longer chain PFAS sorb to solids. In a column study simulating travel through an aquifer, Aly et al., 2018 observed slight retardation of both PFOA (R=1.51) and PFOS (R=4.46). Ottawa sand was used as the column media in this study. In a study quantifying emerging pollutants leaching into biosolid-amended soils, PFOS was found to be highly mobile, only sorbing slightly to the soil matrix (Navarro et al., 2018).

Perchlorate

Perchlorate is a common groundwater and occasional surface water contaminant. The most common sources of perchlorate are from the explosives and fertilizer industries (Cao et al., 2019). As such it is often found in groundwater at weapons manufacture and testing facilities as well as military bases (Gal et al., 2009; Fuller et al., 2019; Cao et al., 2018). In addition to its industrial sources, perchlorate is also a degradation product of hypochlorite and as such may be introduced into drinking water or wastewater at trace concentrations during disinfection (Coulombe et al., 2019). Currently, perchlorate is not regulated by the SDWA, but has a health advisory limit in some states, e.g. 6µg/L in California. Perchlorate is very soluble in water and

does not sorb significantly. Thus, the most efficient method of perchlorate removal is chemical or biological reduction, as with nitrate and bromate. Reduction of perchlorate in an aquifer was observed by Fuller et al., 2019. Fuller et al. injected emulsified oil into a groundwater plume to act as an electron donor for the reduction of perchlorate and other contaminants. The injected oil created a bio-barrier in which reducing conditions were established and >90% reduction of perchlorate was observed. Other than organic carbon, other electron donors have been shown to act as an electron donor in the reduction of perchlorate. In a lab-scale culture, Ju et al., 2007 was able to grow chemolithotrophic utilizing sulfur as an electron donor. The microbial reduction was able to occur in the absence of carbon, but carbon addition did enhance the growth of the culture.

Other Trace Compounds

Redox conditions play a large role in the degradation rates of various compounds. While reducing conditions are generally favorable for the degradation of oxidized DBPs, e.g. perchlorate and bromate, oxidizing conditions enhance the degradation of most trace organic compounds (Ke et al., 2012; Lekkerkerker-Teunissen et al., 2012; Hellauer et al., 2017). He et al., 2018 found that both strongly oxidizing and strongly reducing conditions enhanced trace organic degradation. The lowest degradation rates observed in this study were at weakly oxic and anoxic conditions.

Hellauer et al., 2017 found that trace compounds were degraded most effectively in aerobic conditions where the availability of readily biodegradable organic carbon was scarce. Addition of recalcitrant carbon compounds, e.g. humic acids, were not found to enhance the removal of most trace compounds, however (Hellauer et al., 2019). Rauch-Williams et al., 2010 also observed the importance of oligotrophic environments to the degradation of trace organics.

Acclimation of a microbiological community to trace organics was also found to be important in this study. Over the course of three spike tests, an increased degradation of certain trace contaminants was observed.

Generally, higher degradation rates of trace compounds are observed at higher initial concentrations and the degradation of certain compounds is not observed below a certain threshold concentration (Wiese et al., 2011).

Some trace compounds, e.g. primidone, carbamazepine, show little to no degradation during SAT regardless of travel time or redox conditions (Trussell et al., 2018; Hellauer et al., 2017; Filter et al., 2017)

Arsenic

Arsenic is a metal contaminant sometimes found in natural sediments, regulated by the SDWA at a concentration of 10µg/L. It is naturally found in sediment in one of three oxidation states: 0, +III, and +V. While arsenic is not typically in abundance in water used for aquifer recharge, several different mechanisms have been reported for the mobilization of arsenic from sediment to groundwater during MAR. The most common of these is reduction of Fe (III) minerals (Ahmann et al., 1997; Bose and Sharma, 2002; Das et al., 2016; Duan et al., 2009; Gupta and Singh, 2019; Hassan et al., 2012; Stolze et al., 2019), as arsenic is often found either co-occurring with or adsorbed to oxidized iron in sediment. Iron reducing conditions may be created by the addition of labile organic carbon, either intentionally during MAR projects, or unintentionally during hydrocarbon spills and leaks. The reduced iron either dissolves or has a lesser sorptive capacity, allowing for arsenic to dissolve and potentially mobilize downgradient (Burton et al., 2011).

Another source of arsenic is through the oxidation of pyrite (FeS_2), a reduced iron mineral that often contains trace levels of arsenic (Darling, 2016; Rhine et al., 2008). Arsenic released from pyrite is initially found in the +III oxidation state (Neil et al., 2018), but may be further oxidized to +V. Rhine et al., 2008 isolated a bacterial species capable of both pyritic iron and arsenic oxidation in aerobic cultures at circumneutral pHs. This study found that most of the arsenic released through biological activity was in the +V oxidation state. While arsenic in the +V oxidation state is generally less mobile, both As (III) and (V) are potentially mobile depending on pH and availability of sorption sites and concentrations of coprecipitates, e.g. sulfide (Hering et al., 2011).

One oxidation product of pyrite is iron hydroxide, a mineral compound with very low solubility that has a large capacity for arsenic adsorption (Jang et al., 2008; Jovanovic et al., 2011; Wang and Mulligan, 2006). The precipitation of iron hydroxide creates sorption sites for the released arsenic, limiting its mobility. Therefore, under oxidizing conditions in a pyritic aquifer, the mobility of arsenic may be inversely dependent on the stability of iron hydroxide surfaces (Langner and Inskeep, 2000). When the redox condition in the aquifer changes, reduction of the ferric hydroxide may occur. Therefore, continuously changing redox conditions may create a cycle of dissolution, sorption, and desorption that can cause slugs of arsenic mobilization (Jin et al., 2016).

In addition to redox conditions, arsenic mobilization can also be triggered via differing ionic composition of the recharge water compared to the native groundwater. Fakhreddine et al., 2015 found that the divalent cations Mg^{2+} and Ca^{2+} were necessary to prevent arsenic desorption from phyllosilicate mineral surfaces. In addition to dissolution and sorption, Lim et al., 2007 found that re-precipitation of reduced arsenic is an important mechanism controlling overall arsenic

mobility. In reducing conditions, arsenic could coprecipitate with iron to reform pyrite minerals, potentially limiting arsenic mobility.

MATERIALS AND METHODS

Column Design and Configuration

Four columns, configured in two sets of two columns in series, were operated at SWIFT RC to simulate transport in a saturated aquifer. The first column in each set had a height of 2.4m (8ft); the second column had a height of 4.0m (13ft). Both columns had a diameter of 0.3m (1ft.). The large size of the columns was necessary to obtain the effluent sample volumes required for analysis of multiple parameters at long travel times. The targeted travel times of the 2.4m columns and 4.0m columns throughout the course of these experiments were 3 days and 30 days, and henceforth, the columns will be referred to as 3-day and 1-month columns. In order to meet these travel times, flow rates of 13mL/min and 2.2mL/min were targeted for the 3-day and 1-month columns respectively. These target flow rates were based on previous tracer studies performed on the columns (Pradhan, 2018) and confirmed in a tracer performed on one set of columns during Phase 2 of testing.

The column media was collected from the Potomac Aquifer during construction of the test well at HRSD's Nansemond Treatment Plant site. The media was then washed to remove clay and drilling mud and sieved to remove particles larger than 4mm. This was done to minimize the creation of large pores or channels and ensure uniform flow across the column. Sieve analysis data for the column media is presented in the appendix (Figure 39).

To fill the columns initially, aquifer media and SWIFT effluent water were poured into the column in small batches. After each batch, a concrete vibrator was used to ensure the media compacted and there were no large pores or channels. Some space was left at the tops of the

columns above the media to allow for the installation of dissolved oxygen analyzers: 10cm (4in.) in the 3-day columns, 30cm (1ft.) in the 1-month columns.

The columns themselves were constructed out of clear PVC, an inert material that does not exhibit significant sorbent properties. The columns were covered with a black polyethylene plastic wrap to avoid light penetration into the columns, which could cause photolytic reactions or promote phototrophic microbial growth. The aquifer media was packed onto a beaded IMS cap acting as an underdrain plate. The plate was utilized to allow for uniform distribution of feed water and to prevent loss of media. During operation, the columns were fed from the bottom to simulate a saturated aquifer, i.e. no vadose zone. In order to feed at the low, consistent flows required, Masterflex peristaltic pumps were used. Tygon tubing was used for the peristaltic pumps. Teflon tubing was used in the remainder of the sample lines as it is non-reactive and non-sorptive of the majority of solutes (Hebig et al., 2014).

In order to operate the columns in series, configurations shown in Figures 3 and 4 were used for Phase 1 and 2 of testing, respectively. The columns were fed with water collected in batches and stored in 20gal HDPE containers. Water was fed continuously to both sets of columns, even while not being sampled, from June 2018 to October 2019. Three peristaltic pumps run at 16, 13, and 2.2mL/min, were used to maintain the flowrate to and between the columns. The excess flow between pumps was collected in 5-gallon containers, from which samples were taken. The 20-gallon influent and 5-gallon effluent containers are shown in Figure 2.

Column Influents

All SAT column influents through the course of these experiments were taken from the HRSD 1MGD SWIFT Demonstration Facility and advanced treatment pilot. The demonstration facility is an advanced water treatment plant which uses secondary clarifier effluent of HRSD's Nansemond Treatment Plant as its influent. Nansemond WWTP is a 5-stage Bardenpho process with consistently low effluent TN (<4mg/L-N) and TOC (<12mg/L). The SWIFT advanced treatment train consists of coagulation, flocculation, sedimentation, followed by ozonation, biofilters, GAC, UV disinfection, then injection into the Potomac Aquifer. Coagulation/flocculation/sedimentation at the front of the advanced treatment process removes turbidity, TOC, and provides log removal credit of pathogens when combined with filtration. Ozone provides log removal credit for pathogens in addition to breaking down recalcitrant TOC for use in biofilters. Ozonation also creates the DBPs NDMA and bromate, both suspected carcinogens. Monochloramine is fed into the system during ozonation in order to inhibit the formation of bromate. Biofilters remove a large fraction of TOC, some trace contaminants, and provide log removal credit of pathogens. The GAC acts as a polishing step to remove additional recalcitrant TOC as well as trace contaminants. The low-pressure UV system provides disinfection credit as well as degradation of select trace contaminants via direct photolysis, e.g. nitrosamines.

Figure 2: Image of refrigerated 20 gallon influent and 5 gallon influent and effluent sample containers.

Phase 1:

Phase 1 of testing took place from July to November 2018. During this phase one set of columns was fed by "BAF INF" which was taken from the combined biofilter effluent of the SWIFT facility. This water was then treated with a Viqua PRO30 UV system at a dose of approximately 30mJ/cm^2 before being used as column influent. The second set of columns was fed by "GAC INF", which was taken from the UV effluent of the SWIFT demonstration facility. Due to the ozonation step in the treatment process, DO was supersaturated (>15mg/L) in both influents at the time of collection. However, since influents were collected in batches, the DO slowly

reached equilibrium with the atmosphere over time. Both influents were stored in 20gal HDPE containers in a refrigerator to avoid biological growth.
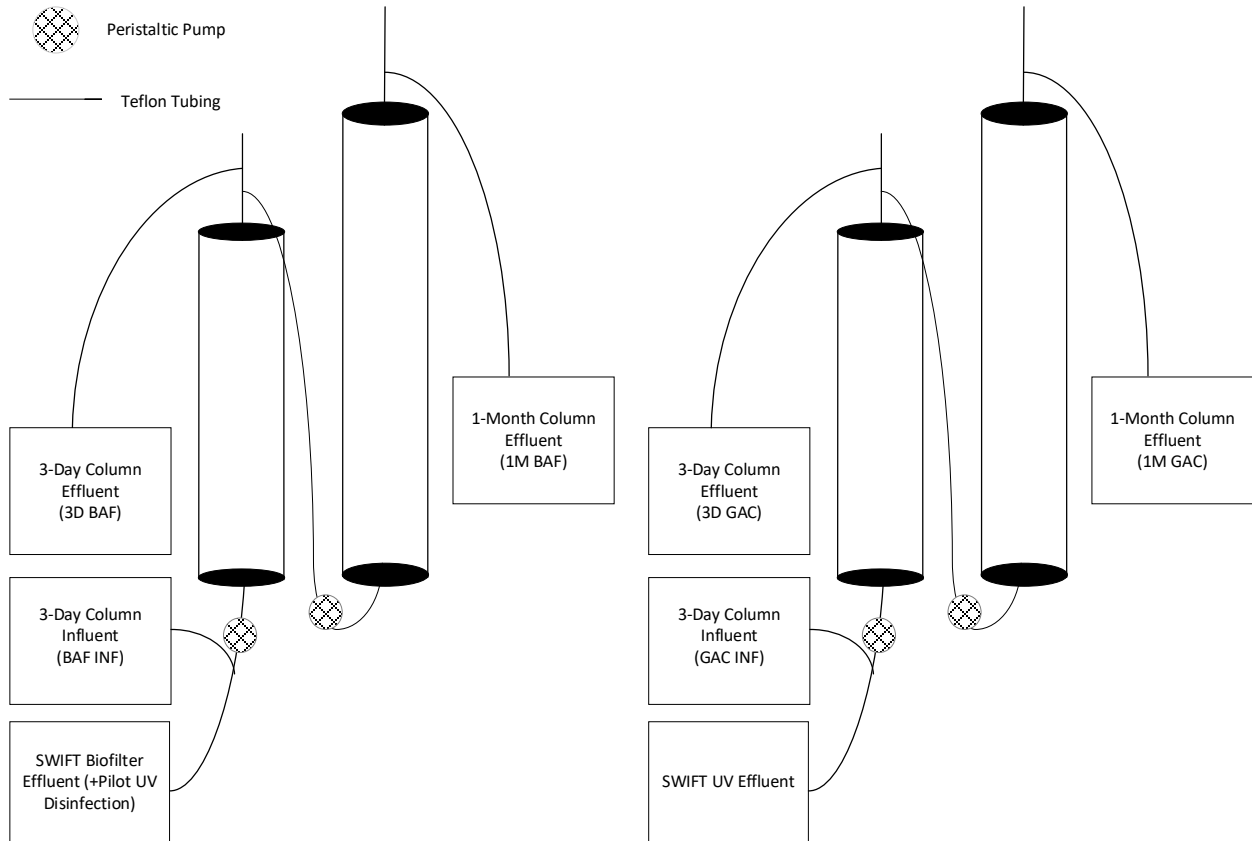
Figure 3: Soil column configuration during Phase 1 of testing. Sample point names are given in parentheses.

Phase 2:

Phase 2 of testing took place from June to September 2019. During Phase 2 of testing 950L (250gal) of water was collected from the SWIFT RC biofilter pilot effluent to use as influent for the spike test. The SWIFT RC pilot follows the same treatment process train as the 1MGD demonstration facility. At the time of collecting the spike influent water, the empty bed contact time (EBCT) of the pilot biofilter was 10min. The collected batch of biofilter effluent was then spiked with several compounds: bromide, bromate, NDMA, nitrate, PFOA, PFOS, primidone,

phenytoin (Dilantin), carbamazepine, perchlorate, DEET, atenolol, ethinyl estradiol, estradiol, triclosan, and cotinine. The spike concentrations were chosen based on the background concentrations and the method reporting limit (MRL) of the analysis method for each compound. If a compound was not previously detected in pilot biofilter effluent, then it was spiked at 50 times its MRL. If a compound was previously detected in pilot biofilter effluent, it was spiked at 10 times the max concentration observed. This method was chosen so that the spiked compounds' breakthrough curves could be clearly observed regardless of the pre-spike background concentrations. This spiked batch was used as the influent to one series of columns for 35 days. The water was stored in a 500gal HDPE tank. The tank was covered with insulation to prevent photolysis of trace compounds and the water was circulated through a chiller maintaining a temperature of 4C to prevent microbial growth in the tank. Along with the spiked influent, monochloramine was fed to the soil columns during Phase 2 of testing. A 100mg/L-Cl_2 monochloramine stock was created from ammonium sulfate and sodium hypochlorite stock solutions. Monochloramine was fed to maintain a concentration ranging from 0.5 to 1.0mg/L-Cl_2 in the column influent.
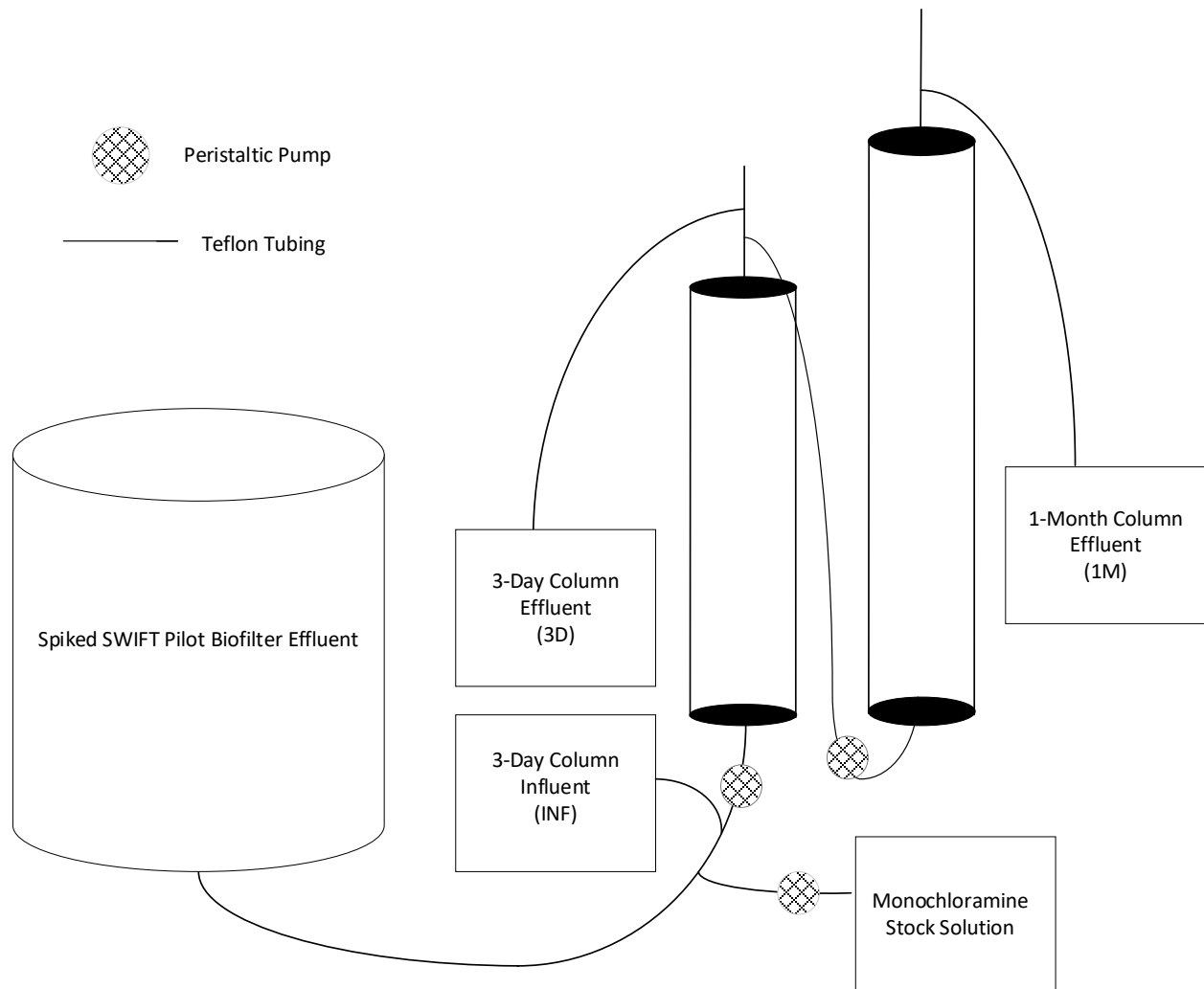
Figure 4: Soil column configuration during Phase 2 of testing.

Sampling and Analysis

Phase 1:

During Phase 1 of testing, the influent and 3-day effluent of both sets of columns were sampled three times per week. The 3-day sampling events occurred approximately three days after the influent samples were taken to correct for travel time. The 1-month effluent was sampled once per week. The influent and effluents of all columns were sampled for the following parameters:

nitrogen species (TKN, NO_2^-, NO_x), TOC/DOC, BrO_3^-, and NDMA. Sample analysis was carried

out by HRSD's Central Environmental Laboratory (CEL). Field analyses for pH, UVT-254, and

DO were also performed regularly. Specific analyses and methods are listed in Table 3.

Table 3: Field and lab instruments and methods used in the course of this study

Analyte	Lab	Instrument/Method	Equivalent EPA Method
Field Instruments			
DO (Inf)	Field	HACH LDO 101	
DO (Eff)	Field	Insite IG MPA -48	
pH	Field	Thermoscientific Orion Star A211	
UVT-254	Field	Thermoscientific Genesys 150 UV-Vis Spectrophotometer	
NH_2Cl	Field	HACH SL1000 Portable Parallel Analyzer	
Shimadzu TOC Analyzer			
TOC	CEL	SM 5310B/C	
Lachat Ion Chromatograph			
TKN	CEL	10-107-06-2-I	EPA 351.2
NO_x	CEL	10-107-04-1-A	
NO_2^-	CEL	10-107-04-1-C	
Br^-/SO_4^{2-}	CEL		EPA 300.0
ICP-MS			
Iron	CEL		EPA 200.7
Arsenic	CEL		EPA 200.8
GC-MS			
NDMA	CEL	In-House 521/522[a]	EPA 521
1,4-Dioxane	CEL	In-House 521/522[a]	EPA 522
LC-MS			
PFAS[b]	Eurofins		EPA 537/537.1
Hormones[b]	Eurofins		EPA 539
CECs[b]	Eurofins	In-House LC-MS-MS[c]	
Perchlorate	Eurofins		EPA 331.0

a – In-house method that performs solid-phase extraction on 1,4-dioxane and NDMA simultaneously
b – A detailed list of analytes can be found in the appendix
c – In-house SPE-HPLC-MS/MS method developed for analysis of PPCPs, EDCs, pesticides, degradates

Phase 2:

During Phase 2 of testing the influent, 3-day effluent, and 1-month effluent of only one set of columns were sampled. Although the influent water was one batch, it was sampled three times to confirm that no loss of spiked contaminant occurred via degradation, photolysis, sorption, or volatilization. The 3-day effluent was sampled three times per week. Bromide was sampled more often at the beginning of the spike to create a more robust breakthrough curve. The 1-month effluent was sampled twice per week. Bromide was sampled more often on the 1-month columns once breakthrough was expected (after ~30 days). The following parameters were monitored in the influent and effluent: nitrogen species (NO_2^-, NO_x^-, TKN), TOC, bromate, bromide, sulfate, NDMA, NMOR, 1,4-dioxane, iron, and arsenic. Samples were also sent to Eurofins Eaton Analytical, LLC contract laboratory for additional analysis on a less frequent basis. The contract lab analyzed for CECs including flame retardants, pesticides, hormones, and pharmaceuticals and personal care products (PPCPs). A sample from the batch influent was sent to the contract lab before and after spiking, as well as near the end of the 35 days to check for degradation or volatilization of spiked compounds. Four samples from the 3-day effluent were sent to the contract lab at times corresponding to approximately 1, 2, 5, and 10 pore volumes. Three samples from the 1-month effluent were sent at times corresponding to 1, 1.35, and 1.7 pore volumes. The PFAS samples for the 3-day effluent corresponding to 10 PVs and the 1-month effluent corresponding to 1.7PVs were accidentally discarded before analysis. As such, one additional 1-month effluent PFAS sample was sent at a date corresponding to 2.7PVs.

Other Sampling:

Samples of media post-installation in the columns were taken to measure solid-phase TOC as well as metals. To avoid greatly disturbing the operation of the columns, solid phase samples were only taken from the top six inches of each column. The analysis of solid-phase TOC was done by Air, Soil, and Water Environmental Laboratory of Richmond, VA by EPA Method 9060A. Analysis of metals was carried out by HRSD's Central Environmental Laboratory by acid digestion, followed by ICP-MS.

RESULTS AND DISCUSSION

Bromide Tracer

Bromide was spiked into one set of columns during Phase 2 of testing to act as a conservative tracer. The spiking period lasted 35 days, sampling continued after the spike for an additional 15 days on the 3-day column, and an additional 60 days on the 1-month column. With breakthrough defined as the effluent concentration reaching half the maximum concentration (C/C_{max}=0.5), the effluent concentration in the 3-day column effluent rose above 50mg/L on the fourth day of spiking (Figure 5; C_{max}=103mg/L). In the effluent of the 1-month column, the bromide concentration rose above 47mg/L on day 34 (Figure 5; C_{max}=86.9mg/L). Using this bromide data as the input to a 1-dimensional advection-dispersion model (see appendix Figures 40 and 41), the travel times of the 3-day and 1-month columns were determined to be 3.3 and 31.6 days, respectively. The sharp decrease of the 3-day effluent Br^- concentration at the end of the spiking period demonstrates that minimal sorption/desorption of bromide occurs in the column.

The mass of bromide recovered in the 3-day column effluent represented 101.7% of the total bromide spiked during the 35-day period. The mass of bromide recovered in the 1-month column effluent represented 107.1% of the expected bromide based on the 3-day effluent concentrations throughout the spiking period. Due to its conservative nature, bromide can be used as a surrogate for the spiked water and its BTC can be compared to those of other spiked compounds to evaluate their potential attenuation during SAT.
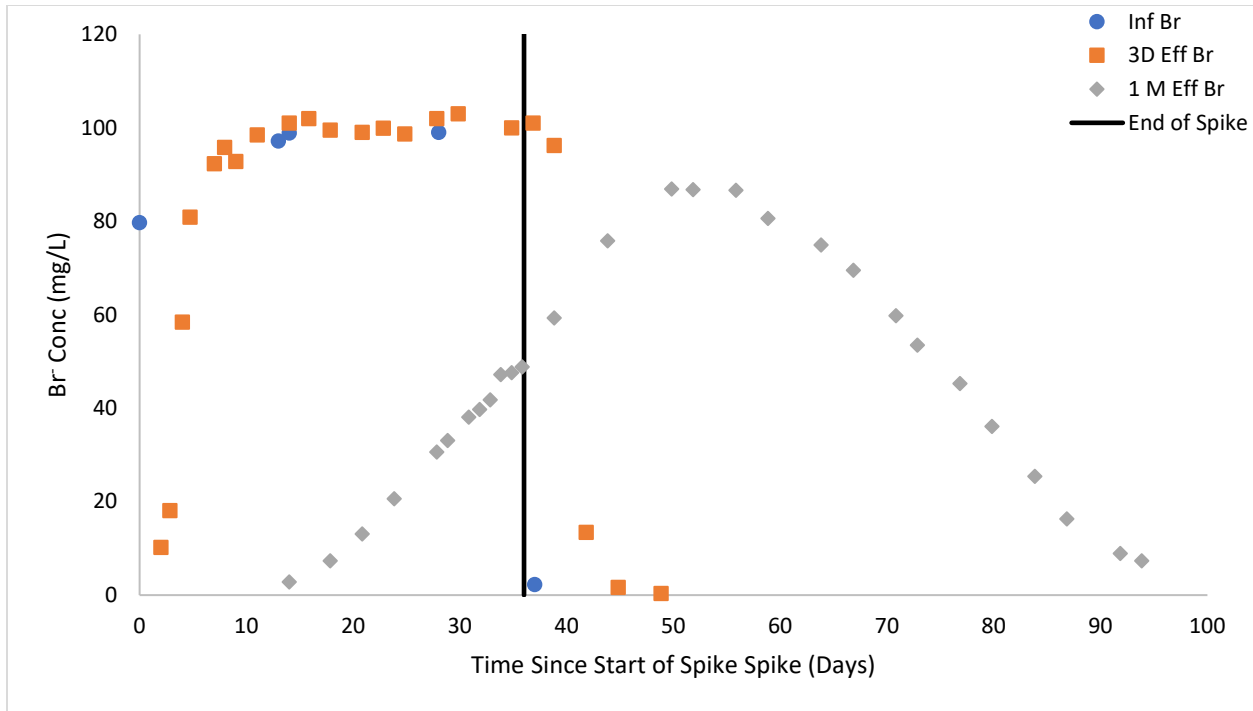
Figure 5: Breakthrough curve of bromide on the 3-day and 1-month effluents during Phase 2 of testing.

Total Organic Carbon

During Phase 1 of testing, TOC on both sets of columns decreased by an average of 45% over the 3-day columns (see Figure 7). A similar level of removal (50%) was observed during Phase 2 of testing (Figure 9). Counterintuitively, with a much longer travel time, no additional removal was observed across the 1-month columns. There are a few possible reasons for this lack of additional removal. Firstly, while the DO in the influent to the 3-day columns is high (10-15mg/L on average), the DO was consumed before reaching the top of the columns. Thus the 1-month columns were anoxic-anaerobic, and less consumption of TOC was expected. As seen in Figure 7, the average TOC appeared to increase across the 1-month column fed by GAC INF. This was possibly due to the timing of sampling. As seen in Figure 6, TOC was increasing in GAC INF in the middle of sampling, then decreased sharply. Adjusting 33 days for travel time,

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only one sample was taken in the 1-month effluent after this sharp decrease, whereas many 3-day effluent samples were taken, resulting in a lower average concentration.

Figure 6: TOC concentrations in the influent, 3-day, and 1-month effluents during Phase 1 of testing. 3D and 1M data time shifted 3 days and 33 days respectively, to correct for travel time.
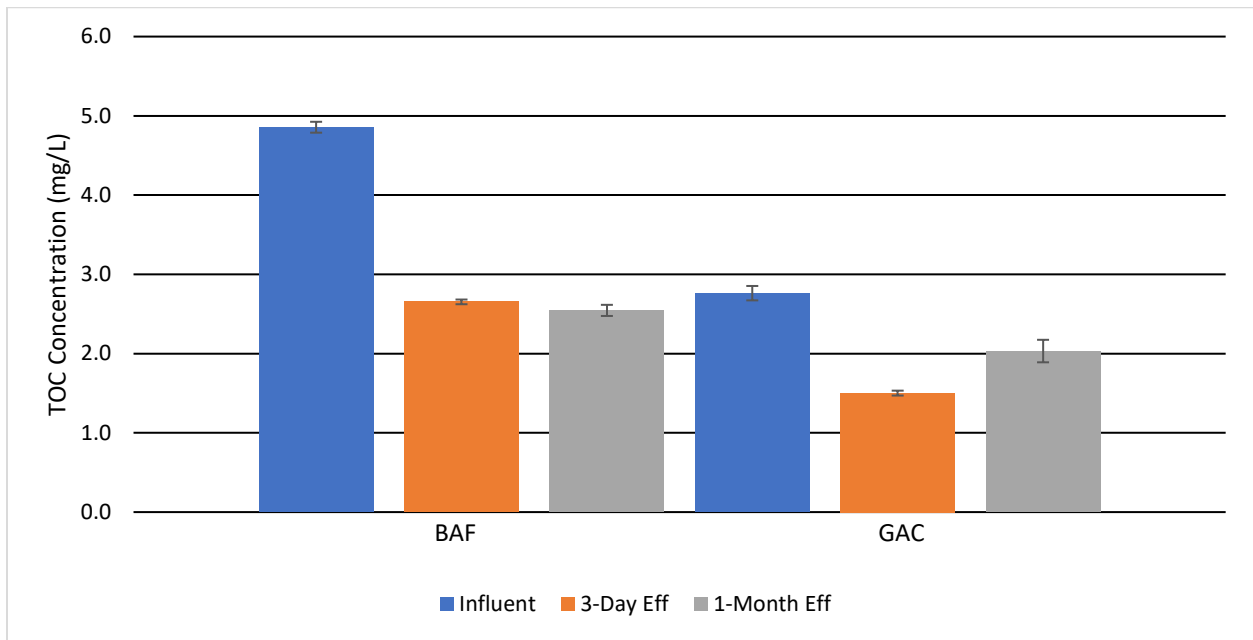
Figure 7: TOC measurements on the influent, 3-day, and 1-month effluents of both sets of columns during Phase 1 of testing.

The lack of additional removal of TOC in the 1-month columns also suggests that the removal observed in the 3-day columns was due to degradation and not sorption. The 1-month columns, being larger, had much more capacity for sorption and would have removed more carbon than the 3-day columns if the primary mechanism was irreversible sorption. The level of solid phase carbon as shown in Table 4 was also very low. A 0.01% by weight solid-phase carbon concentration is approximately equal to or lower than in the studies Patterson et al., 2011 (0.02%) and Burke et al., 2013 (0.2%). Both these column studies observed high mobility of most organic compounds. This supports the claim that the removal observed was degradation, as sorption is generally correlated with fraction of organic carbon in the soil.

Table 4: Solid phase TOC concentrations of the four columns

	3DBAF Column	3DGAC Column	1MBAF Column	1MGAC Column
Sample 1 (mg/kg)	128	81.5	92.1	75.3
Sample 2 (mg/kg)	103	106	81.2	88.5
Average (mg/kg)	115.5	93.75	86.65	81.9
% by weight	0.012	0.009	0.009	0.008

The lack of TOC removal could be attributed to the recalcitrance of the carbon. The TOC in the influent of both columns had already gone through multiple chemical and biological treatment processes meaning that what was left was relatively recalcitrant. It is possible that the more easily degradable fraction of this carbon was used quickly in the columns and what was left would take much longer to degrade.

During Phase 1 of testing UVT-254 was closely monitored along with TOC. Using these two values, the SUVA of the influent, 3-day, and 1-month effluents could be calculated as seen in Table 5.

Table 5: Average TOC, UVT-254, and SUVA for the influent, 3-day, and 1-month effluents of both sets of columns during Phase 1 of testing.

	BAF Inf	3D BAF	1M BAF	GAC Inf	3D GAC	1M GAC
TOC (mg/L)	4.89	2.61	2.55	2.75	1.47	1.78
%T	88.67	93.15	88.4	94.36	95.05	91.04
SUVA	1.07	1.18	2.10	0.92	1.50	2.29
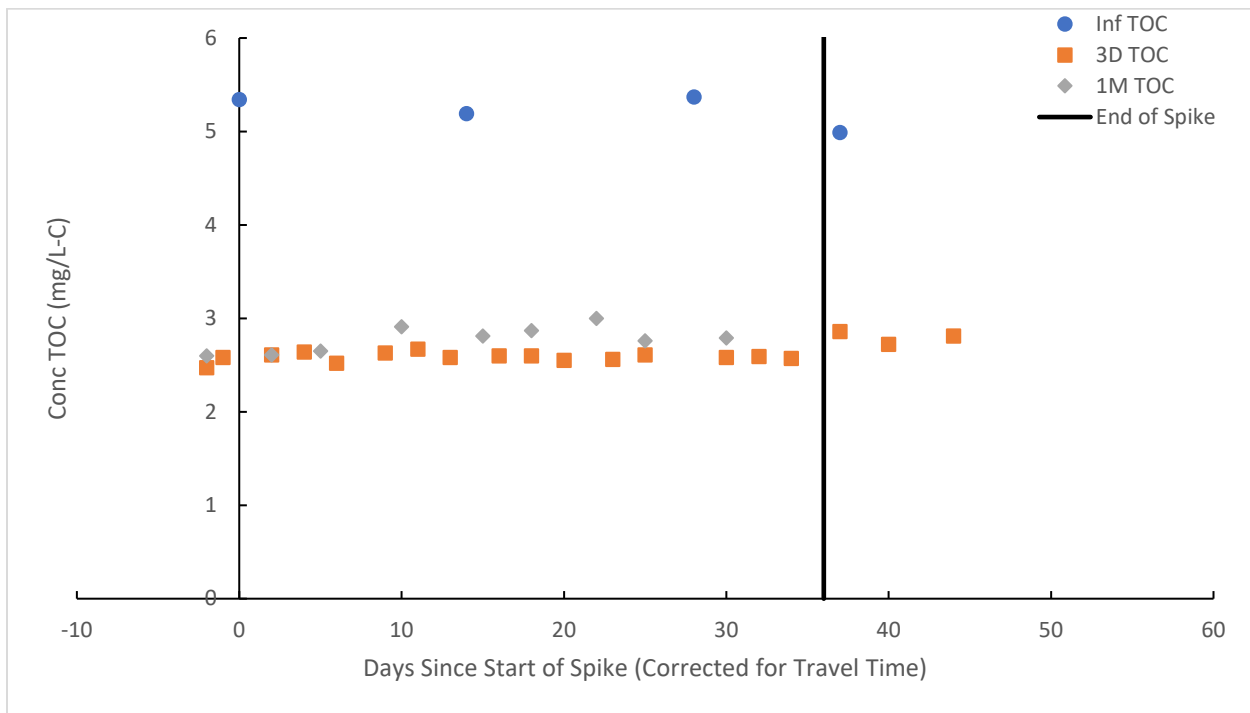
Figure 8: Concentration of TOC in the influent, 3-day, and 1-month column effluents during Phase 2 of testing.

Although the concentration of TOC did not decrease over the length of the 1-month columns, the SUVA did significantly increase on both sets of columns. This indicates that, although the TOC was not mineralizing, the nature of the TOC was still changing through chemical or biological processes in the anoxic/anaerobic columns and with longer travel times additional TOC removal may have be possible.
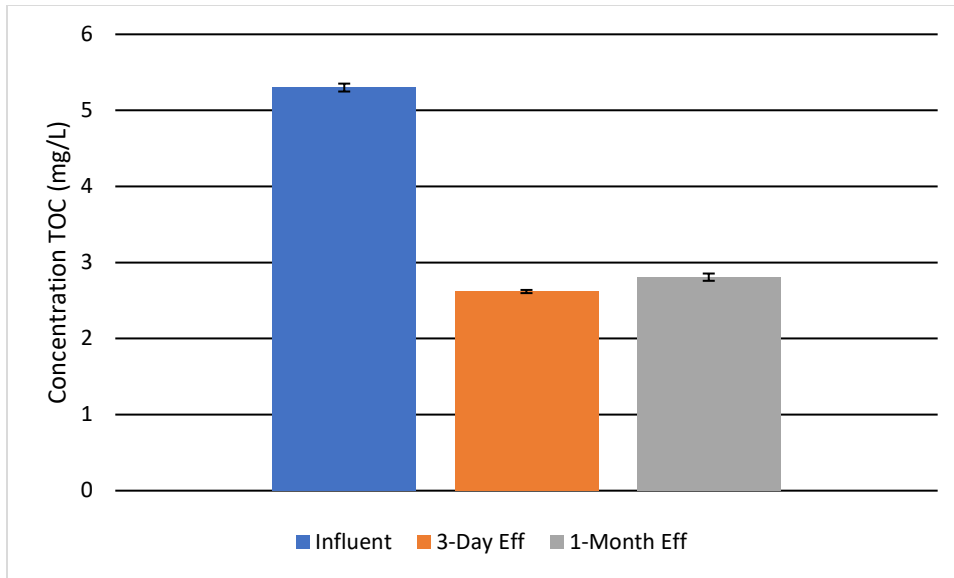
Figure 9: TOC measurements on the influent, 3-day, and 1-month effluents of the spiked set of columns during Phase 2 of testing.

Nitrogen

Multiple nitrogen species were measured during both phases of the column study: NO_x, nitrite, and TKN. Total nitrogen concentrations were calculated based on the sum of NO_x and TKN. Nitrite was consistently low in both the influent and effluent of the columns, indicating that nitrate was the predominate form of oxidized nitrogen.

A small amount of nitrogen removal (~0.4mg/L-N) was observed across the 3-day columns, whereas a much larger fraction of nitrogen (up to 3.5mg/L-N) was removed in the 1-month columns (Figure 13). The loss of TN in the 3-day columns, with no removal of NO_x suggests that there was assimilation of reduced nitrogen species (TKN) by the native microbes in the columns. This loss of TKN is seen in Figure 11. As the influent TKN was often just above, and the effluent was often just below the detection limit (0.5mg/L-N), it was difficult to determine how much reduced nitrogen was transformed, assimilated, or removed in the 3-day columns.
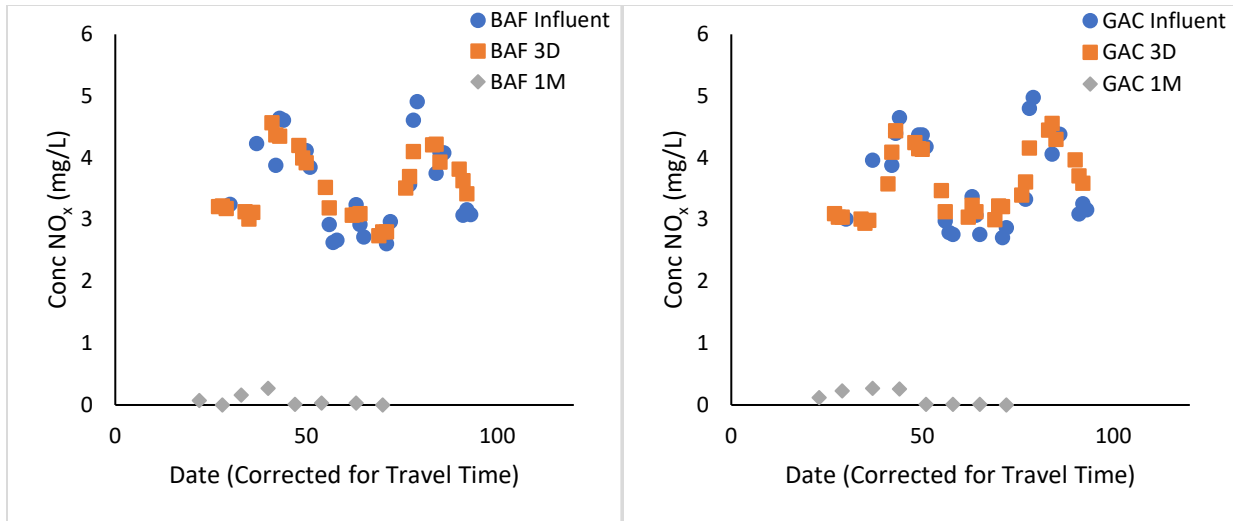
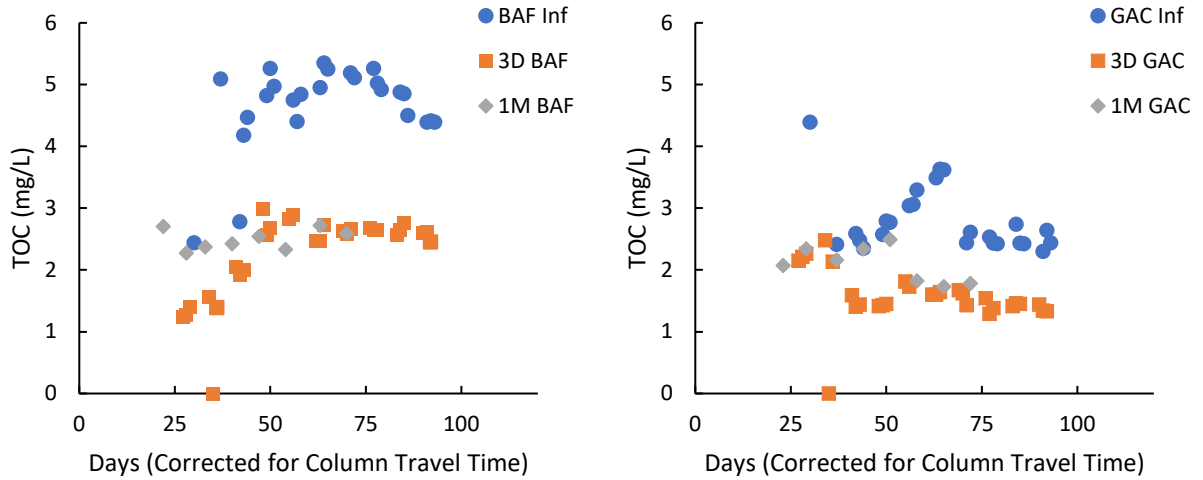**Figure 10: Combined nitrate and nitrite concentrations in the influent, 3-day, and 1-month effluents of the soil columns during Phase 1 of testing. 3D and 1M data time shifted 3 days and 33 days, respectively, to correct for travel time.**

During Phase 2 of testing, ~0.3mg/L-N was added to the influent of the columns in the form of monochloramine. Again, a small decrease of TKN was observed across the 3-day columns with no increase in NO_x (nitrification), indicating that the added ammonia had been assimilated.
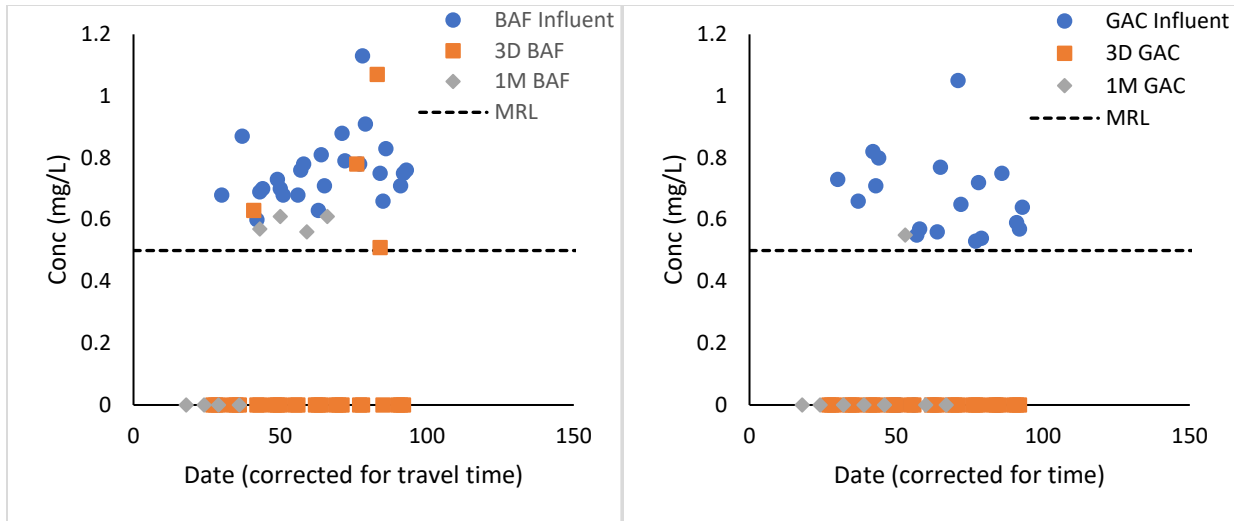
Figure 11: TKN concentrations in the influent, 3-day, and 1-month effluents of the soil columns during Phase 1 of testing. 3D and 1M data time shifted 3 days and 33 days, respectively, to correct for travel time.

The assumption that the 3-day column is mostly aerobic, and the 1-month column is anoxic-anaerobic is supported by the NO_x concentrations across the columns. Figures 10 and 12 show that NO_x is conservative across the 3-day columns. These data, combined with the fact that DO is consumed by the end of the 3-day column, imply that the microbial activity in the 3-day columns is mostly aerobic. The complete denitrification that is observed in the 1-month column effluent indicates that anoxic conditions had been well established in those columns.
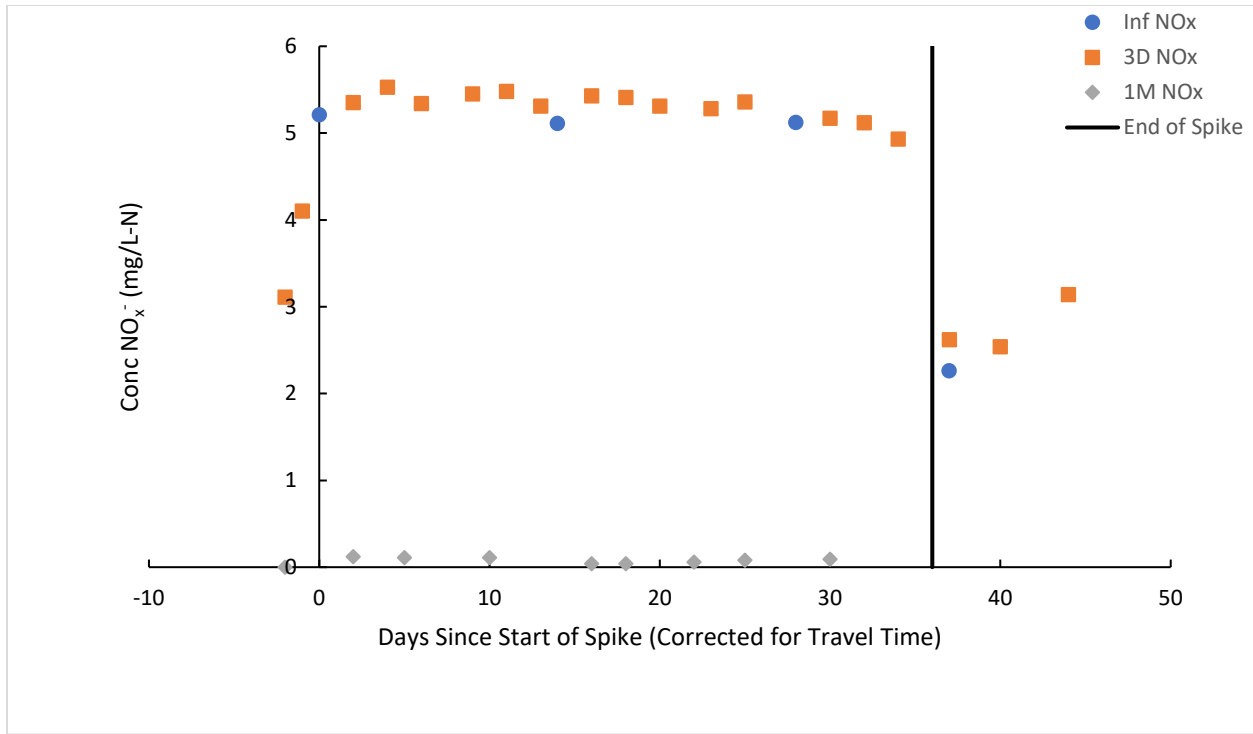
Figure 12: Concentration of NOx across the 3-day and 1-month columns during Phase 2 of testing. 3D and 1M data time shifted 3 days and 33 days respectively, to correct for travel time.

However, since no TOC mineralization is observed in the 1-month columns, the denitrification that occurs is highly unlikely to be supported by carbon as the terminal electron donor as is typical in wastewater treatment. Since the influent for the columns was taken downstream of an ozone-biofiltration process, it is also unlikely that there were electron donors apart from carbon in the water that could support denitrification on the order of milligrams nitrogen per liter. The most probable source of electrons, therefore, was from the media itself. Denitrification in the subsurface, either by solid phase carbon, or by native minerals, is well documented (Parmentier et al., 2014; Aquilina et al., 2018; Pauwels et al., 2010).
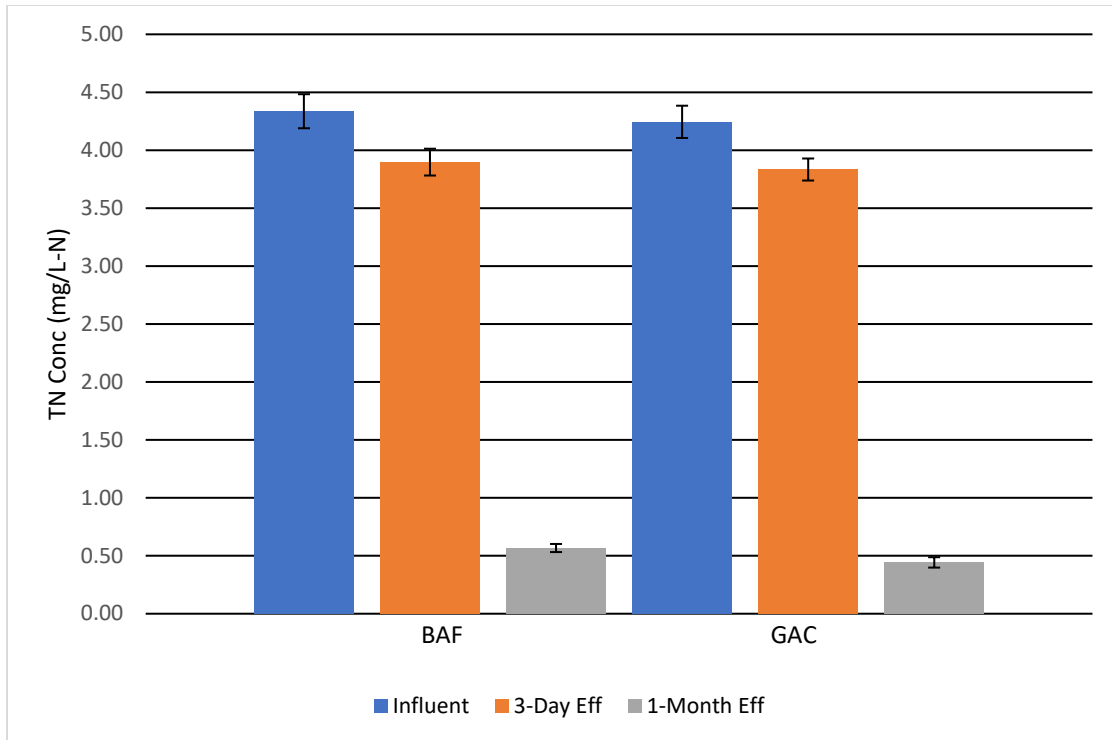
Figure 13: TN measurements in the influent, 3-day, and 1-month effluents of the soil columns during Phase 1 of testing.

As the amount of solid phase carbon in the column media was very low (<0.01%), the most likely electron donors were reduced minerals, e.g. Fe, S. If reduced sulfur acted as an electron donor, the sulfate concentration would be expected to have increased across the 1-month columns. If reduced iron acted as an electron donor, oxidized iron would form in the 1-month column. However, since oxidized iron is not very soluble, no change in effluent iron concentration would have been expected unless iron reducing conditions were established farther downstream in the column.

Bromate

As shown in Figures 14 and 15, significant bromate reduction occurred in the 3-day columns (90% in 3D BAF, 94% in 3D GAC). Microbial bromate reduction in low oxic/anoxic conditions is well documented (Hübner et al., 2016; Kirisits and Snoeyink, 1999). Multiple studies showed

that reduced mineral iron (Wang et al., 2018 (1); Fan et al., 2006) and sulfur (Chairez et al., 2009) compounds could act as the electron donor. In these studies, bromate was reduced rapidly, even in the presence of other electron acceptors, e.g. oxygen and nitrate.
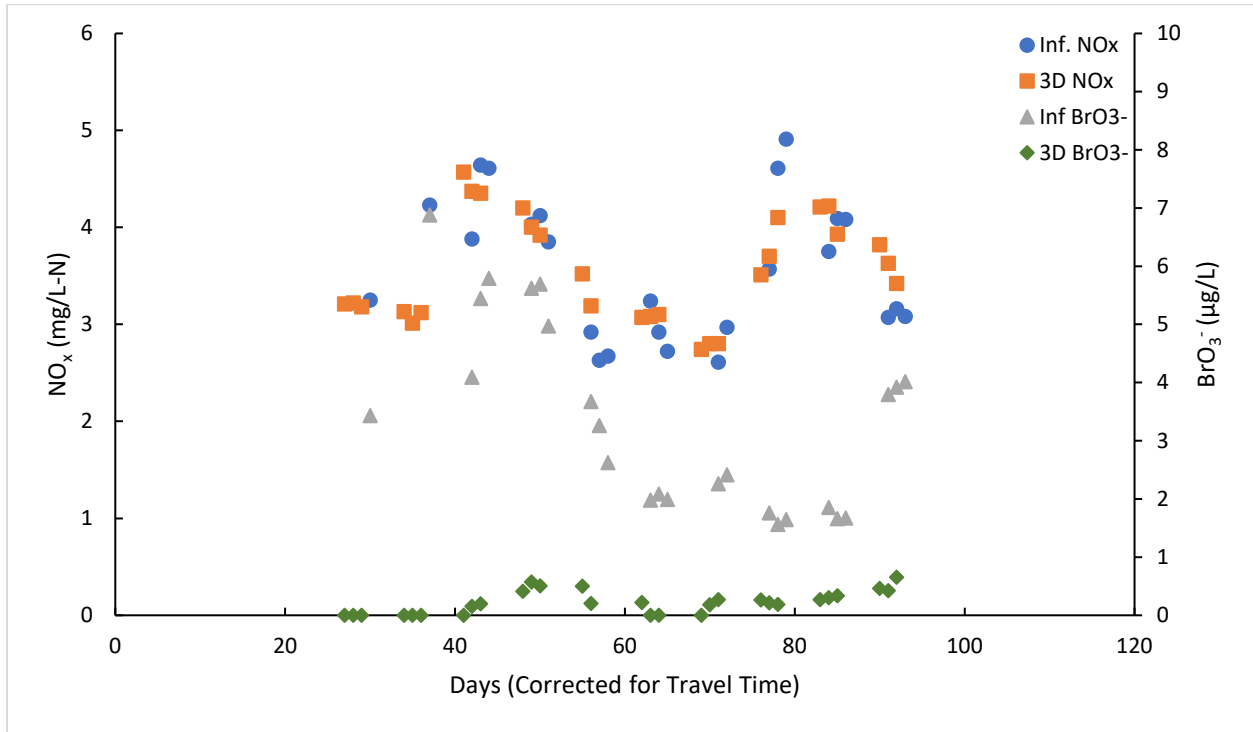
Figure 14: NOx and bromate concentrations in the influent and effluent of the 3-day BAF column during Phase 1 of testing. 3D data time shifted 3 days to correct for travel time.

Reduction has also been shown to occur via denitrifiers (Davidson et al., 2011;) as well as other heterotrophic bacteria that specifically reduce bromate (Davidson et al., 2011; van Ginkel et al., 2005). However, Hijnen et al., 1995 and Wang et al., 2018 (2) found that when bromate was reduced by denitrifiers, nitrate significantly inhibited the process. Figure 14 shows that bromate reduction occurred in the presence of nitrate, with no detectable denitrification, implying that the reduction was not carried out cometabolically by denitrifiers.
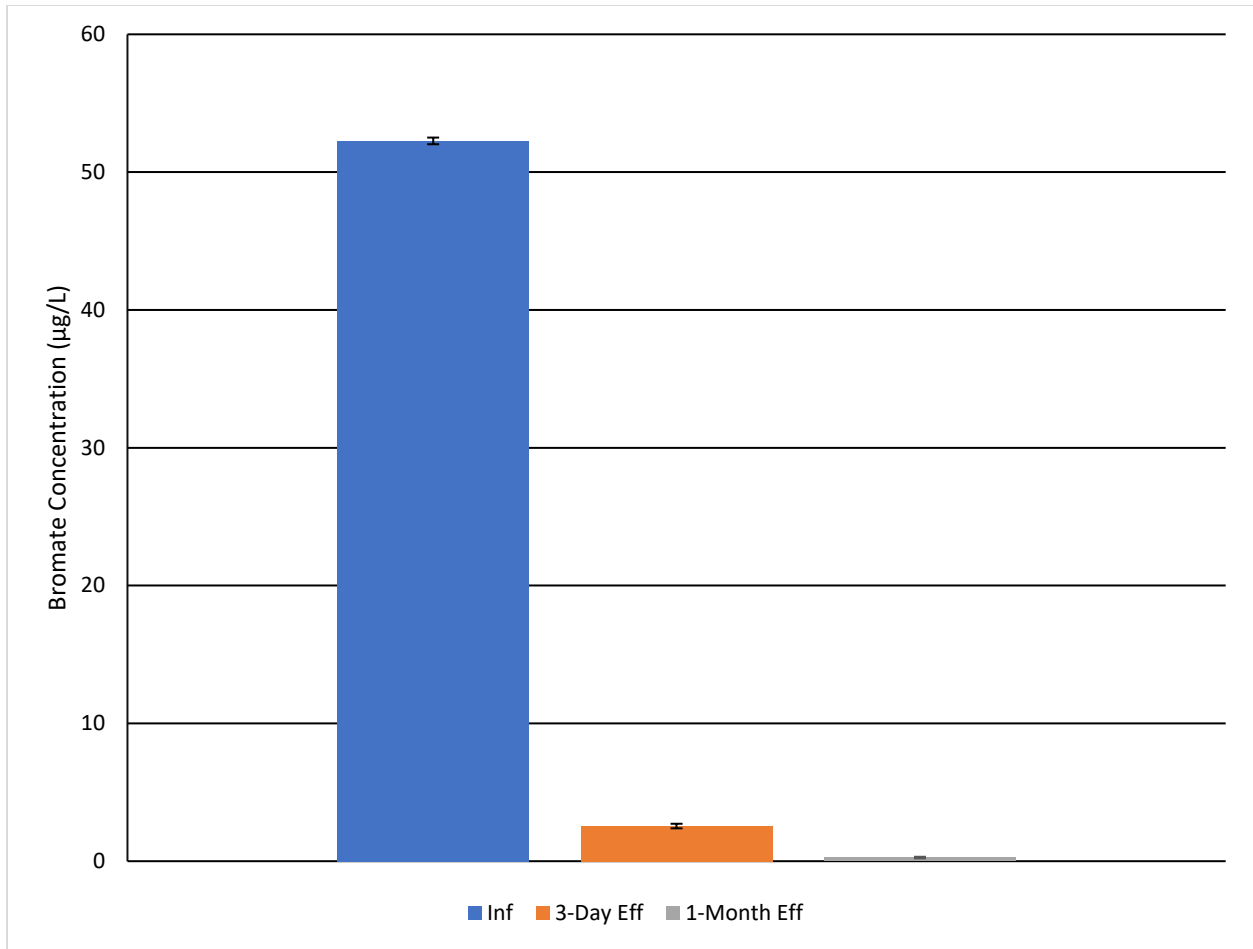
Figure 15: Average bromate concentration in the influent, 3-day, and 1-month effluents during spiking in Phase 2 of sampling.

During Phase 2 of testing, both bromate and nitrate were spiked into the column influent.

Bromate was spiked to 50μg/L to approximate a worst-case scenario in the SWIFT process when

both influent bromide and ozone dose are high with no bromate formation controls. Nitrate was

spiked up to 5mg/L-N, the monthly total nitrogen limit for the SWIFT program. Again, this

concentration would represent a worst-case scenario if nitrate inhibition of bromate reduction

were a factor. At this much higher influent concentration, a high rate of bromate reduction was

maintained (Figures 15 and 16). Over the course of the spike test, 95% removal of bromate was

observed in the 3-day column and bromate was rarely detected in the 1-month effluent. No

desorption of bromate was observed at the end of the spiking period.
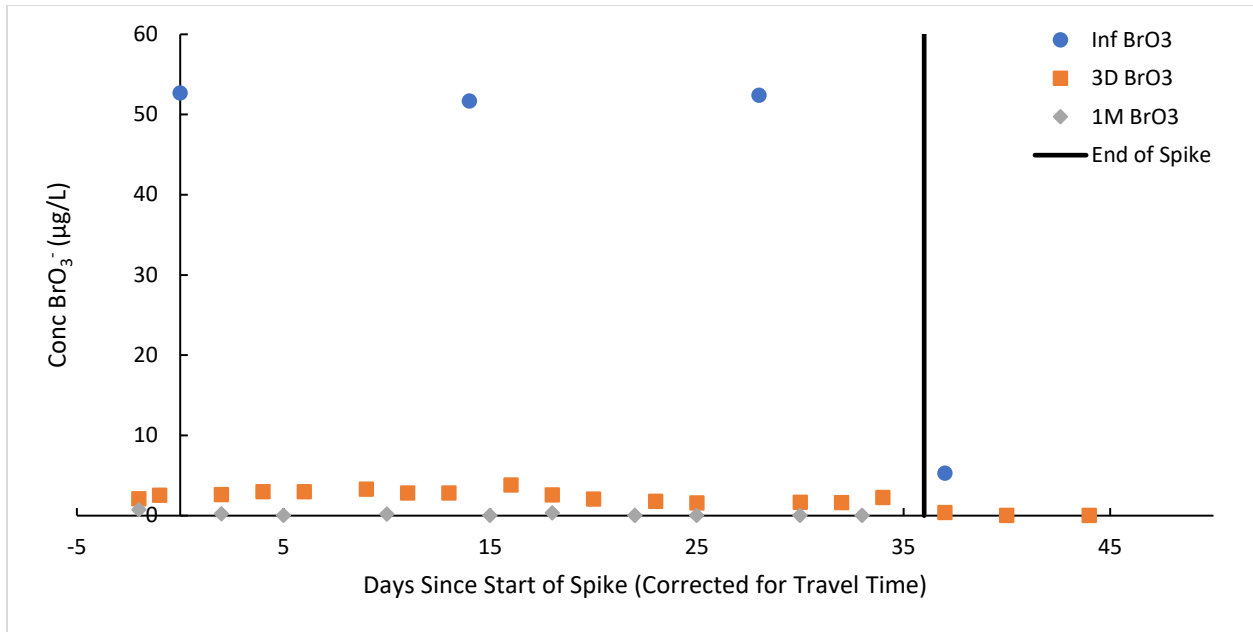
Figure 16: Bromate concentrations in the influent, 3-day, and 1-month effluents of the spiked columns during Phase 2 of testing. 3D and 1M data time shifted 3 days and 33 days respectively, to correct for travel time.

These results demonstrate that even at relatively high concentrations for advanced treatment MAR projects, bromate can be reduced quickly in the subsurface. This reduction does not appear to be inhibited by the presence of other electron donors, e.g. nitrate, even at concentrations multiple orders of magnitude higher than bromate. However, the rapid reduction may be coupled to the oxidation of iron and sulfur minerals and so bromate removal may be site specific during MAR.

CECs

During Phase 2 of sampling, the column influent and effluents were sampled for a large range of CECs. These CECs included pharmaceutical and personal care products, pesticides, flame retardants, and perfluorinated compounds. Of the 120 compounds analyzed, 32 were detected in the background pre-spiking (see Table 6). A total of 43 compounds were detected in the influent over the three sampling events after spiking (see Table 7), 26 compounds were detected in the 3-

day effluent over 4 sampling events, and 22 compounds were detected in the 1-month effluent over 3 sampling events.

Table 6: List of Pre-Spike Influent CEC detections

Compound	Max Conc. Detected	Detection Limit	Units
TCEP	110	10	ng/L
Primidone	32	5	ng/L
DEET	18	10	ng/L
TCPP	790	100	ng/L
TDCPP	240	100	ng/L
Lidocaine	18	5	ng/L
Oxolinic Acid	7.2	5	ng/L
Atrazine	5.3	5	ng/L
Amoxicillin	47	20	ng/L
Atenolol	18	5	ng/L
Carbamazepine	12	5	ng/L
Cotinine	13	10	ng/L
Lopressor	38	20	ng/L
Sucralose	29000	100	ng/L
Meprobamate	11	5	ng/L
Caffeine	26	10	ng/L
Testosterone	0.15	0.05	ng/L
Theophylline	19	10	ng/L
Iohexol	1500	5	ng/L
Dehydronifedipine	5	5	ng/L
Sulfamethoxazole	19	5	ng/L
Trimethoprim	8.6	5	ng/L
BPA	610	10	ng/L
Theobromine	31	20	ng/L
Quinoline	12	5	ng/L
2,4-D	12	5	ng/L
NDMA	6.36	2	ng/L
1,4-D	0.44	0.07	µg/L
PFBS	10	2	ng/L
PFHxA	21	2	ng/L
PFHxS	5	2	ng/L
PFHpA	3	2	ng/L
PFOA	9	2	ng/L
PFOS	8	2	ng/L

Of the 120 CECs, 18 are non-regulatory performance indicator compounds. These compounds, some of which are on the EPA's contaminant candidate list (CCL4) were chosen for monitoring

by the SWIFT project to evaluate the performance of individual treatment processes in addition to the SWIFT process in general. 11 of the 18 compounds were detected in the column influent (pilot biofilter effluent) before spiking, however none of the compounds were detected above their notification or health advisory limit.

Table 7: List of spiked CECs during Phase 2 of testing. Background concentration indicates compounds detected before spiking. Influent concentrations 1, 2, and 3 were sampled on the 1st, 15th, and 29th days of spiking respectively. Analysis of 1,4-Dioxane and NDMA was done in-house so more samples were able to be collected.

Solute	Background Conc	Influent Conc 1	Influent Conc 2	Influent Conc 3
1,4-Dioxane (µg/L)	0.24	2.40	2.11	2.43
NDMA (ng/L)	2.47	70.7	56.3	38.5
Primidone (ng/L)	32	5600		5000
DEET (ng/L)	18	11000		4700
Atenolol (ng/L)	18	6700		4600
Carbamazepine (ng/L)	12	600		660
Cotinine (ng/L)	13	5300		10000
17-Beta-Estradiol (ng/L)	ND	ND		15
Estrone (ng/L)	ND	ND		28
Ethinyl Estradiol (ng/L)	ND	19		140
Triclosan (ng/L)	ND	ND		22
Dilantin (ng/L)	ND	290		540
Perchlorate (µg/L)	ND	42		43
PFOA (ng/L)	8.8	84		76
PFOS (ng/L)	8	69		54

Expected Sorptive Behavior

As multiple attenuation mechanisms take place in soil columns, it is useful to estimate possible overall removal rates for individual trace compounds. Retardation is one attenuation mechanism that can be estimated using the following formula: $R = 1 + \frac{K_{OC} * f_{OC} * \eta}{\rho}$ where R is the retardation coefficient representing how much slower a solute travels compared to the bulk flow of water. K_{oc} is the empirical water-organic carbon partition coefficient, f_{oc}, η, ρ are the fraction of organic carbon, porosity, and density of the media respectively. Table 8 details the K_{oc} and calculated retardation coefficients for the trace compounds spiked during Phase 2 of soil column

testing. Since k_{oc} is an empirical measurement and varies depending on the nature of organic carbon in the media, these R calculations are an approximation. When K_{oc} values could not be found, K_{ow} was used in the calculation. K_{ow} is usually not considered a suitable substitute for K_{oc} when predicting travel through soil (Chiou and Kile, 1994). However, the approximate order of theoretical breakthrough on the columns in the absence of chemical or microbial degradation can be inferred from this table.

Table 8: Koc and Kow (when Koc was unavailable) values for select trace compounds of interest during this study. Retardation coefficient calculated from literature Koc/Kow values, column media porosity, density, and organic fraction. (National Center for Biotechnology Information, 2020)

Compound	Koc	Kow	$R_{Calculated}$
Atenolol		1.4	1.00
Primidone		8.1	1.01
Sucralose	10		1.01
1,4-Dioxane	17-29		1.01-1.02
TCEP		60	1.04
NDMA	68-118		1.04-1.07
DEET		105	1.07
Cotinine	130		1.08
PFHxA	43-224		1.03-1.14
PFOA	83-389		1.05-1.24
Carbamazepine	510		1.32
Ethinyl Estradiol	510		1.32
Dilantin	520		1.32
PFOS	250-50,100		1.16-32.1
17-b-Estradiol	30000		19.6

NDMA

The disinfection byproduct NDMA was spiked into one set of soil columns during Phase 2 of testing at a concentration of approximately 70ng/L. Over the course of the spike test, the

concentration of NDMA in the feed tank decreased either due to volatilization, sorption, or photolysis. The tank was covered throughout the course of the test, so photolysis is possible, but unlikely. Sorption of NDMA to the tank was also unlikely as NDMA is highly soluble in water and HDPE tends to have a low sorptive capacity. As the water in the tank was continuously circulated through a chiller, the surface of the water was turbulent and may have allowed for some volatilization over time despite NDMA's low Henry's law constant. Even accounting for the removal of NDMA in the influent tank, >70% degradation was observed across the 3-day soil columns (Figure 18). NDMA was never detected in the effluent of the 1-month columns, demonstrating that degradation can continue in anoxic/anaerobic conditions and down to very low concentrations (<2ng/L) during SAT.
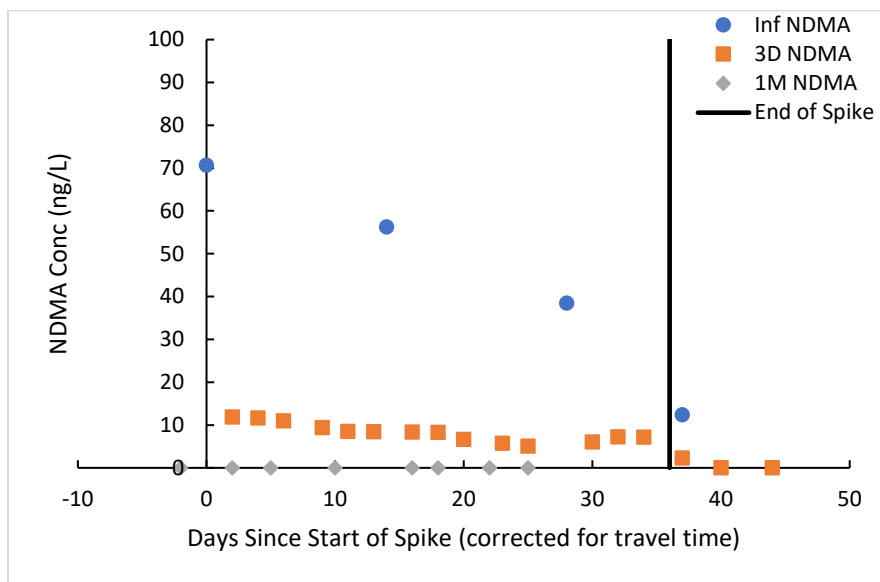
Figure 17: NDMA concentrations in the influent, 3-day, and 1-month effluents during Phase 2 of testing. Sample times are corrected for column travel time. 3D and 1M data time shifted 3 days and 33 days respectively, to correct for travel time.

Long acclimation times have been reported before the onset of NDMA biodegradation in the subsurface (Drewes et al., 2006). However, no lag period was observed during the spike (Figure

17) indicating that additional acclimation was not necessary after the sharp increase in influent NDMA.
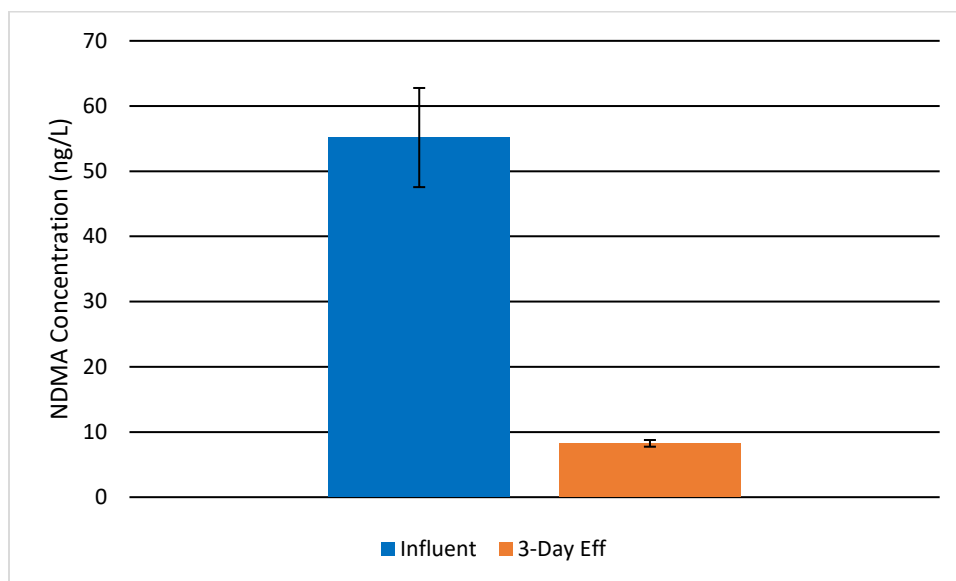
Figure 18: Average NDMA concentration in the influent and 3-day effluent of the spiked set of columns during Phase 2 of testing. 1-month effluent concentration not shown as all measurements were non-detect (<2ng/L).

1,4-Dioxane

During Phase 2 of testing, 1,4-dioxane was spiked to a concentration of 2.4µg/L. As seen in Figure 19, 1,4-dioxane quickly broke through the 3-day column at 70% of the influent concentration and remained steady until the end of the spiking period. After the end of the spiking period, the 3-day effluent concentration quickly dropped below the new influent concentration, implying little to no desorption of 1,4-dioxane occurred. The 1,4-dioxane concentration in the 1-month column effluent was approximately 5% (See Figure 20) of the influent concentration and did not increase over the course of the spike test. This rate of 1,4-dioxane degradation is much higher than observed in most studies, both lab-scale (Nishimura et al., 2014; Shen et al., 2007) and full-scale (Chiang et al., 2008). Inoue et al., 2020 observed slightly enhanced degradation of 1,4-dioxane in the presence of iron and manganese, but this

occurred in aerobic cultures. The continuation of 1,4-dioxane degradation in anoxic/anaerobic

conditions and without the addition of a co-substrate is especially uncommon.
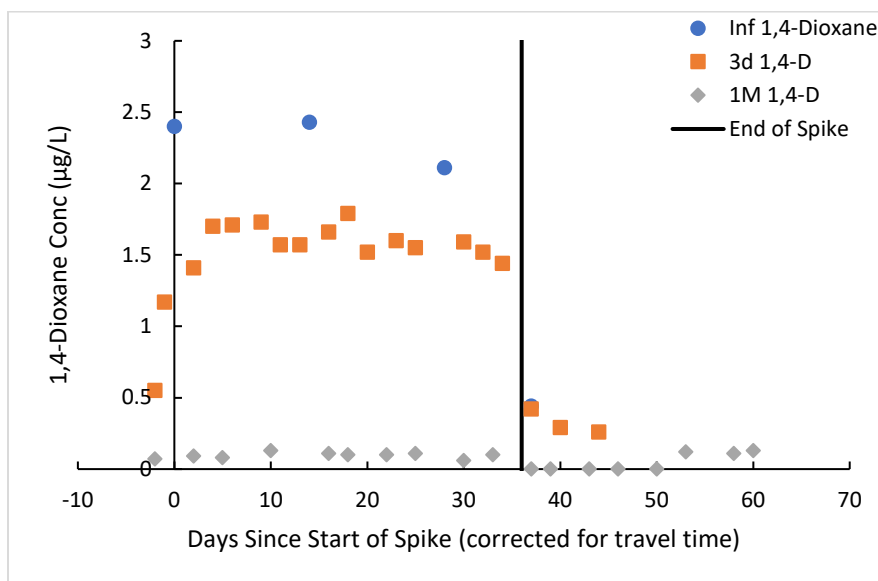
Figure 19: Concentration of 1,4-Dioxane in the influent, 3-day, and 1-month effluents during Phase 2 of testing. Sample times are corrected for column travel time. 3D and 1M data time shifted 3 days and 33 days respectively, to correct for travel time.

In the week following the end of the spike test, the 1,4-dioxane concentration in the 1-month

effluent decreased to non-detect levels (<0.07µg/L). One week after the end of the spiking

period, the concentration rebounded to 0.12µg/L in the 1-month effluent, approximately 30% of

the background influent concentration. There are two possible explanations for the increase and

subsequent decrease in removal after the end of the spiking period. Desorption of 1,4-dioxane

may have occurred after the influent concentration to the 1-month column decreased. However,

the amount of desorption is probably minimal. There was no sorption or desorption observed on

the 3-day columns and removal of 1,4-dioxane was consistent in both columns throughout the

spike test. Another possibility is that some threshold concentration of 1,4-dioxane is necessary

for biodegradation to take place. Higher rates of biodegradation are often observed when higher

initial concentrations of the target substrate are fed into a biological system (Inoue et al., 2018;

Zhang et al., 2017). This would also explain the non-detect measurements immediately following the end of the spike. Immediately after the spike feed was removed, higher degradation was observed as a larger community of 1,4-dioxane degraders had been cultivated. After a week, the community shrank, and the 1-month column could no longer support enough 1,4-dioxane degrading microbes to remove the contaminant to non-detect levels.
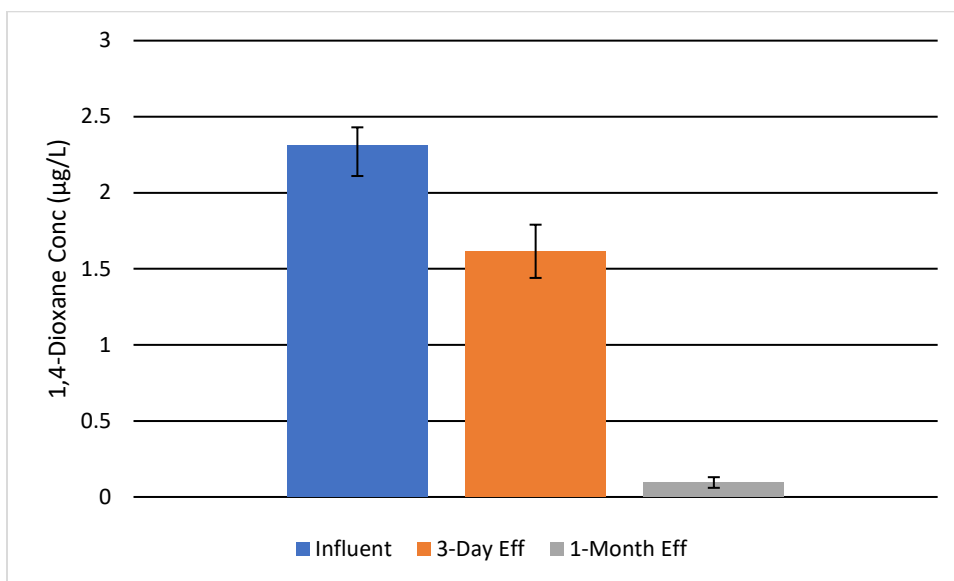
Figure 20: Average influent, 3-day, and 1-month effluent concentrations of 1,4-dioxane on the spiked set of columns during Phase 2 of testing.

Primidone

Primidone is a pharmaceutical compound sometimes detected in wastewater. During Phase 2 of testing, primidone was spiked up to a concentration of approximately 5000ng/L. No significant removal or retardation of primidone was observed across the 3-day or 1-month columns. This was consistent with Trussell et al., 2018, who observed no significant change in concentration of primidone over a 6-month travel time in soil columns. The breakthrough curves of primidone compared to the breakthrough curves of bromide are shown in Figure 21.
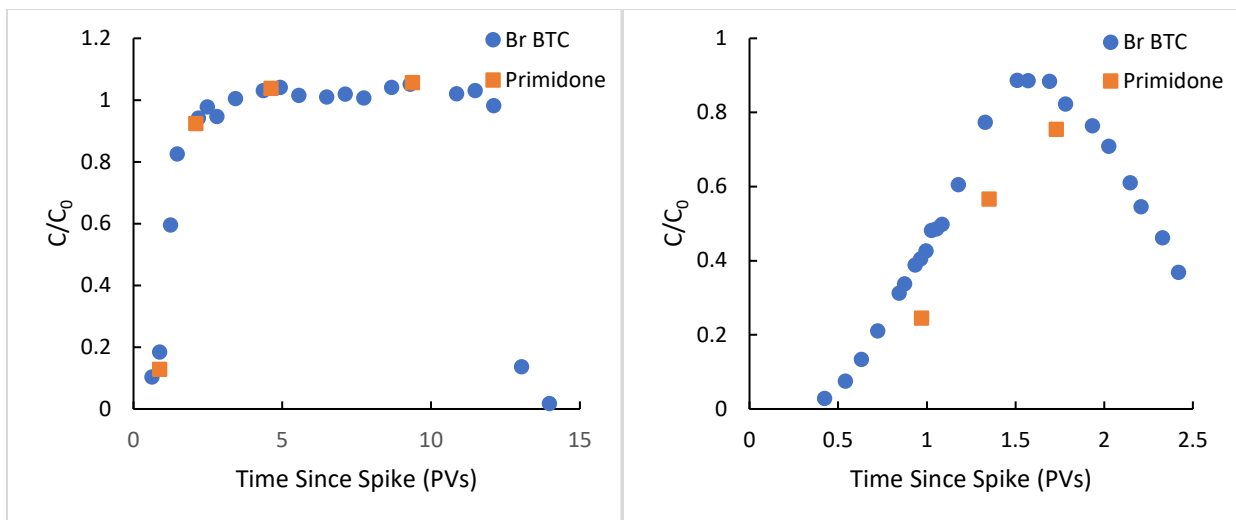
Figure 21: BTCs of primidone on 3-day (left) and 1-month (right) columns compared to bromide

PFAS

Perfluorinated and polyfluorinated alkyl substances (PFAS) are comprised of thousands of compounds characterized by a carbon-fluorine bond. Two perfluorinated compounds were spiked during Phase 2 of testing: perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS). PFOA and PFOS were spiked to concentrations of approximately 80ng/L and 60ng/L respectively. As seen in Figure 22, PFOA behaved conservatively through both the 3-day and 1-month columns. According to the BTC PFOS appeared to be slightly removed through both columns. However, biodegradation of PFOS is not expected because of the extreme stability of the carbon-fluorine bond and lack of reported PFAS degradation. As such, this apparent removal could most likely be attributed to sorption. The apparent sorption of PFOS and lack of PFOA is consistent with literature. Siriwardena et al., 2019 observed that PFOS had a higher preference to sorb to GAC than PFOA due to the hydrophobic sulfonate group.
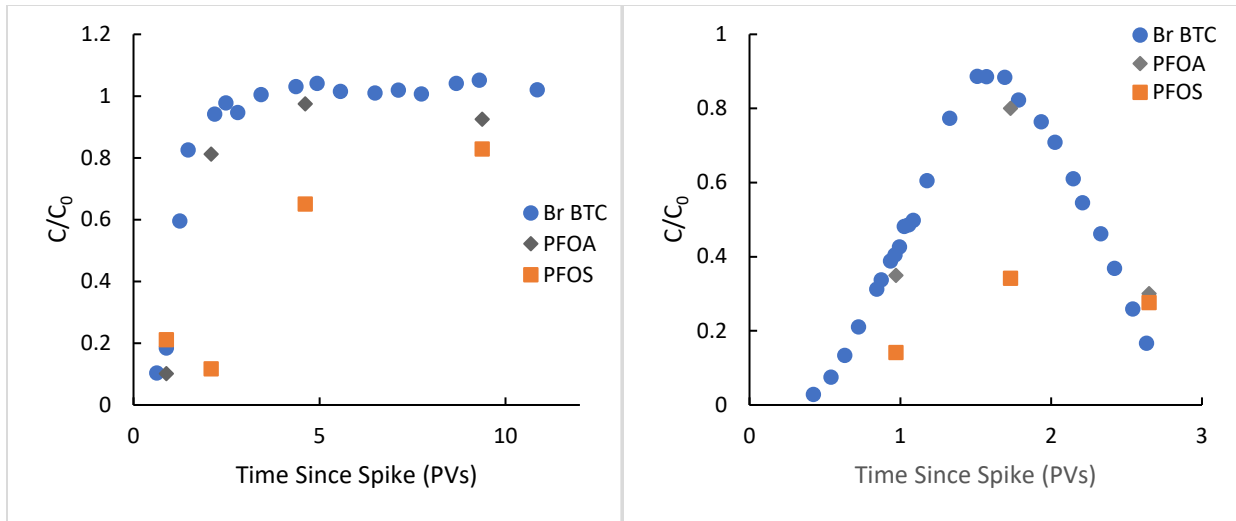
Figure 22: Breakthrough curves of PFOA and PFOS compared to bromide on the 3-day (left) and 1-month (right) column effluents

Perchlorate

Perchlorate is a degradation product of hypochlorite and, as such, is sometimes detected in drinking water and wastewater disinfection with chlorine. During Phase 2 of testing, perchlorate was spiked at a concentration of 50µg/L. In the 3-day (mostly aerobic) column, perchlorate breaks through along with bromide, implying little to no sorption of perchlorate occurs. However, after 1-month of travel time in anoxic-anaerobic conditions, the perchlorate is consistently decreased to less than 5% of the influent concentration (Figure 23).

Figure 23: Breakthrough curves of perchlorate compared to bromide on the 3-day (left) and 1-month (right) column effluents

Notably, the reduction of perchlorate occurred after bromate during spiking, implying that perchlorate reduction is less energetically or thermodynamically favored in microaerophilic conditions, even in the presence of reduced minerals.

Carbamazepine

Carbamazepine is an anti-convulsant drug sometimes found in wastewater. During Phase 2 of testing, carbamazepine was spiked to a concentration of approximately 600ng/L in the column influent. By 30 days into the spiking period, carbamazepine reached a C/C_0 of 1 – the effluent concentration was equal to the influent concentration. This indicates that no degradation of carbamazepine occurred in the 3-day column. Carbamazepine did, however, show slight retardation in the 3-day column, taking nearly 10 pore volumes (PVs) to reach a C/C_0 of 1. The effects of retardation are even more clear in the 1-month effluent data as seen in Figure 24. Carbamazepine clearly takes much longer to break through the column, compared to bromide. It is possible that some degradation of carbamazepine took place in the 1-month column, but

unfortunately not enough samples were able to be taken to observe what the maximum concentration of carbamazepine would have been at complete breakthrough.
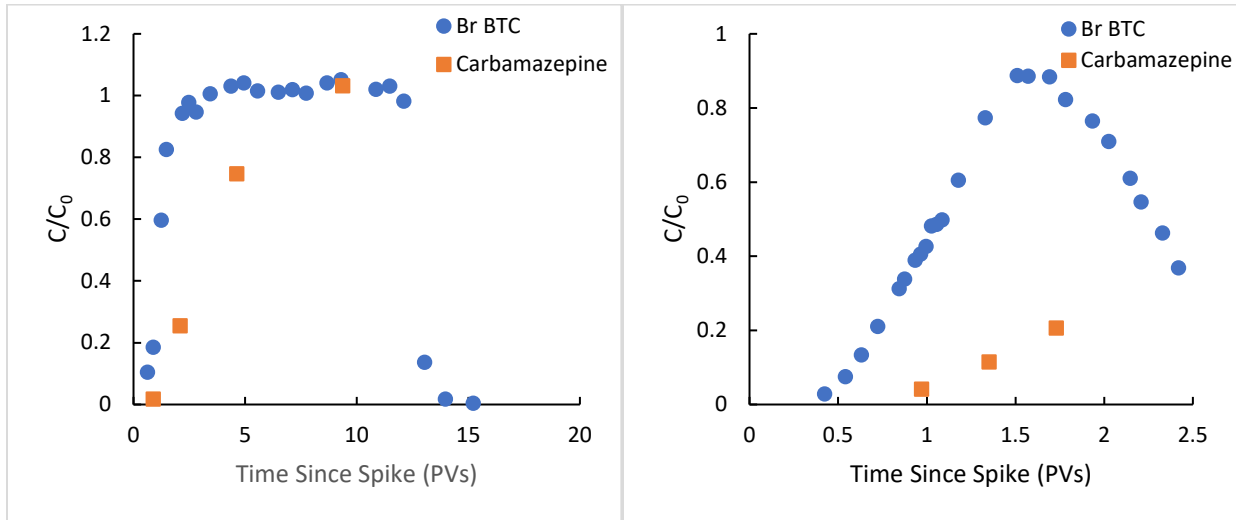
Figure 24: Breakthrough curves of carbamazepine compared to bromide on the 3-day (left) and 1-month (right) column effluents

Dilantin (Phenytoin)

During Phase 2 of testing, Dilantin was spiked into the SAT columns at approximately 400ng/L. Dilantin broke through the 3-day column shortly after bromide, implying that it was slightly retarded. This retardation is more evident based on the 1-month effluent concentrations shown in Figure 25. As with carbamazepine, a full Dilantin BTC was not able to be developed for the 1-month column, so potential degradation with longer travel times in anaerobic conditions was unable to be assessed.
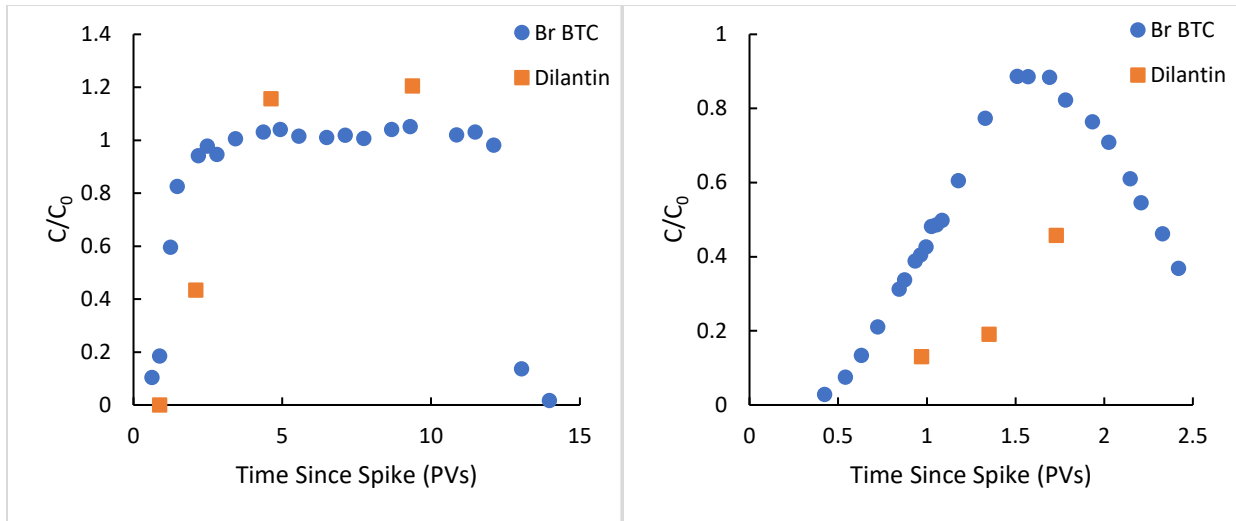
Figure 25: Breakthrough curves of Dilantin compared to bromide on the 3-day (left) and 1-month (right) column effluents

DEET

DEET was spiked to the SAT columns at a concentration of approximately 8000ng/L during Phase 2 of testing. It appeared to start breaking through the 3-day column but was later removed by >95% (Figure 26). Based on k_{oc} values, DEET is expected to sorb less strongly than PFOS, Dilantin, or carbamazepine. Since some breakthrough of all three of those compounds occurred during the spike test, it is reasonable to assume that at least some of the removal of DEET observed was the result of degradation. The early breakthrough supports this theory, as often an acclimation period is necessary for microbes to begin biodegrading certain compounds previously not present (or present at much lower concentrations) in the environment.
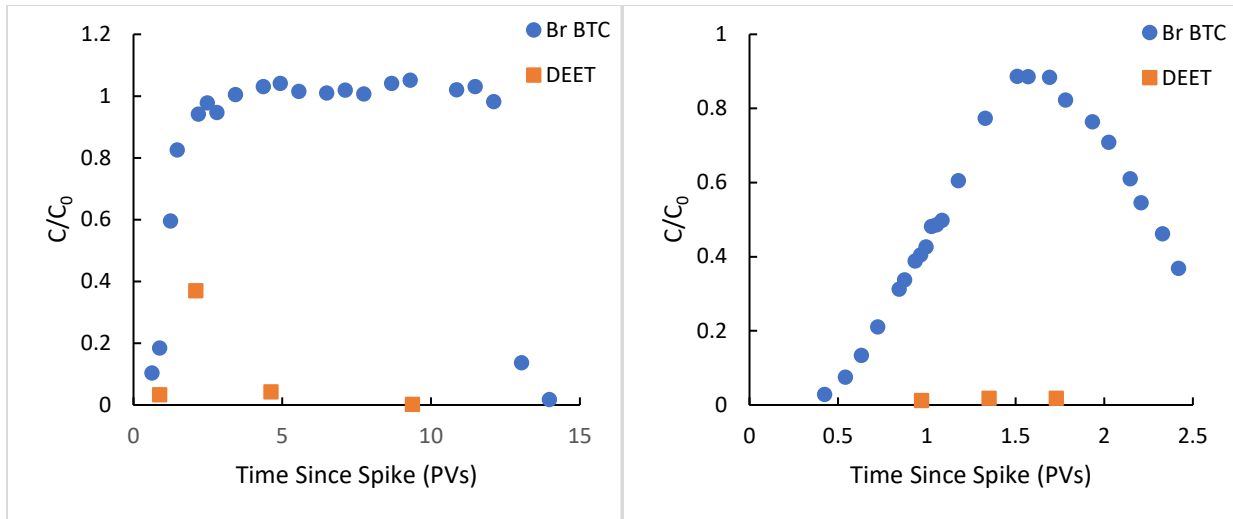
Figure 26: Breakthrough curves of DEET compared to bromide on the 3-day (left) and 1-month (right) column effluents

Cotinine

Cotinine was spiked to the SAT columns at a concentration of approximately 8000ng/L during Phase 2 of testing. It appeared to begin breaking through the column at 20% of the influent concentration after 2PVs, but then the concentration decreased and stayed low (<3% of influent concentration) throughout the remainder of the spiking period (Figure 27). Cotinine was not detected in the effluent of the 1-month column. The quick increase then subsequent decrease in cotinine concentration in the 3-day effluent implies a brief acclimation period followed by robust biodegradation.
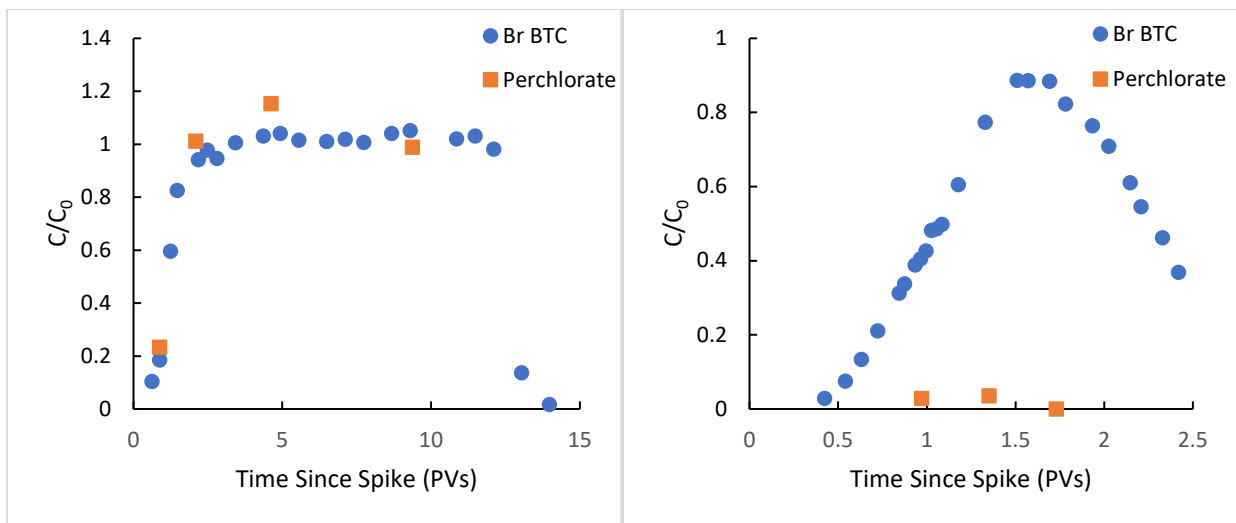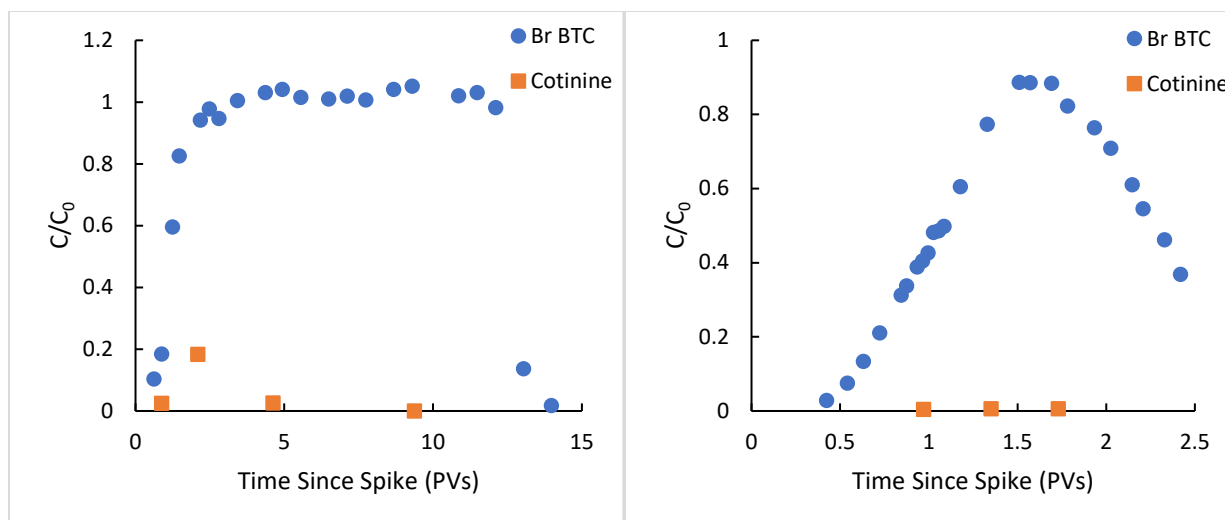
Figure 27: Breakthrough curves of cotinine compared to bromide on the 3-day (left) and 1-month (right) column effluents

Atenolol

During Phase 2 of testing, atenolol was spiked into the columns at a concentration of approximately 5600ng/L. Atenolol was never detected in the effluent of either the 3-day or 1-month column during the test (Figure 28). Based on the k_{ow} value for atenolol, little to no sorption is expected. However, Burke et al., 2013 observed significant (R>6) retardation of atenolol in a soil column experiment. Even accounting for potential retardation, the complete removal of atenolol, even after 10 pore volumes (PVs) implies that some degradation occurs as Burke et al., 2013 eventually saw breakthrough of the compound. This robust degradation is consistent with similar studies. Trussell et al., 2018 observed near complete degradation in a soil column study simulating 30 days of travel time. In a full-scale surface spreading operation, Laws et al., 2011 observed >90% degradation over the course of 70 hours, and complete degradation in two months.
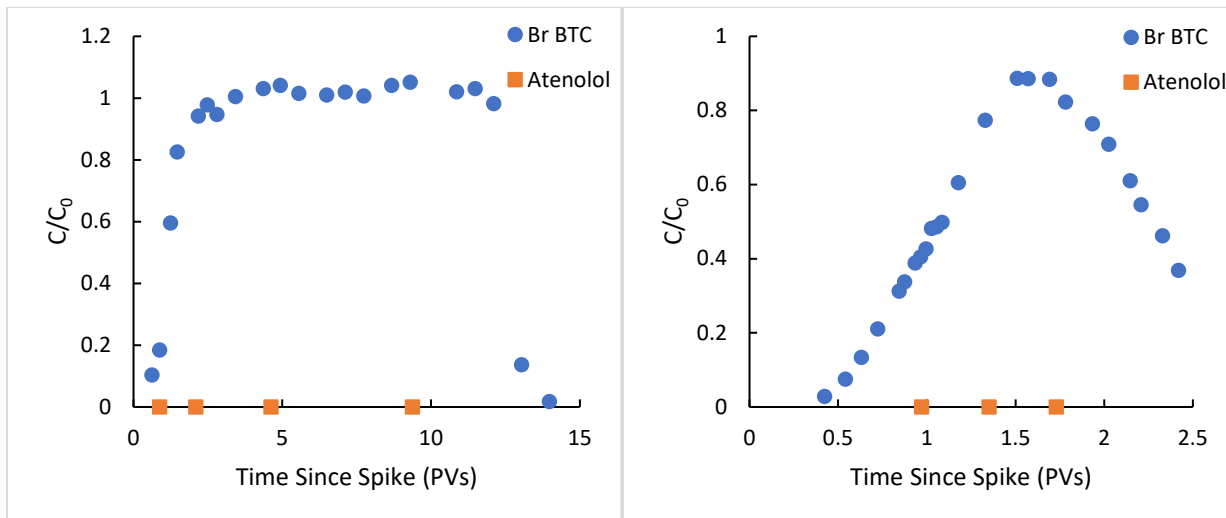
Figure 28: Breakthrough curves of atenolol compared to bromide on the 3-day (left) and 1-month (right) column effluents.

Sucralose

Sucralose is an artificial sweetener with very recalcitrant behavior and as such, is frequently found in wastewater. Sucralose was one of the CECs sampled for on the spiked columns during Phase 2 of testing. Due to its high background concentration, it would have been necessary to spike sucralose to near mg/L concentrations to accurately monitor its travel through the columns and develop a BTC. Therefore, in order to avoid adding a significant amount of TOC to the columns, sucralose was not spiked.
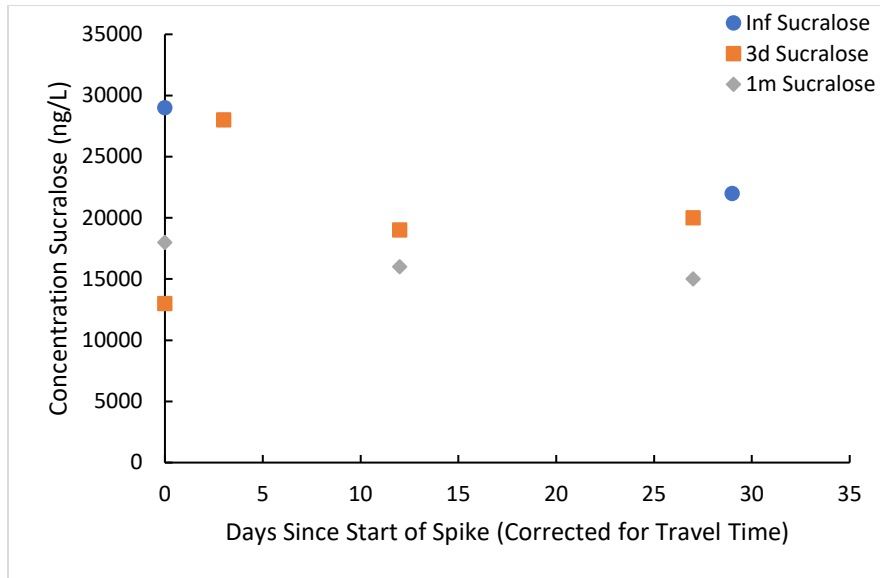
Figure 29: Concentration of sucralose in the influent, 3-day, and 1-month effluents of the spiked columns during Phase 2 of testing. 3D and 1M data time shifted 3 days and 33 days respectively, to correct for travel time.

Still some removal of sucralose can be observed in the soil columns. On average, 20% removal of sucralose was observed across the 3-day column, and 36% removal was observed across the 1-month column seen in Figures 29 and 30. However, some of the apparent removal may have be an artifact of the feeding schedule. The initial low 3-day effluent concentration was possibly indicative of the switch from SWIFT RC final effluent, which is low in TOC and trace organics, to the spiked pilot biofilter effluent.
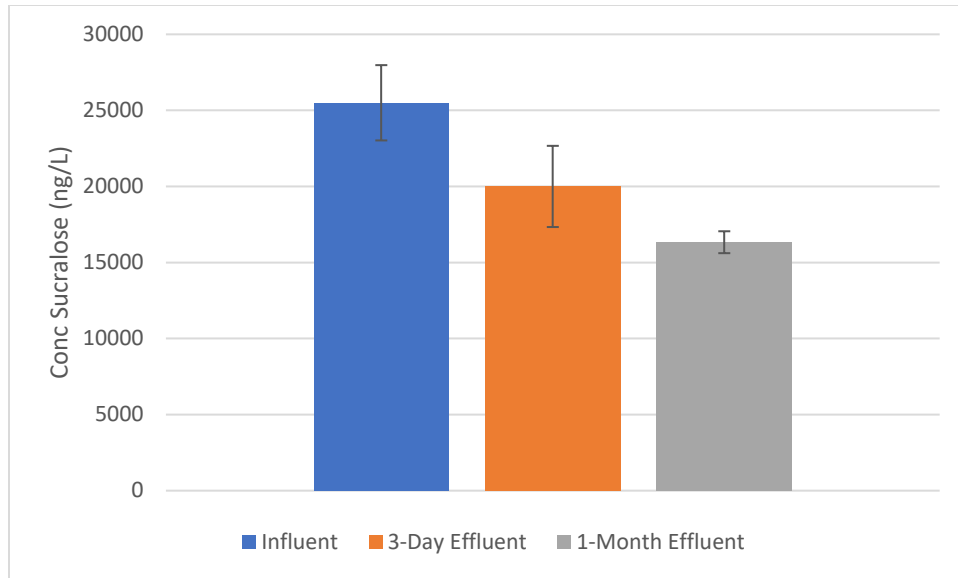
Figure 30: Average concentration of sucralose in the influent, 3-day, and 1-month effluents of the spiked set of columns during Phase 2 of testing.

TCEP

TCEP was one of the CECs sampled on the spiked set of columns during Phase 2 of testing. An attempt to spike TCEP was made, but no increase from the background concentration of 110ng/L was observed. This was possibly due to solubility issues in the stock solution of spiked compounds.

Figure 31: Concentration of TCEP in the influent, 3-day, and 1-month effluents of the spiked columns during Phase 2 of testing. 3D and 1M data time shifted 3 days and 33 days respectively, to correct for travel time.

A small amount of TCEP removal was observed across the 3-day column (Figure 31), however as with sucralose, this may have been due to the switch in influent feed. Again, a low initial 3-day effluent concentration was observed with what appeared to be breakthrough later in the spiking period. An average of 30% removal of TCEP was observed across both columns (Figure 32).

Figure 32: Average concentration of TCEP in the influent, 3-day, and 1-month effluents of the spiked set of columns during Phase 2 of testing.

Metal Mobilization

During Phase 2 of testing, arsenic was monitored on the influent, 3-day, and 1-month effluents of the spiked set of columns. Influent concentrations of arsenic were consistently just above the detection limit of 0.5µg/L. Concentrations increased across the 3-day and 1-month columns as seen in Figure 33, occasionally rising above the SDWA PMCL of 10µg/L in the 1-month column effluent.

Figure 33: Average concentration of arsenic in the influent, 3-day, and 1-month effluents of the spiked set of columns during Phase 2 of testing.

This increase in arsenic concentration was likely due to mobilization from the soil column media. An arsenic speciation test was performed on a sample taken near the end of the spike test. As shown in Table 9, it was found that most of the effluent arsenic in both columns was in the +V oxidation state, implying that it was released via the oxidation of sediments.

Table 9: Arsenic speciation test measuring oxidation states of the spike column's effluent arsenic.

Column	Total As (µg/L)	As (III) (µg/L)	As (V) (µg/L)	Detection Limit (µg/L)
Spiked 3-day	3.7	ND	3.2	2
Spiked 1-month	8.5	ND	8.1	2
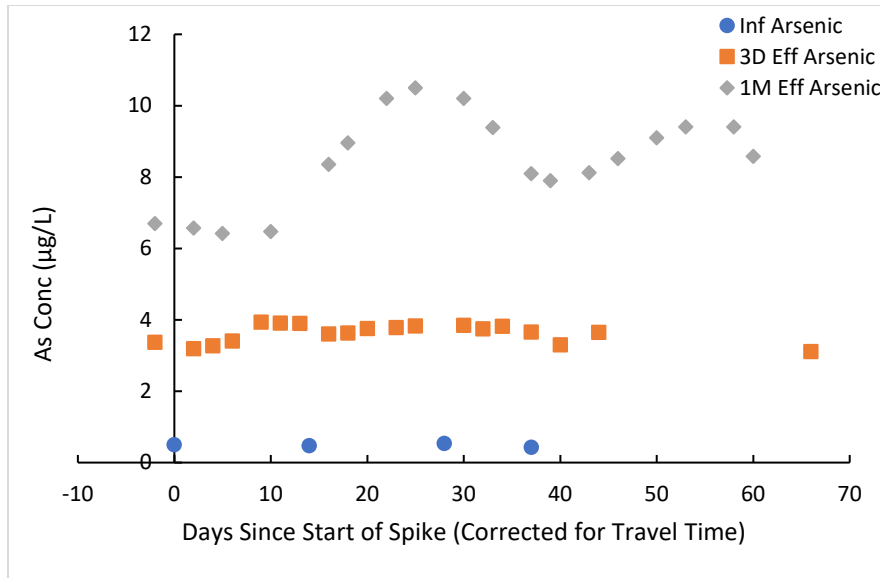
Figure 34: Concentrations of arsenic in the influent, 3-day, and 1-month effluents of the spiked columns during Phase 2 of testing. 3D and 1M data time shifted 3 days and 33 days respectively, to correct for travel time.

The column media was tested for solid phase metal concentrations to confirm the possibility of arsenic release from sediment. The non-spiked column media was tested as taking media samples required opening the column and disturbing the media and the spiked set of columns was being actively sampled. However, all columns were filled with media from the PAS that had been washed and screened using the same method so the solid phase metal concentrations should be similar across all tested columns. As seen in Table 10, a low level of arsenic was detected in the non-spiked column media. However, release of arsenic from sediments containing low mg/kg concentrations is consistent with other groundwater studies (Bose and Sharma, 2002).

Table 10: Solid phase metal concentrations (mg/kg) of the non-spiked columns

Metal	3-Day Column	1-Month Column
Al	1150	1420
Ca	16950	14785
Fe	2395	3005
Mg	306	411.5
K	355	493
Na	218	181
Mn	54.45	67.85
As	1.15	1.37

As seen in Figure 34, the 1-month effluent arsenic appeared to increase over the course of the spike test. As arsenic is known to be mobilized due to competitive desorption (Hering et al., 2011), it was suspected that the elevated bromide in the spiked influent may have been contributing to the release of arsenic. Batch tests were performed using aquifer media and SWIFT final effluent amended with elevated concentrations of bromide and chloride. The results of this test showed that bromide did not affect the release of arsenic (see appendix Figure 42).

Iron was also monitored in the influent, 3-day, and 1-month effluents during Phase 2 of testing. As with arsenic, mobilization of iron was observed in the 3-day and 1-month columns (Figure 35). The release of iron from the 3-day columns was somewhat unexpected as oxidizing conditions prevail in the 3-day column and oxidized iron is not particularly soluble. However, this release of iron may explain the release of arsenic, as arsenic co-occurs with both oxidized and reduced iron minerals. Oxidation of reduced iron minerals, e.g. pyrite, by DO (in the 3-day columns) or nitrate (in the 1-month columns) could have mobilized arsenic (Darling, 2016; Rhine et al., 2008). As most of the effluent arsenic from both the 3-day and 1-month columns was in the +V oxidation state, it is likely that the arsenic was released before the iron-reducing zone of the 1-month columns.
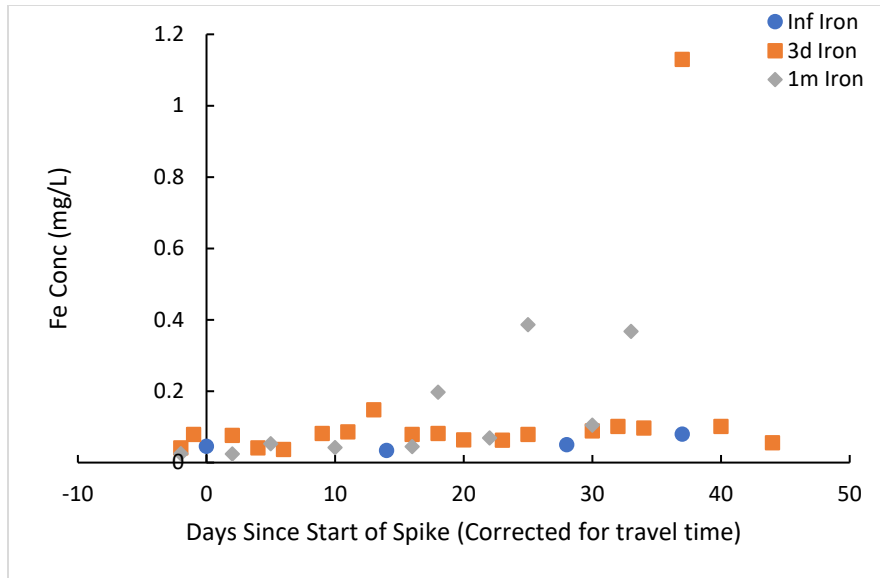
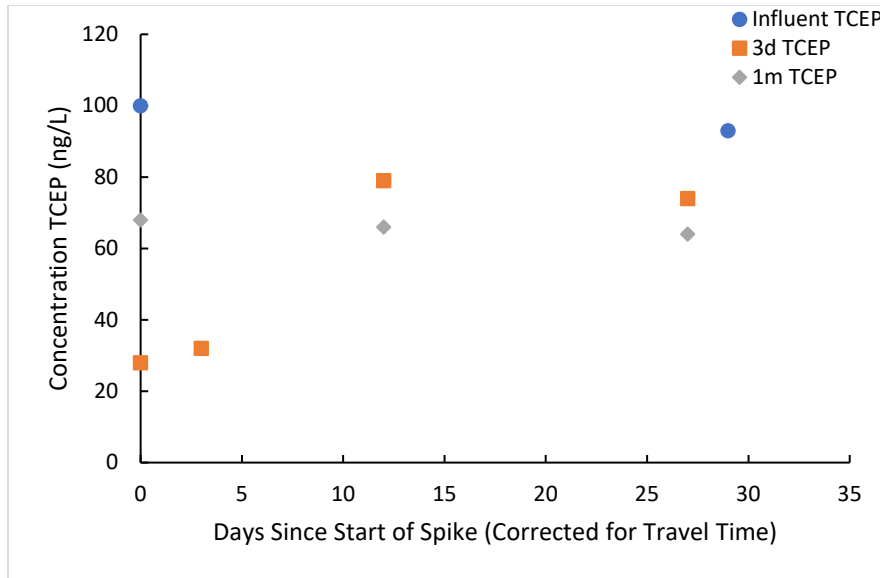**Figure 35: Concentration of iron in the influent, 3-day, and 1-month effluents during Phase 2 of testing. 3D and 1M data time shifted 3 days and 33 days respectively, to correct for travel time.**

Buildup of iron precipitate was observed in the effluent tubing of the 1-month columns throughout both phases of soil column testing. The precipitate was most likely formed by the oxidation of soluble Fe^{2+} as it was exposed to the atmosphere in the effluent tubing of the column. This precipitation implies that the measured effluent iron concentration is lower than the actual iron leaving the column. It may also explain the wide variance in 1-month iron concentration as seen in Figure 36.
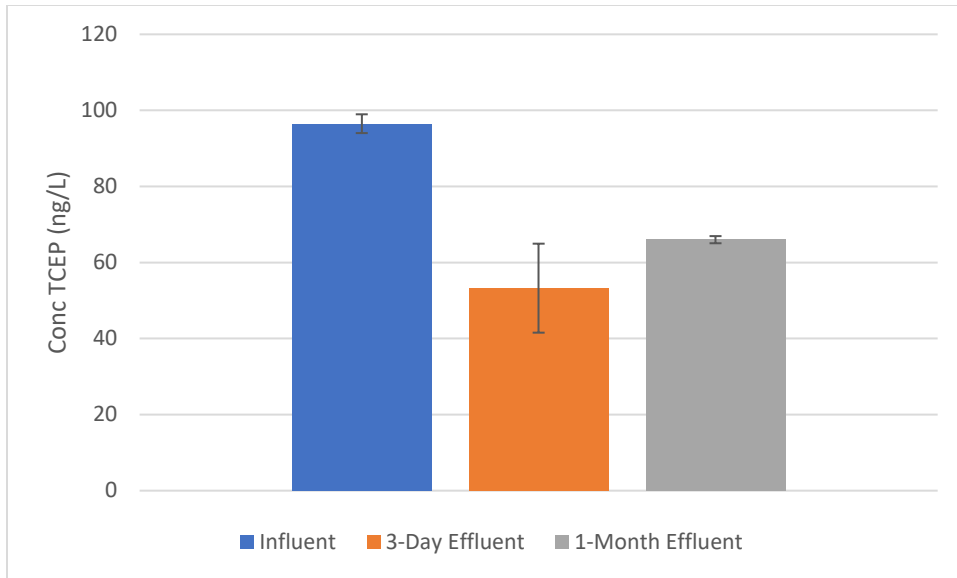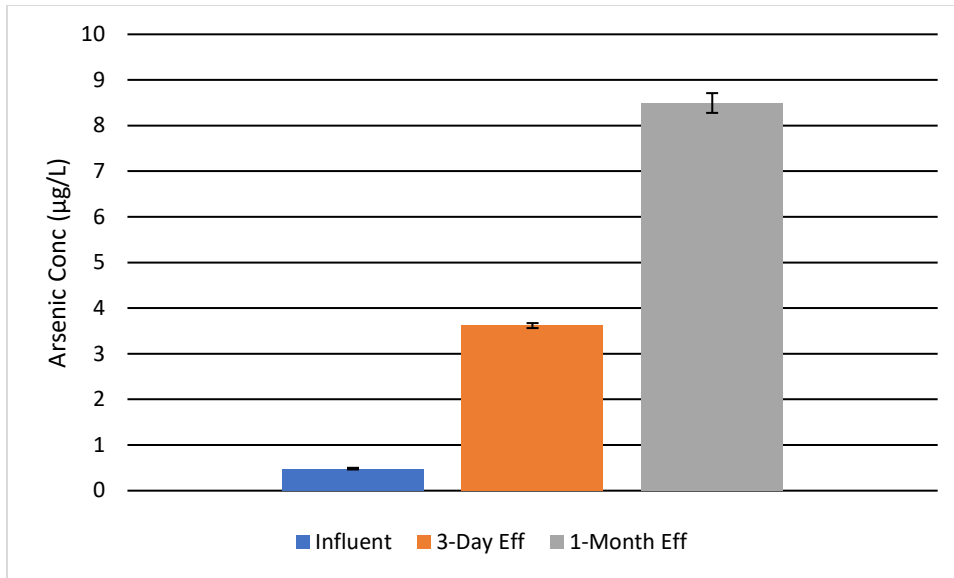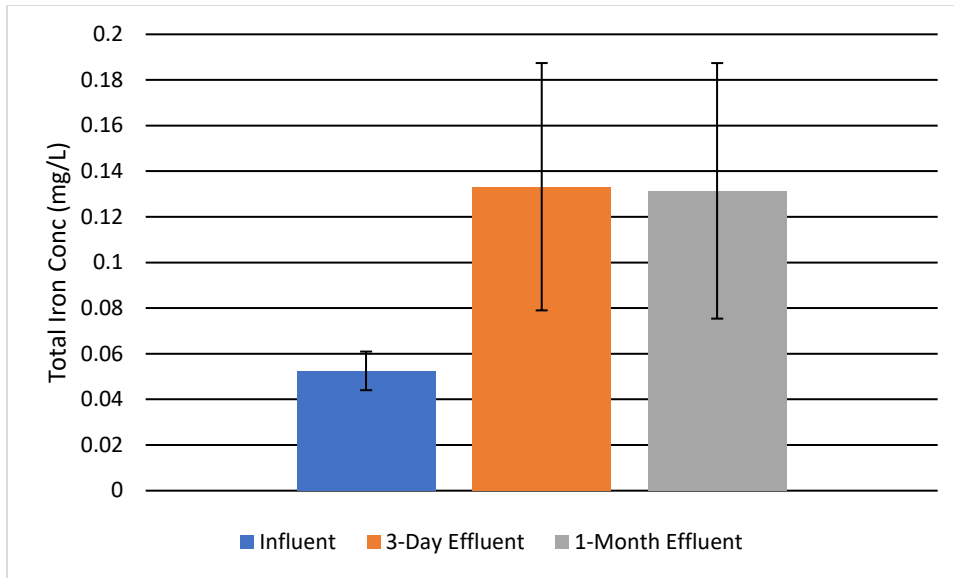
Figure 36: Average concentration of total iron in the influent, 3-day, and 1-month effluents of the spiked set of columns during Phase 2 of testing.
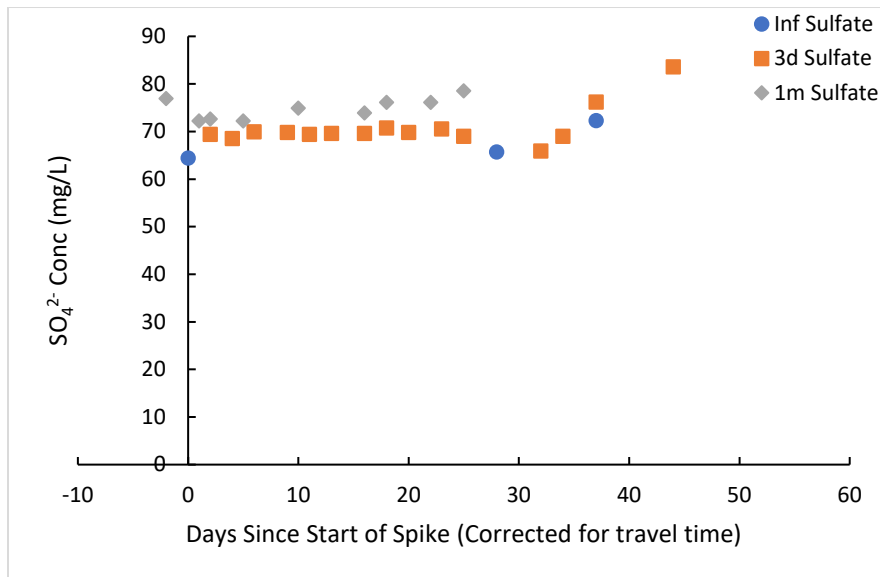
Sulfate

Figure 37: Concentration of sulfate in the influent, 3-day, and 1-month effluents during Phase 2 of testing. 3D and 1M data time shifted 3 days and 33 days respectively, to correct for travel time.

During Phase 2 of testing, sulfate was monitored on the spiked 3-day and 1-month columns

(Figure 37). Due to the observed DO and nitrate reduction as well as suspected pyrite oxidation,

it was hypothesized that sulfate concentrations would increase across the columns. As seen in

Figure 38, sulfate increased approximately 5mg/L in each column. This consistent increase supports the theory that arsenic mobilization in the columns was the result of pyrite oxidation. Pyritic sulfide oxidation could also contribute to nitrate reduction, however 5mg/L production of sulfate is not stoichiometrically sufficient to reduce 5mg/L NO_3^- to N_2. As anoxic/anaerobic conditions were established in the 1-month columns, some sulfate reduction may be expected. Sulfide was only measured occasionally on the 1-month column effluent but was never measured at high enough concentrations for sulfate reduction to be a major factor in the overall sulfur mass balance.
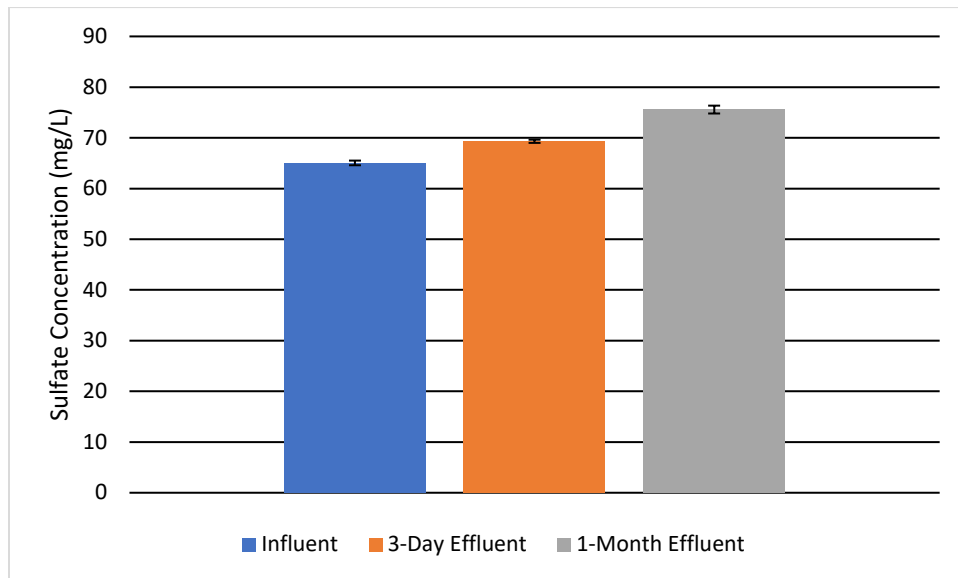
Figure 38: Average concentration of sulfate in the influent, 3-day, and 1-month effluents of the spiked set of columns during Phase 2 of testing.

CONCLUSION

This column study has helped to elucidate the fate and transport of various contaminants, both regulated and non-regulated, during managed aquifer recharge. The study has demonstrated that SAT is an excellent strategy post advanced treatment for additional removal of both bulk and trace contaminants. During both phases of this study, 40-50% removal of TOC was observed in 3 days of travel time. While no additional removal was observed in 30 days, the SUVA of the water continued to change, indicating further TOC transformation. Nitrate was not removed in the 3-day columns but was completely and consistently reduced in the 1-month columns. Bromate was reduced by >90% in the 3-day columns in the presence of nitrate. It was also reduced from influent concentrations representing a "worst-case-scenario" for ozonation of treated wastewater with moderate levels of bromide. NDMA was also reduced greatly in the 3-day columns, and completely removed within 30 days of travel. After a sharp increase in influent concentration of both DBPs studied, no acclimation period was necessary to maintain a high level of removal. Of the CECs studied, compounds fell into one of three groups: compounds that remained conservative through both columns, compounds that were slightly retarded but did not degrade, and compounds that were significantly retarded and/or degraded. Primidone and PFOA were conservative in both the 3-day and 1-month columns. Perchlorate was conservative in the 3-day column but was fully reduced in the 1-month column. PFOS, Dilantin, and carbamazepine appeared to be slightly retarded in both columns, but fully broke through on the 3-day column indicating no degradation. Atenolol, DEET, and cotinine appeared to be well degraded with possible lag periods necessary to establish removal of DEET and cotinine.

ENGINEERING SIGNIFICANCE

In the face of increasing global water scarcity evaluating the feasibility of new sources of potable

water has become increasingly important. Indirect potable reuse through managed aquifer

recharge is a strategy that could help to provide such sources. In coastal regions, MAR projects

have the additional benefit of protection against saltwater intrusion. Until this point, potable

reuse projects have mainly focused on membrane filtration and advanced oxidation with high

pressure UV systems. Both these treatment processes have a high energy cost and limit the

feasibility of reuse projects. As MAR is a relatively passive treatment process, it is an

inexpensive option for providing additional treatment to a reuse treatment train. Evaluating the

ability of soil aquifer treatment to remove contaminants is vital to the development of MAR

reuse projects. As the mobilization of trace metals is also possible during MAR, the evaluation of

mobilization and possible mitigation strategies is also necessary.

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APPENDICES

Appendix A: Sieve Analysis

Particle Size Distribution Report

% +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		

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

* (no specification provided)

Source of Sample: Newport News   **Depth:** 2.00-4.00
Sample Number: S-1   **Date:** 9/25/2017

ECS MID-ATLANTIC, LLC
108 Ingram Road, Suite 1
Williamsburg, VA 23188
Phone: (757) 229-6677
Fax: (757) 229-9978

Client: HRSD
Project: HRSD SAT Column Sieve Analysis
Project No: 13976   **Figure**

Tested By: MK   Checked By: SDP

Figure 39: Sieve analysis performed on aquifer material prior to installation in soil columns

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Appendix B: Bromide Tracer

Bromide Tracer Advection-Dispersion Model

$$C(x,t) = \frac{C_0}{2}\left[erfc\left(\frac{x - v_x t}{2\sqrt{D_L t}}\right) + \exp\left(\frac{v_x x}{D_L}\right)erfc\left(\frac{x + v_x t}{2\sqrt{D_L t}}\right)\right]$$
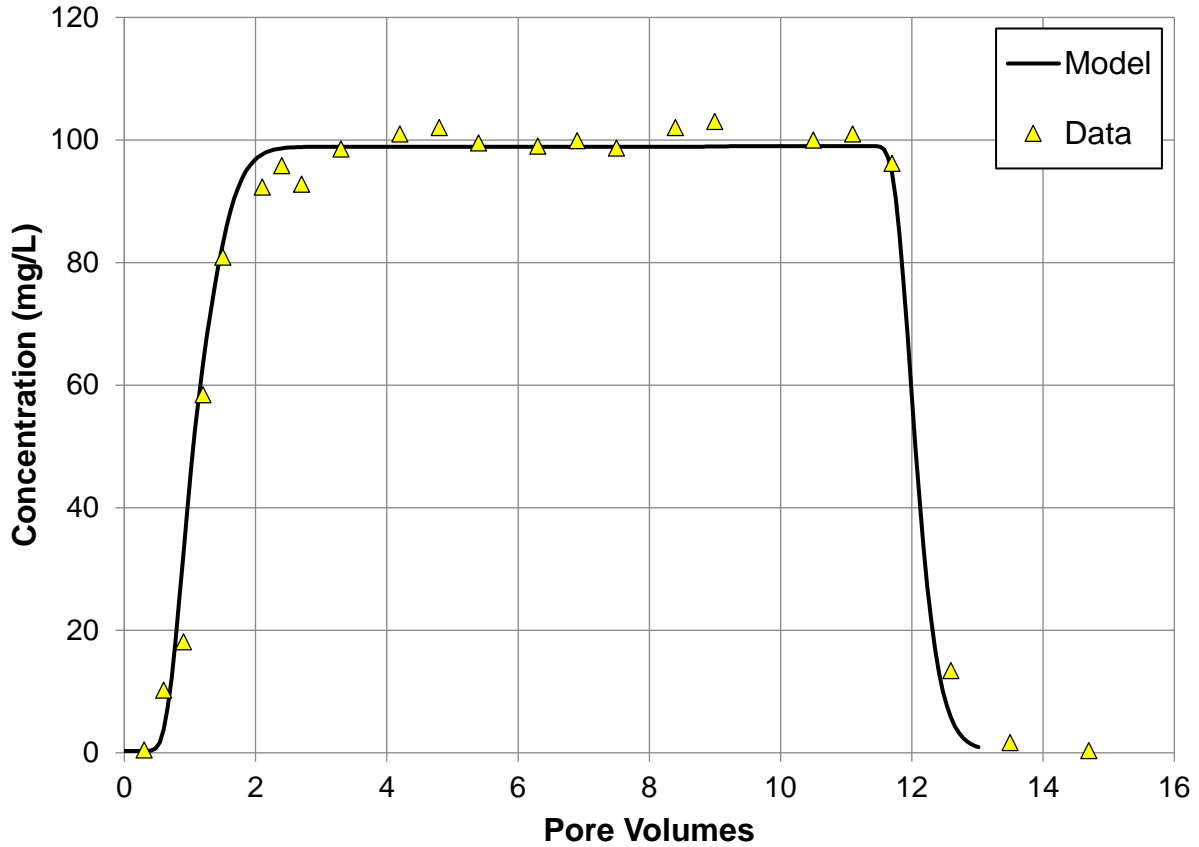

Figure 40: Comparison of 1-dimensional advection-dispersion model to experimental bromide data. Porosity: 0.38; Dispersivity: 0.3ft
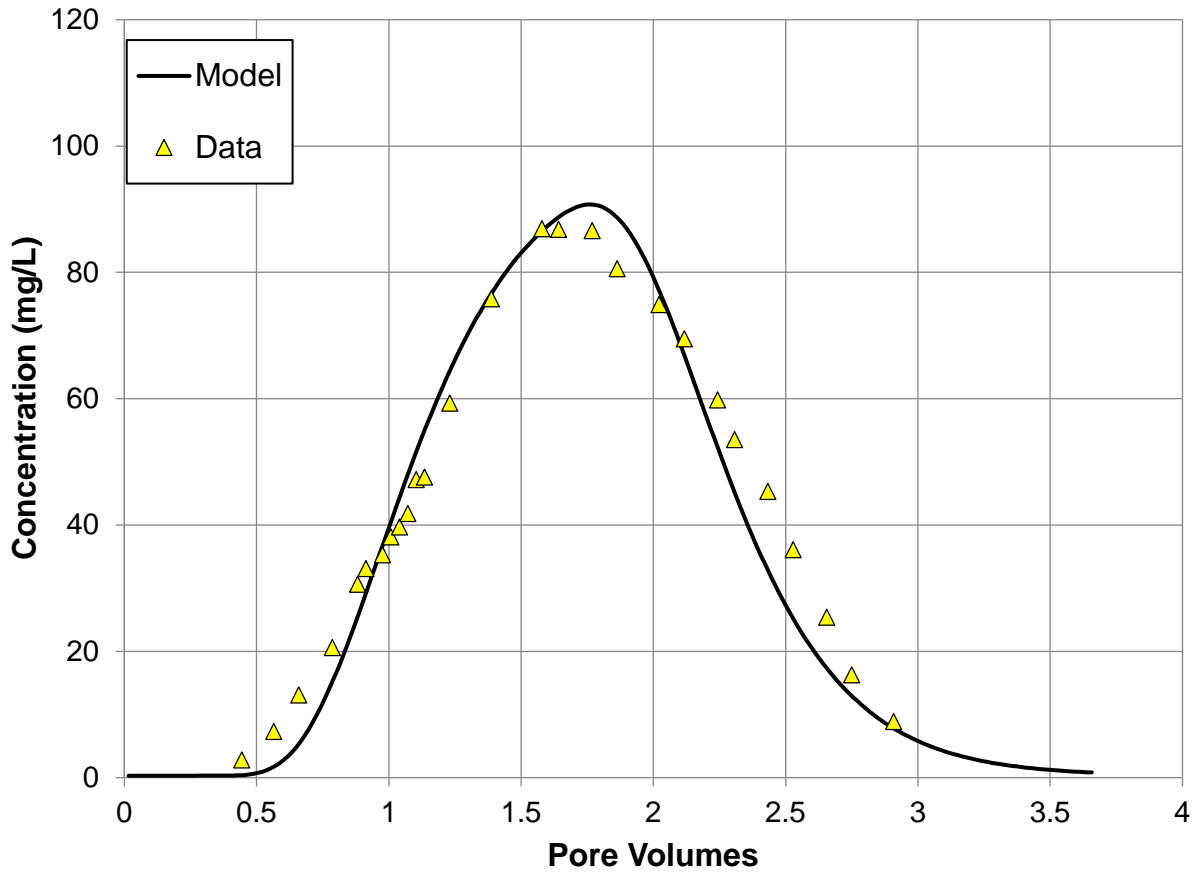
Figure 41: Comparison of 1-dimensional advection-dispersion model to experimental bromide data. Porosity: 0.38; Dispersivity: 0.8ft

Appendix C: CECs

Table 11: List of 120 emerging contaminants analyzed during Phase 2 of testing.

Compound	Detection Limit (ng/L)
DIA	5
Triclocarban	20
Acetaminophen	5
4-nonylphenol - semi quantitative	400
Erythromycin	10
TCEP	10
Ethylparaben	20
Sulfadimethoxine	5
Simazine	5
Primidone	5
Sulfamerazine	5
DEET	10
TCPP	100
TDCPP	100
Lidocaine	5
Propazine	5
4-tert-Octylphenol	50
Sulfamethizole	5
Oxolinic acid	5
Thiabendazole	5
Diclofenac	5
Lincomycin	10
Chlorotoluron	5
Ibuprofen	10
Chloridazon	5
Albuterol	5
Atrazine	5
Cyanazine	5
Nifedipine (semi quantitative)	20
Ketoprofen	5
Naproxen	10
Gemfibrozil	5
Amoxicillin (semi-quantitative)	20
Atenolol	5
Carbamazepine	5
Bromacil	5
Diuron	5
Linuron	5
Triclosan	20
DACT	5
Isoproturon	100

Bezafibrate	5
Diltiazem	5
Isobutylparaben	5
Flumeqine	10
Diazepam	5
Equilin	4
Cotinine	10
Estriol	5
Estradiol	5
Lopressor	20
Cimetidine (semi quantitative)	5
Estrone	2
Estrone	5
Fluoxetine	5
Acesulfame-K	20
Sucralose	100
Chloramphenicol	5
Dilantin	20
Meprobamate	5
17 alpha-ethynylestradiol	0.9
Sulfamethazine	5
Progesterone	5
Caffeine	10
Testosterone	5
Theophylline (semi-quantitative)	10
Phenazone	5
1,7-Dimethylxanthine	5
DEA	5
4-androstene-3,17-dione	0.3
Andorostenedione	10
Meclofenamic Acid	5
Pentoxifylline	5
Iohexal	10
Dehydronifedipine	5
Metazachlor	5
Carbadox	5
Norethisterone	5
Sulfadiazine	5
Sulfathiazole	5
Sulfamethoxazole	5
Iopromide	5
Bendroflumethiazide	5
Trimethoprim	5
Ketorolac	5
OUST (Sulfometuron,methyl)	5
Butalbital	5

|	
Ethinyl Estradiol - 17 alpha	5
Carisoprodol	5
BPA	10
Sulfachloropyridazine	5
Warfarin	5
Theobromine	5
Clofibric Acid	5
Quinoline	5
Propylparaben	5
Butylparaben	5
2,4-D	5
Methylparaben	20
Perchlorate	500
Perfluorooctanesulfonic acid	2
Perfluoroundecanoic acid	2
N-methyl Perfluorooctanesulfonamidoacetic acid	2
N-ethyl Perfluorooctanesulfonamidoacetic acid	2
Perfluorohexanoic acid	2
Perfluorododecanoic acid	2
Perfluorooctanoic acid	2
Perfluorodecanoic acid	2
Perfluorohexanesulfonic acid	2
Perfluorobutanesulfonic acid	2
Perfluoroheptanoic acid	2
Perfluorononanoic acid	2
Perfluorotetradecanoic acid	2
Perfluorotridecanoic acid	2

Appendix D: Batch Arsenic Test
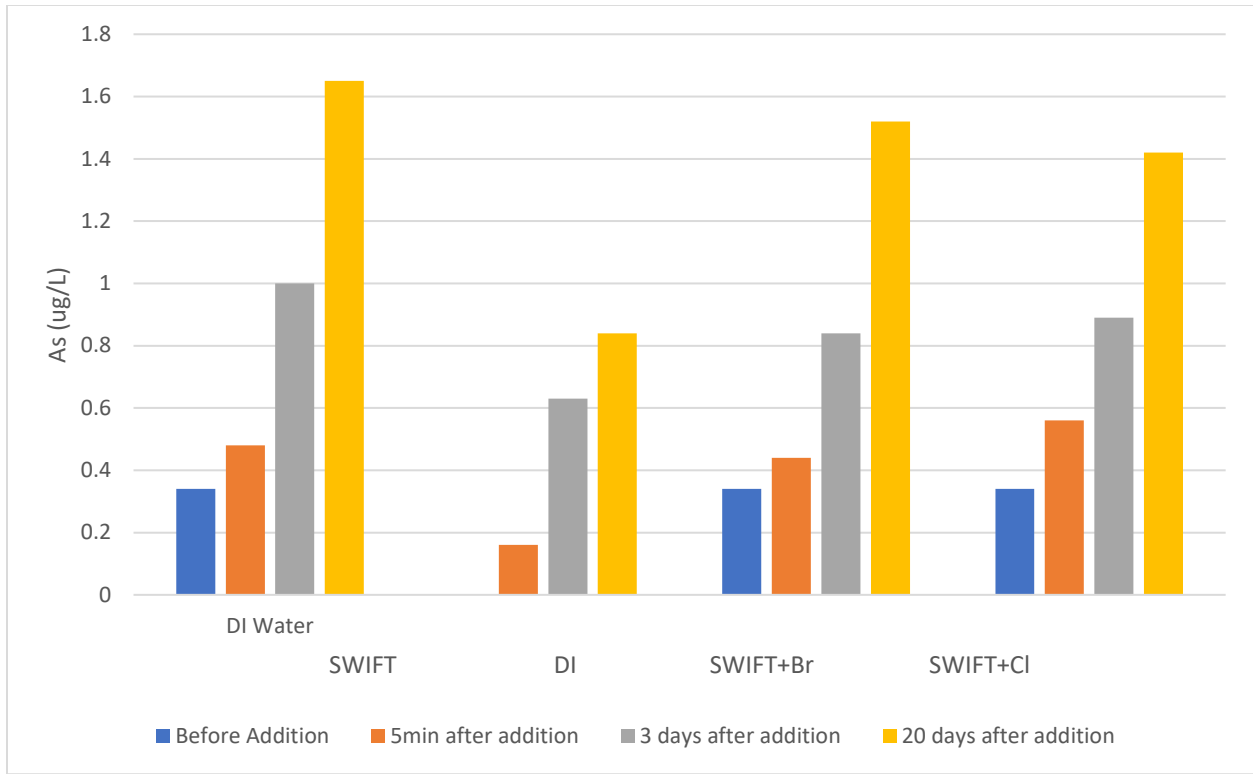
Figure 42: Concentration of arsenic in SWIFT water, deionized water, SWIFT water with 200mg/L added bromide (NaBr), and SWIFT water with 2g/L added chloride (NaCl) after addition to aquifer media. Tests were performed in buckets, separate from column experiment.