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Performance Dynamics of Trace Organic Chemicals in Onsite Treatment Units and Systems

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PERFORMANCE DYNAMICS OF TRACE ORGANIC CHEMICALS IN ONSITE TREATMENT UNITS AND SYSTEMS

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Colorado School of Mines

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1.0 Introduction

The purpose of this work is to improve our understanding regarding presence and attenuation of TOrC in onsite wastewater systems. A full-scale septic tank and sequencing batch membrane bioreactor (SBMBR) were used to provide water for the experiments conducted. Bench-scale soil columns were used to simulate the performance of soil absorption systems. Effluent from both STE and SBMBR were used in soil column experiments.

The objectives of this study were to investigate the fate and occurrence of trace organic contaminants (TOrC) in Onsite Wastewater Systems (OWS). The data collected over the course of this study highlighted the lack of detailed TOrC occurrence data for onsite systems. As such a more robust sampling campaign was completed to characterize the occurrence and standard deviation of TOrC occurrence in septic tank effluents (STE). These results were compared with the variability of TOrC occurrence in advanced above ground treatment effluent. The main objective of the study was to detail the role of the quantity and type of organic matter in infiltrating water on the attenuation of TOrC. The rate at which water is applied to the subsurface may be important in the performance of soil absorption systems.

The analytical methods and experimental approach used for this study are presented in Chapter 2.0. The occurrence of TOrC in septic tanks serving different unique sewersheds and above ground treatment steps are detailed in Chapter 3.0. Chapter 4.0 discusses the role of soil absorption systems on further treatment of TOrC in OWS, specifically the role of loading rate and the amount and type of organic carbon present in infiltrating water. Finally some conclusions and recommendations for future work are presented.

2.0 Experimental Approach

2.1 Field Site

Colorado School of Mines, located in Golden, Colorado is home to a pilot-scale SBMBR. The system collects wastewater from approximately 400 student-housing units into a subsurface septic tank before delivery to SBMBR. The full-scale 6-12 gpm SBMBR system (Figure 1) was designed and constructed by Aqua-Aerobic Systems, Inc. (Rockford, IL) and consists of two alternating side-by-side SBMBR trains. Occurrence sampling and soil column experiments were conducted from January through August of 2009. During the June-August portion of this study only half the student units were occupied.

Figure 1. The Hybrid SBMBR System at Colorado School of Mines, Golden, CO.

2.2 Soil Columns Experiments

Bench-scale packed soil columns were used to simulate the performance of soil absorption system. Eight soil columns (30 cm in length with an inner diameter of 8 cm) were operated under saturated conditions (Figure 2). Four columns were fed with STE and four with SBMBR effluent. A peristaltic pump and silicon tubing were used to deliver water to each column. Columns were saturated in up-flow mode. However, the columns were operated in down-flow conditions in order to reduce any possible porosity issues caused by the force of the water pushed through the columns. The columns were wrapped with contact paper and fed from opaque feed containers to minimize photodegradation of micropollutants and algae growth.

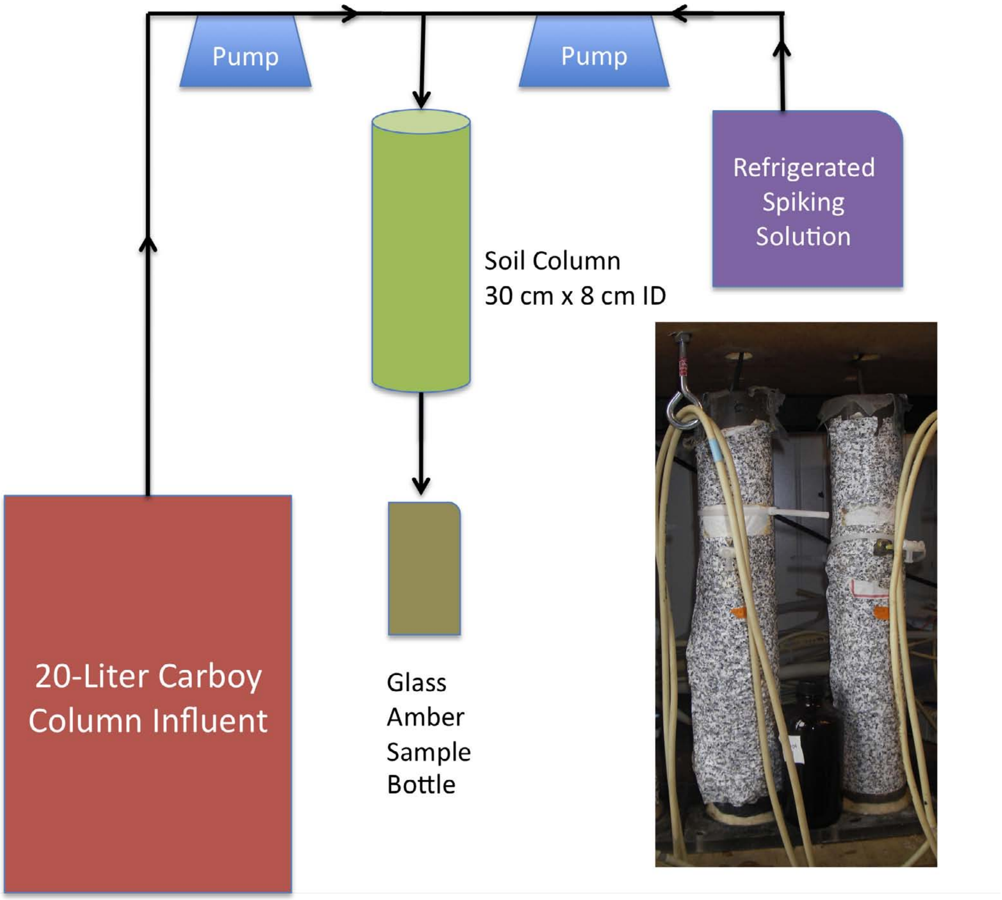


Figure 2. Soil Column Experimental Setup.
Columns operated under saturated conditions.
Additional low flow peristaltic pump was only used for SBMBR spiked experiments.

2.3 Operating Procedures

2.3.1 Sampling Protocol

The water used during these experiments was collected from the STE and SBMBR at Mines Park. The STE was collected from the influent port of the SBMBR utilizing the system pumps for delivery. In order to minimize clogging of tubing and columns STE was passed through a 200-µm screen. SBMBR effluent was collected from a sampling port on the system. The final stage of SBMBR treatment is membrane treatment through a 0.1-µm filter. Water for each effluent type was delivered from a 20-Liter carboy in single pass mode through soil columns. The water in the carboys was replaced approximately every three days.

During sampling a fresh batch of water was allowed to percolate through columns for approximately eight hours before sampling began. Water samples were collected in 250 mL glass amber bottles for chemical and physical measurements. Samples were immediately refrigerated with hold times of less than three days for all analysis. Water samples for TOrC analysis were collected into 1-Liter amber glass bottles, cleaned and pre-rinsed with methanol and a 1 g/L dose of sodium azide to minimize any biotransformation after sampling. Samples were then refrigerated prior to solid phase extraction.

2.3.2 Spiking Procedures

Results from initial screening efforts revealed that the SBMBR effluent did not have measurable concentration of many TOrC in our analytical suite. As a result, the feed solution was spiked with five TOrC representing compounds with a range of biodegradability (i.e., ibuprofen, naproxen, gemfibrozil, diclofenac, and clofibric acid) to a target concentration of 500 ng/L each. To avoid or minimize any biotransformation losses, compounds were spiked into the feed line with an additional low flow peristaltic pump (Figure 2). Concentrated stock solution was kept in a refrigerator. While spiking experiments targeted a nominal concentration of 500 ng/L, the apparent influent concentration was measured on each sampling campaign.

2.4 Analytical Methods

The analytical methods used during these experiments followed Standard Methods where available (APHA, 2005). More advanced analysis (e.g., NOM characterization and TOrC analysis) had been previously developed and validated at Colorado School of Mines.

2.4.1 Physical and Chemical Measurements

pH was measured with a dual-probe Oakton Waterproof 300 series hand-held meter (Oakton Instruments, Vernon Hills, IL) (Standard Method 4500-H). DO was measured with a portable YSI 85 oxygen, conductivity, salinity, and temperature meter (YSI Incorporated, Yellow Springs, OH) (Standard Method 4500-O).

2.4.2 Nutrients and Anions

The anion composition of the aqueous samples was determined using a Dionex ICS-90 Ion Chromatography System (IC) using an AS14 column and a sodium hydroxide eluent (Standard Method 4110B). Ammonia and nitrate were measured independently using a Hach DR/2500 (Hach Company, Loveland, CO) according to Hach methods 8038 and 10020, respectively. This ammonia method is designed for ranges between 0.02 and 2.50 mg/L. The nitrate test is designed to measure a range of 0.2 to 30 mg/L

2.4.3 Cations and Metals

The anion composition of the samples was evaluated with an Optima 3000 Inductive Coupled Plasma (ICP) Spectrometer (Standard Method 3120B). Manganese was measured independently using Hach DR/2500 according to Hach method 23508 ranging 0.0 and 0.700 mg/L.

2.4.4 Bulk Organic Characterization

Quantifying and characterizing the organic matter present in infiltrating water is important to develop a clear understanding of the fate of TOrC in these systems.

UV, DOC, SUVA

Additional characteristics of the organic matter in aqueous samples were measured using UV absorbance (UVA) and dissolved organic carbon (DOC). The UVA was measured with a

Beckman Coulter DU 800 spectrophotometer with a 1-cm quartz cell (Standard Method 5910 B). The samples were measured at UV wavelength of 254 nm; UV absorbance at this wavelength corresponds to the concentration of unsaturated and aromatic organic constituents in the sample. The samples were prefiltered with a 0.45 µm Supor-450 filter before analysis. Samples were then placed in 17 mL glass vials and acidified to a pH of less than two with phosphoric acid.

The ratio of UVA and DOC measurements were used to calculate values of specific UV absorbance (SUVA). The SUVA of the aqueous sample is a measure of the aromatic character of the natural organic matter in the sample. The value relates the natural organic matter to the level of the aromaticity per carbon unit. The SUVA is calculated according to the following equation:

$$SUVA = \frac{UVA}{DOC}$$

SUVA = specific UV absorbance [L/(mg · m)]
UVA = UV absorbance [1/m]
DOC = dissolved organic carbon [mg/L]

3D Fluorescence

The fluorescence of DOC is due to the presence of fluorophores that absorb photons, followed by the excitation to a higher electronic energy state. Then the absorbed energy is released to the environment at a greater wavelength (Amy and Drewes, 2007; McKnight et al., 2001). Fluorescence spectrometry can be used to distinguish humic-like organic matter from protein-like organic matter. 3D-Fluoresence can be used to gain a measure of the protein-like and humic-like relative abundances. There are three main peaks identifiable in the excitation and emission matrix (EEM). These three peaks and their associated excitation and emission wavelengths are as follows and can be identified on the SBMBR EEM (Figure 3).

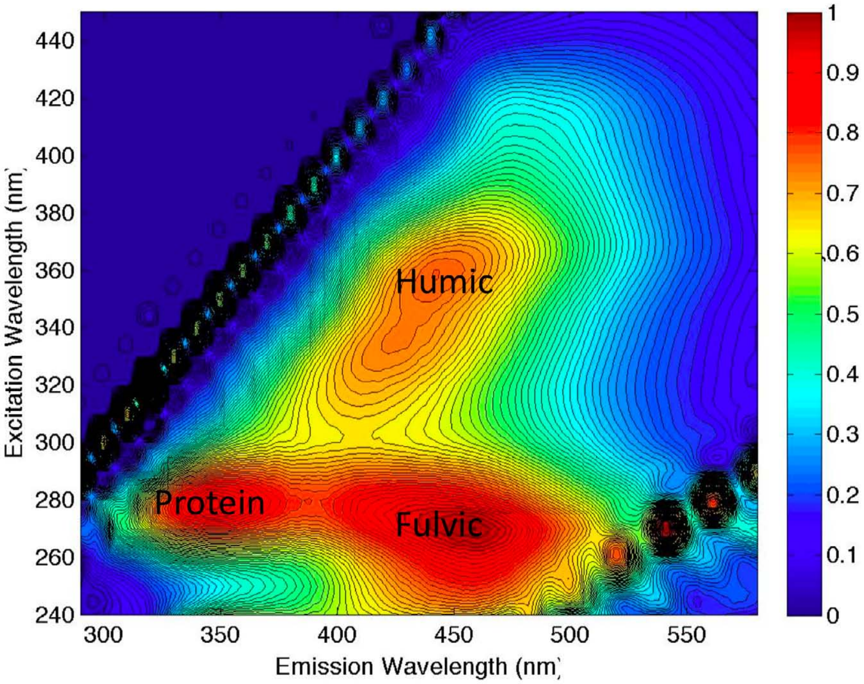


Figure 3. Excitation Emission Matrix. Protein, Humic, and Fulvic Peaks as Labeled.

Size Exclusion Chromatography

Size Exclusion Chromatography (SEC) with online UV absorbance and dissolved organic carbon (DOC) detection can be used to identify the relative distribution of molecular weight fractions of DOC (Figure 4). The largest compounds move quickly through the column, while the smallest organic carbon compounds are retained in the column. In a typical drinking water sample four key peaks can be identified; polysaccharides, humic substances, humic building blocks, and low molecular weight acids. For the samples described herein, the MBR effluent exhibits each of these peaks. This method will enable a measure of relative total mass of each molecular weight fraction and relative aromaticity.

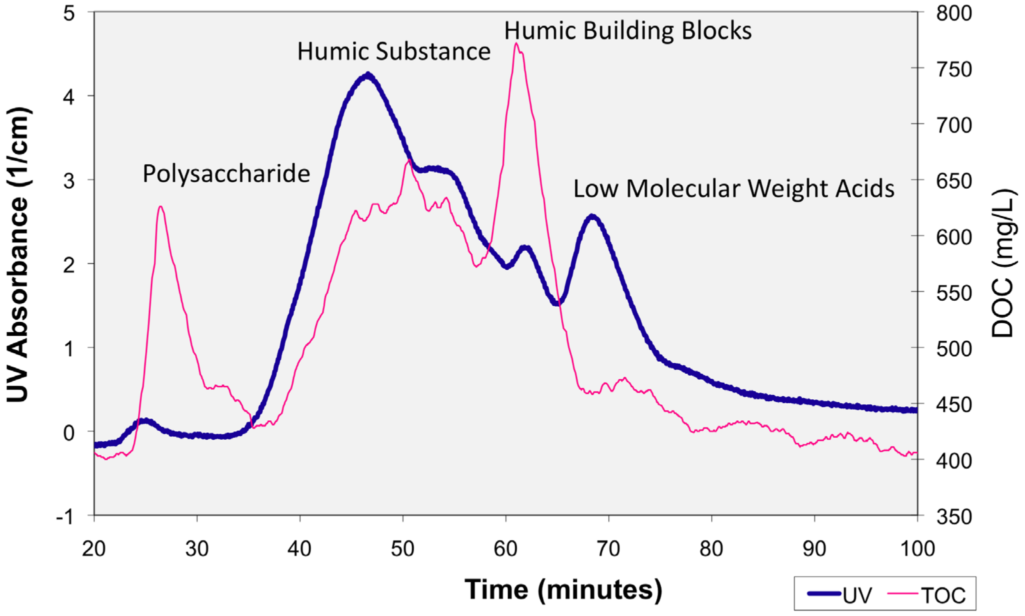


Figure 4. Example SEC Chromatogram with Polysaccharide, Humic Substances, Humic Building Blocks, and Low Molecular Weight acid Peaks as Labeled.

2.4.5 Trace Organic Chemicals

The method used for TOrC analysis at CSM is a gas chromatography mass spectrometry (GC-MS) method developed after Redderson and Heberer (2003). Detection limits have been verified down to the tens of ng/L for sample matrices low in DOC (<2 mg/L). The compounds included in the suite have been selected to represent compounds from readily degradable to poorly degradable (Table 1).

Preparation steps of aqueous samples prior to GC-MS analysis include solid phase extraction (SPE), elution, and derivatization. The volume of aqueous sample concentrated during SPE is related to initial concentration. For the analysis in this study all STE related samples 20 mL and 300 mL for all SBMBR related samples. The pH of aqueous samples is adjusted to below 1.5 (below the pK_a of all compounds in the suite), 1% methanol added, and spiked with isotope labeled surrogate standards to account for losses throughout the method.

Samples are extracted onto 6 mL polyethylene cartridges packed with 1 gram of Bakerbond Polar Plus RP-C-18. Cartridges are conditioned with 5 mL of acetone, 10 mL methanol, and 10 mL Milli-Pore water at pH 2. The cartridges were then fitted on a PreSep 12-port manifold. A gentle vacuum is applied to pass the sample through the cartridges at a flow rate of 3-5 mL/min using Teflon tubing. The cartridges were dried using a light stream of medical-grade nitrogen.

Table 1. GC-MS Analytical Suite with Compound Class and pKa.

Group	Target Compound	pK_a
Stimulant	Caffeine	1.5
Anti-inflammatory analgesic	Clofibric Acid	3.18
	Diclofenac	4.18
	Ibuprofen	4.41
	Ketoprofen	4.23
	Naproxen	4.40
	Salicylic acid	2.97
Blood-Lipid Regulator	Gemfibrozil	4.75
Chlorinated Flame Retardants	TCEP	n/a
	TCPP	n/a
	TDCPP	n/a

Dried cartridges are eluted with acetone into a 2 mL GC vial to concentrate target compounds. Samples are dried down under a stream of medical grade nitrogen. The derivatization agent pentafluorobenzyl bromide (PFB) is added to fragment the compounds for GC analysis. The residual sample is dissolved with 100 µL of a 2% PFB solution prepared in toluene and 4 µL of triethylamine. Samples were baked in an oven for one hour at 100°C and then dried with nitrogen. The resulting residue was once again dissolved in 100 µL toluene. Finally the samples are analyzed with a HP 6890 gas chromatograph and a HP 5973 quadrupole mass spectrometer.

2.4.6 Statistics

The accuracy and impartiality of this study were assured by using proper quality assurance and quality control (QA/QC) procedures. QA/QC affects every aspect of this project, beginning with the design of the experiments, the analytical methods, bench and field studies, and ending with the analyses of the data and production of the final report.

To ensure the data generated through the research were both appropriate and in compliance with quality assurance objectives for accuracy, precision, representativeness, completeness, and compatibility, specific quality control practices were followed.

3.0 Occurrence Variability of Trace Organic Chemicals in Onsite Wastewater Treatment Systems as a Function of Sewershed and Above Ground Treatment

3.1 Introduction

Onsite wastewater treatment systems account for approximately one quarter of U.S. wastewater treatment. Water discharged to soil absorption systems ultimately recharge groundwater or surface water nearby. TOrC plumes have been reported beneath onsite wastewater systems (Carrara et al., 2008; Moelants et al., 2008). Many of the communities that rely on onsite wastewater systems also utilize drinking water wells (Verstraeten et al., 2005). Understanding the occurrence, fate, and transport of TOrC in these systems is important to ensure safe drinking water to the communities in which they are utilized.

Each onsite system collects wastewater from a unique catchment or sewershed of users. Individual onsite systems can range in size from a single source (e.g., resident, convenience store, hospital, gas station), to a small community (e.g., 500-1000 users). The type and number of users in each sewershed influences the occurrence and variability of TOrC in these systems. While the occurrence of TOrC in some onsite systems have been reported (Carrara et al., 2008; Conn et al., 2006; Matamoros et al., 2009) the variability in these systems has not been described. In addition the relationship between the size and type of sewershed and TOrC occurrence has not been established.

Advanced above ground treatment systems have been developed to treat wastewater to a quality suitable for surface discharge or subsurface infiltration in regions with not suitable geological conditions. Understanding the occurrence of TOrC in above ground treatment processes is important to optimize soil absorption system loading rates as well as establish decision matrix for selecting above ground treatment in system design.

3.2 Hypotheses

The hypotheses of this study are twofold:

- The variability in TOrC occurrence in STE is a function of the size of serviced sewershed and the type of wastewater generators
- SBMBR effluent exhibits a lower variability and lower occurrence of TOrC as compared to STE and are similar to tertiary treated effluent of centralized systems.

3.3 Results and Discussion

3.3.1 TOrC in STE

The type and number of users in an onsite wastewater sewershed is likely to play a role for TOrC occurrence and variability. Sampling of STE effluent at CSM for TOrC occurrence began in May 2009. The TOrC detected throughout the course of this study (Table 2) were in the range of other onsite systems reported in the literature (Matamoros et al., 2009).

The reported occurrence of TOrC in onsite systems is quite variable and has the potential to vary at a single location as the TOrC usage of people in the sewershed changes. Single source systems may experience greater shock loads and variability than larger systems. Comparing the frequency of detection of some key compounds at Mines Park as compared to those reported for single sources, ibuprofen, naproxen, and salicylic acid are detected more frequently in a sewershed of 400 people, but average reported concentrations are higher in the single source.

Table 2. Table Summarizing Average Concentration and Detection Frequency for Select TOrC.
Add additional specific paper references as available to represent wide variety of sewershed sizes.

Group	Target Compound	STE (µg/L) ~400 people		Conn et al. in review (µg/L) Single Sources		Matamoros et al., 2009 (µg/L) 4-300 people	
		AVG	DF	AVG	DF	AVG	DF
Stimulant	Caffeine	34.3	100 (17/17)	130	100 (14/14)	31.9	100 (16/16)
Anti-inflammatory analgesic	Clofibric Acid	<0.5	0 (0/17)	<0.1	0 (0/15)	Not available	
	Diclofenac	<0.5	6 (1/17)	<0.1	0 (0/15)	0.50	31 (5/16)
	Ibuprofen	19.0	100 (17/17)	110	60 (9/15)	1.95	88 (14/16)
	Ketoprofen	<0.5	0 (0/17)	<0.1	0 (0/15)	1.79	13 (2/16)
	Naproxen	9.1	47 (8/17)	150	7 (1/15)	0.09	63 (10/16)
	Salicylic acid	39.3	100 (17/17)	210	87 (13/15)	16.4	100 (4/4)
Blood-Lipid Regulator	Gemfibrozil	<0.5	0 (0/17)	<0.1	0 (0/15)	Not available	
Chlorinated Flame Retardants	TCEP	1.7	35 (5/17)	<0.2	0 (0/15)	Not available	
	TCPP	2.8	100 (17/17)	<0.2	0 (0/15)	Not available	
	TDCPP	<0.5	0 (0/17)	<0.2	0 (0/15)	Not available	

Little is known about the variability of TOrC occurrence of a single source. In July 2009 an intensive sampling campaign was conducted to investigate the variability of TOrC occurrence in Mines Park STE. Sampling focused on the variability over a 24-hour period, and the variability between weekday and weekend use.

During the 24-hour sampling campaign, concentration of some compounds (i.e. caffeine) varied by an order of magnitude. Peak concentration of caffeine and salicylic acid were detected in the composite taken from 10:00 am to 2:00 pm (Figure 5).

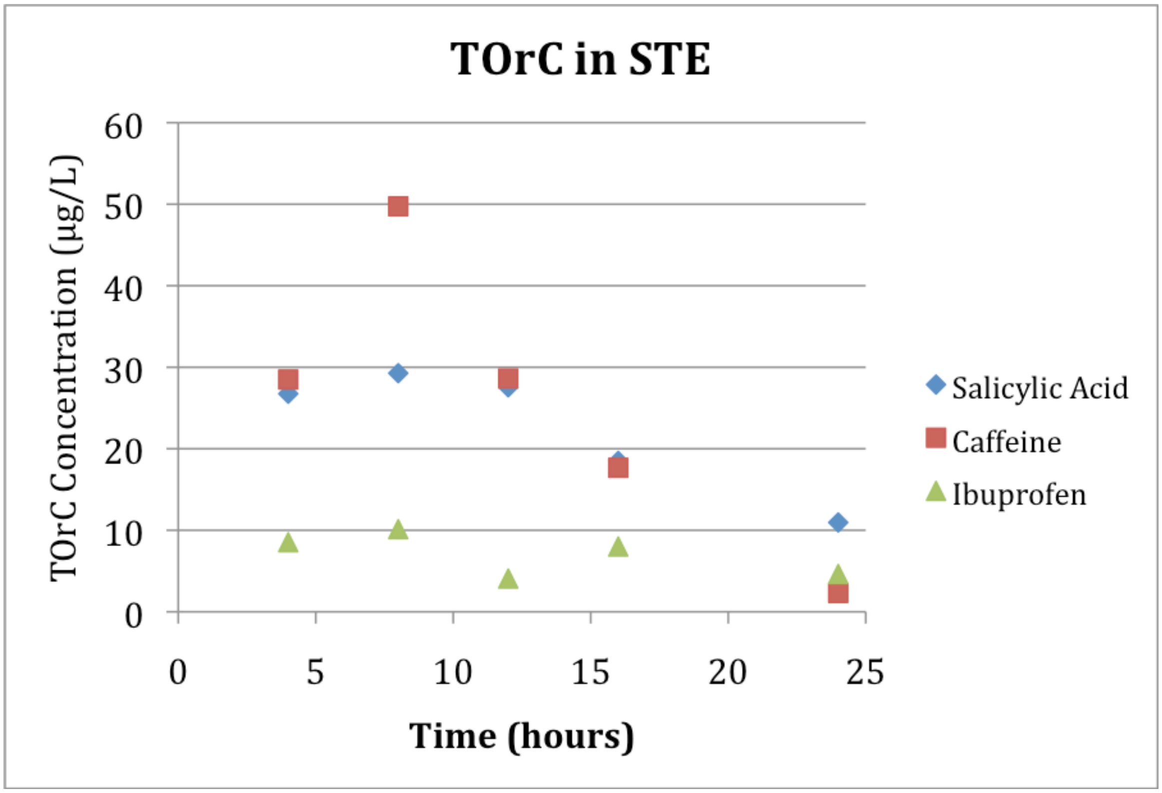


Figure 5. Diurnal Occurrence of Select TOrC in STE Over a 40-Hour Intensive Sampling. Samples represent composite of sampling from last sample collection time. Time zero begins at 6:00 am.

Occurrence of TOrC over the course of a week also exhibited great variability, as much as an order of magnitude (Figure 6). Concentrations of salicylic acid, caffeine, and ibuprofen all peak on Friday and Saturday, with a smaller peak on Monday. Understanding the variability of TOrC occurrence in onsite systems is important to optimize design for any shock loading that may occur.

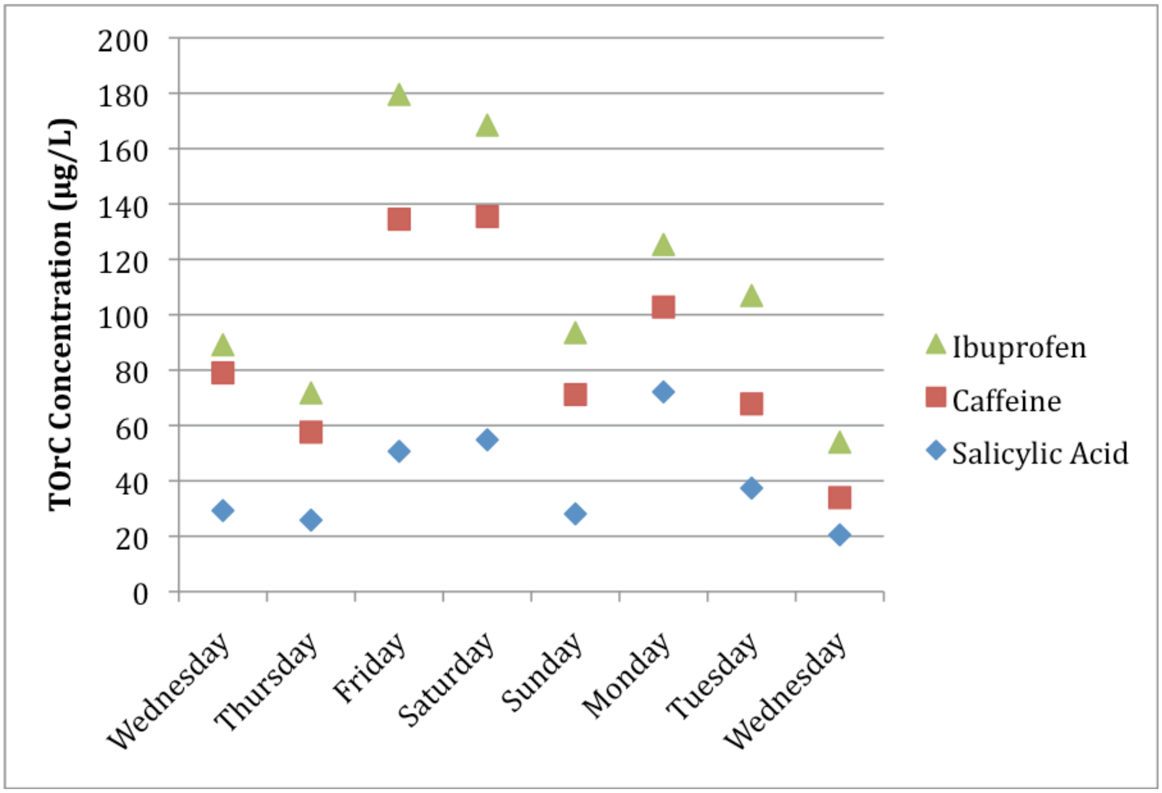


Figure 6. TOrC Occurrence Over One Week Period in Mines Park STE.
All samples were taken as a composite from 6:00 am to 2:00 pm.

3.3.2 TOrC in Above Ground Treated Effluent

Above ground treatment systems are designed to reduce carbon and nutrient concentration in wastewater. The SBMBR utilizes bacterial communities to biotransform constituents in the wastewater in both oxic and anaerobic redox states. Many TOrC are also removed during this process (Table 3) achieving a water quality that is similar to tertiary treated wastewater.

Many compounds are below method detection limits. The complex matrix of the raw wastewater proves an analytical hurdle for detection limits. In the case of the Mines Park system diclofenac, naproxen, TCEP, TCPP, and TDCPP are detected more frequently in the SBMBR effluent than wastewater. This is either a function of the lower detection limit of the SBMBR samples achieved through larger aqueous volume prior to extraction, or interferences through matrix effects limiting the detection of these compounds in the STE samples.

The occurrence of chlorinated flame retardants in SBMBR effluent more frequently than STE could also represent contamination from the unit. Chlorinated flame-retardants have a wide variety of uses. Further work is necessary to determine whether these compounds are released by student residences or contributed somewhere in the full-scale system (i.e., leached from pipe material).

Table 3. TOrC Average Concentration and Detection Frequency for Above Ground Treatment and Water Treated at Centralized Wastewater Treatment System.

Group	Target Compound	MBR		Avg. Tertiary Treated Effluent
		AVG	DF	AVG
Stimulant	Caffeine	<0.1	0 (0/16)	not available
Anti-inflammatory analgesic	Clofibric Acid	<0.1	0 (0/16)	0.006
	Diclofenac	0.102	44 (7/16)	0.015
	Ibuprofen	<0.1	13 (2/16)	0.22
	Ketoprofen	<0.1	0 (0/16)	0.04
	Naproxen	0.06	56 (9/16)	0.07
	Salicylic acid	0.12	100 (16/16)	0.84
Blood-Lipid Regulator	Gemfibrozil	<0.1	0 (0/16)	0.06
Chlorinated Flame Retardants	TCEP	0.58	100 (16/16)	0.35
	TCPP	1.31	100 (16/16)	2.6
	TDCPP	0.61	100 (16/16)	0.13

SBMBR effluent was also sampled more intensively over both 24 hour and weeklong period to ascertain variability in TOrC occurrence. Many of the compounds are known to degrade under oxic conditions (Clara et al., 2005; Heberer et al., 2008; Massmann et al., 2006). The treatment steps and hydraulic retention time would be expected to decrease these compounds either below detection limits or to a more consistent concentration. The lack of trend in either 24 hour sampling or weeklong sampling indicates that the SBMBR effectively decreases easily degradable TOrC concentration. The effluent produced is a more consistent quality than STE.

TOrC that aren't readily biotransformed may persist through the system. There was some variability in chlorinated flame retardant occurrence over the weeklong sampling (Figure 7). The changing concentration TCPP over the week long sampling period suggests there may be a household source. TCEP and TDCPP remain relatively constant suggesting that perhaps the source is within the Mines park system.

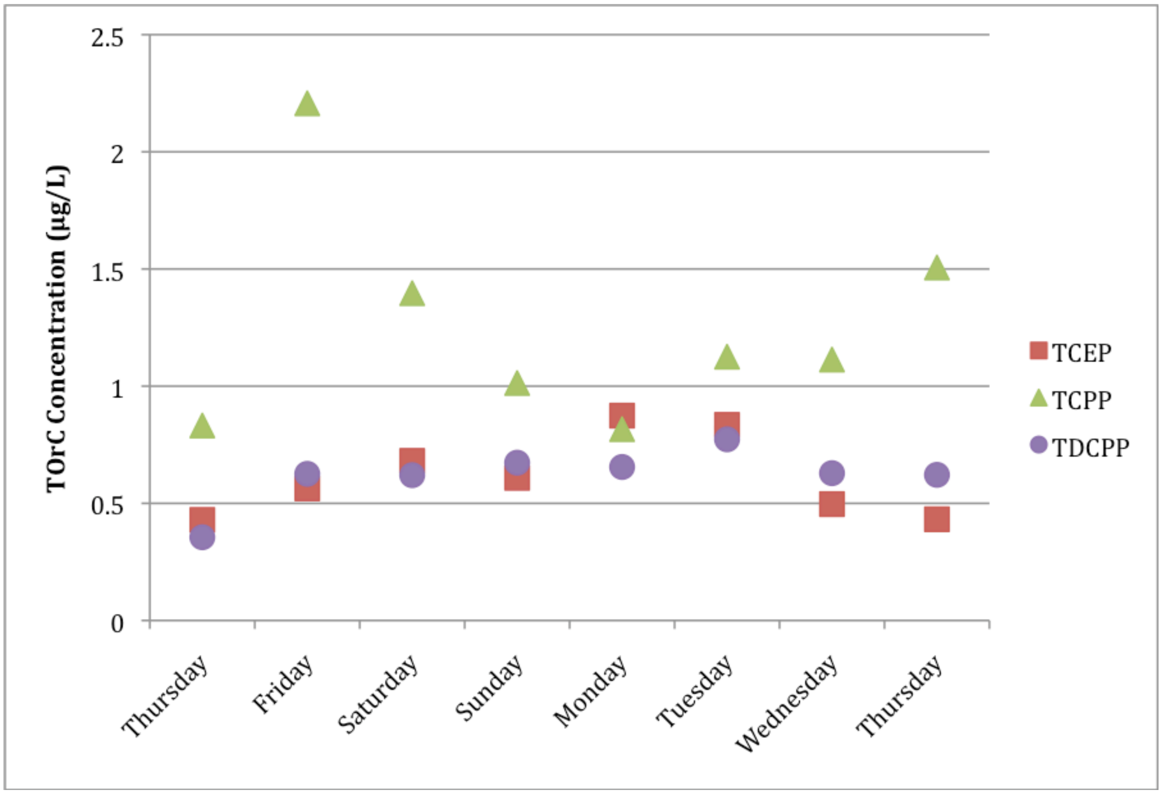


Figure 7. Occurrence of Chlorinated Flame-Retardants Over the Course of a Week Intensive Sampling.
All samples represent a composite taken from 6:00 am to 2:00 pm.

3.4 Conclusions

The occurrence of TOrC in onsite wastewater systems is highly variable. The frequency of detection is inversely related to the size of the sewershed, however the highest average concentration reported have been from single source units. Concentrations of TOrC reported in the literature are up to two orders of magnitude different. This study measured concentration of a single system and found that concentration from one location varied by one order of magnitude. Understanding the variability and shock loads that onsite systems may experience in TOrC loading is imperative to design systems effective at attenuating these compounds.

Advanced above ground treatment, such as SBMBR, can effectively decrease TOrC concentrations often below detection limits. Effluent water achieves a quality comparable to tertiary treated effluent of centralized wastewater treatment plants. Poorly degradable TOrC may not be removed. The fate and transport of these compounds to ultimate receiving environments is not well understood.

4.0 The Role of Organic Carbon and Loading Rate on Removal of Trace Organic Chemicals during Onsite Wastewater Soil Treatment

4.1 Introduction

Over 22 million U.S. homes and businesses (approximately 25% of the population) and 35% of all new housing developments are served by decentralized onsite wastewater treatment systems (EPA, 2002). Water discharged to soil absorption systems ultimately recharge groundwater or surface water nearby. Trace organic chemicals (TOrC) plumes have been reported beneath onsite wastewater systems (Carrara et al., 2008; Moelants et al., 2008). Many of the communities that rely on onsite wastewater systems (OWS) also utilize drinking water wells (Verstraeten et al., 2005). Understanding the occurrence, fate, and transport of TOrC in these systems is important to ensure safe drinking water to the communities in which they are utilized.

Attenuation of TOrC in these systems can occur either in advanced above ground treatment or by optimizing the soil absorption system performance. Attenuation can be improved during infiltration through change in retention time (depth to groundwater), loading rate, or soil type. Adjusting the loading rate is the most easily engineered parameter. Biotransformation of TOrC relies on microbial communities of the subsurface. These communities are supported by the bulk DOC of infiltrating water. The quantity and type of DOC in infiltrating water may also play an important role in TOrC attenuation.

The concentrations of trace organics in treated sewage effluent have been measured from greater than 1,000 ng/L down to detection limits of 10 ng/L or less (Heberer et al., 2001; Kolpin et al., 2002; Sedlak and Pinkston, 2001). These concentrations are not likely sufficient to support microbial biomass growth. Biodegradation of trace organic contaminants thus requires degradable organic matter or DOC to support biomass growth. DOC can range in molecular size from a few hundred to 100,000 Daltons (Leenheer and Croue, 2003) and the composition of DOC is key to supporting a biologically active environment (Rauch-Williams and Drewes, 2006). The biotransformation of TOrC results from microbial community present in the infiltration zone supported by the bulk DOC in the infiltrating water.

In the case of STE infiltration there is an excess of degradable DOC introduced, and thus the microbial community likely is not very diverse. During infiltration some dissolved oxygen may diffuse into the infiltrating water, however fully aerobic conditions are not likely to exist in the subsurface. Advanced above ground treatment, such as membrane bioreactor processes, will have a much lower concentration of DOC favoring more oxic conditions. The microbial community that this water will support will be more diverse than during STE infiltration (Figure 8).

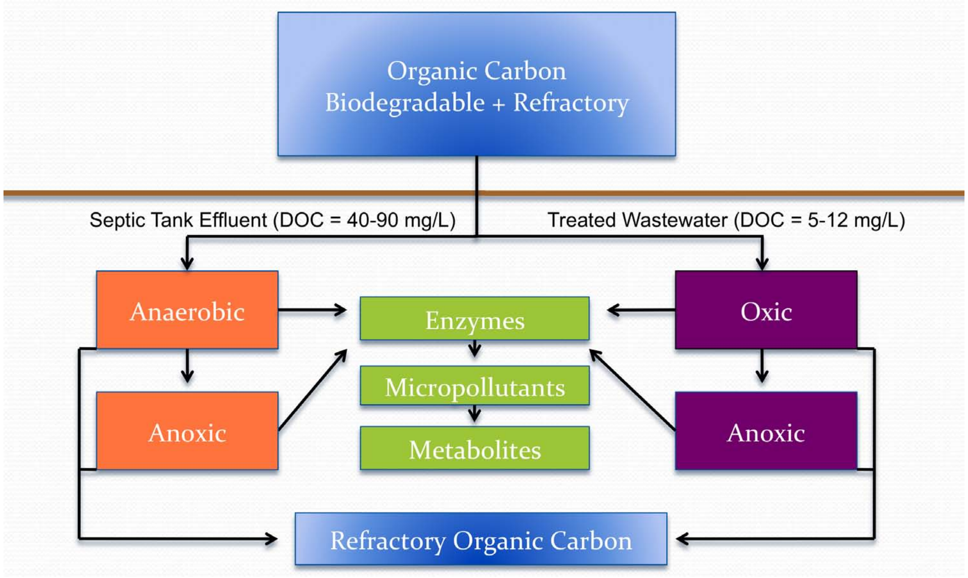


Figure 8. The Type of Organic Carbon Delivered to the Subsurface Results in Different Microbial Communities. STE Delivers Mostly Readily Degradable Carbon While Treated Wastewater Results in a More Diverse Microbial Community.

4.2 Hypotheses

The type of biomass at the infiltrative surface of an OWS is related to the DOC of infiltrating water (Rauch-Williams and Drewes, 2006). The attenuation of TOrC in these systems is likely also related to the type of DOC and the rate at which is applied.

- STE application:
  - Soil absorption systems where STE is applied are overwhelmed by easily degradable DOC. The DOC concentration will decrease and the fraction of easily degradable DOC will decrease.
  - Attenuation of easily degradable TOrC in soil absorption systems fed by STE effluent will be most effective at lower loading rate.
- SBMBR application:
  - Advanced treated wastewater will experience little change to DOC quantity and percent during soil infiltration.
  - Microbial diversity at the infiltrative surface of a soil absorption system may lead to attenuation of relatively recalcitrant compounds.

4.3 Results and Discussion

4.3.1 Removal of TOrC Using STE as a Function of Loading Rate

The nutrients and DOC of infiltrating water support the microbial biomass responsible for the majority of changes to infiltrating water. There is an inverse relationship between ammonia and DOC attenuation and loading rate; as loading rate decreases attenuation efficiency increases (Figure 9). Nitrification of ammonia requires the presence of oxygen. At the highest loading rate ammonia isn’t as effectively removed indicating that oxygen diffusion into the system is favored during a lower loading rate.

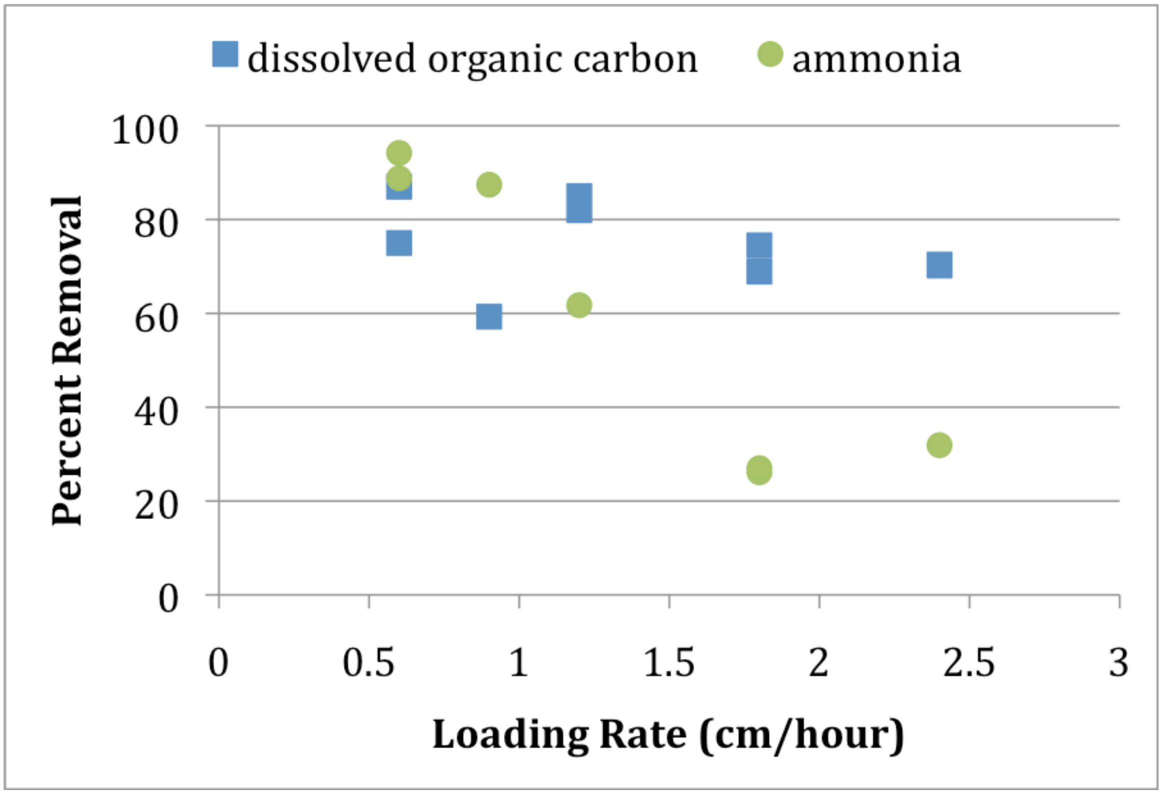
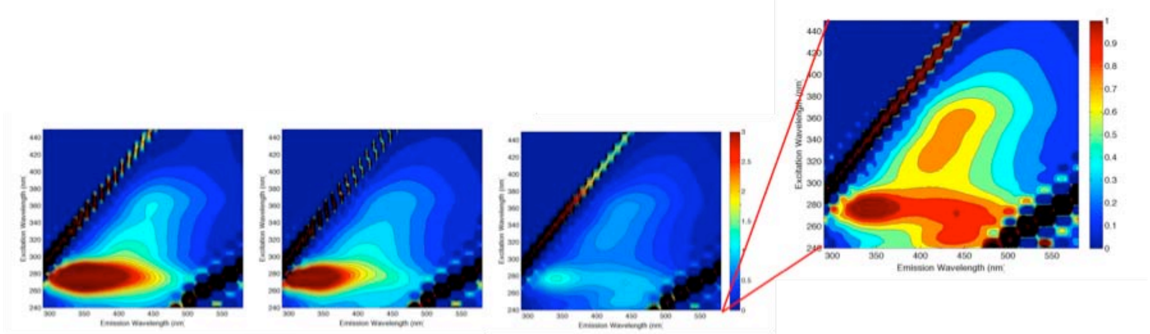


Figure 9. Percent Removal of DOC and Ammonia in STE Fed Soil Columns as a Function of Loading Rate.

Bulk DOC measurements indicate that DOC concentration is decreasing through the soil absorption system. Using 3D-Fluoresence a comparison can be made between the fraction of DOC that is removed during infiltration. The STE EEM is dominated by carbon that represents an easily degradable protein-like peak (Figure 10). As loading rate increases, total DOC concentration decreases and the easily degradable protein peak is removed. As loading rate decreases the increased retention time leads to greater transformation of DOC and distinct humic and fulvic peaks in the column effluent.



Septic Tank Effluent
DOC = 70.7 mg/L

Septic Column Effluent
2.4 cm/hour
DOC = 33.3 mg/L

Septic Column Effluent
1.8 cm/hour
DOC = 11.1 mg/L

Figure 10. Fluorescence Eems from STE and Septic Column Effluent.
The Absorption Scale is the Same for the Three Figures on the Right.

Attenuation of TOrC during soil infiltration was also related to the loading rate (Figure 11). For readily degradable salicylic acid 95% or greater attenuation was achieved at all loading rates tested. Caffeine and ibuprofen exhibited greater attenuation rates at higher lower loading rates. This trend is similar to that of ammonia and DOC removal. Like ammonia these compounds are known to more readily biotransform under oxic conditions (Heberer et al., 2008).

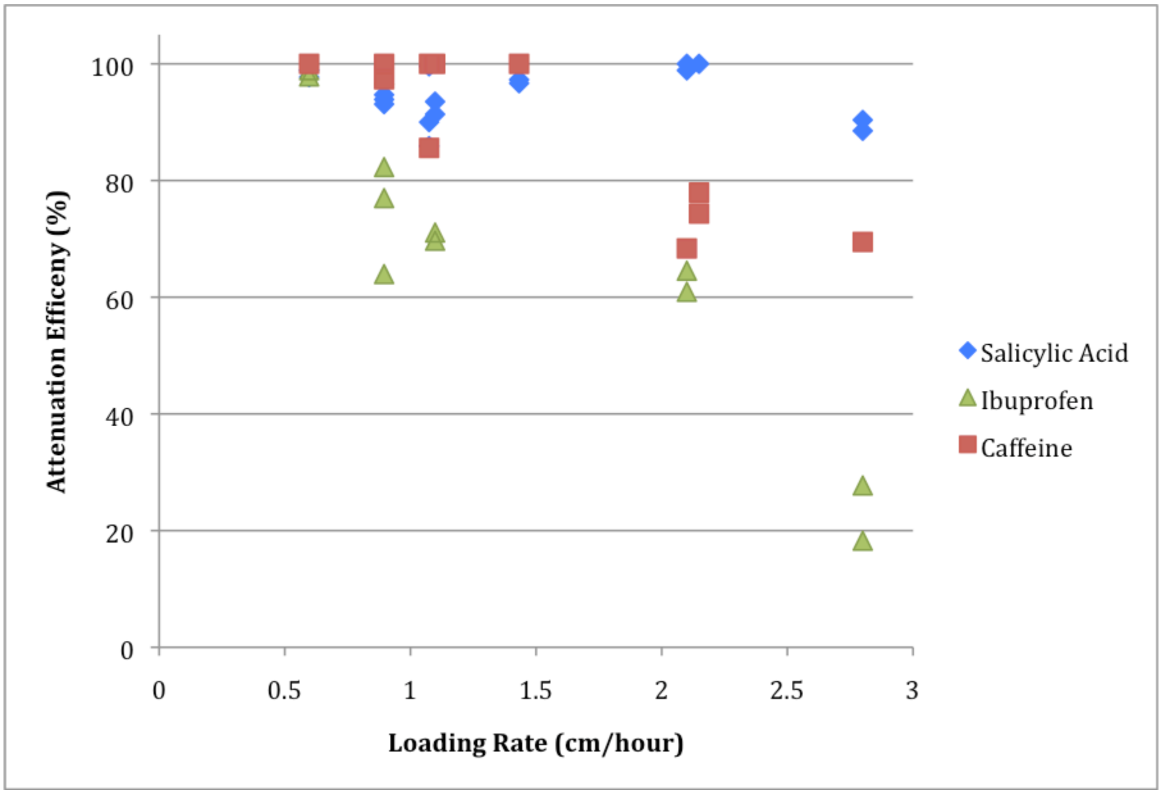
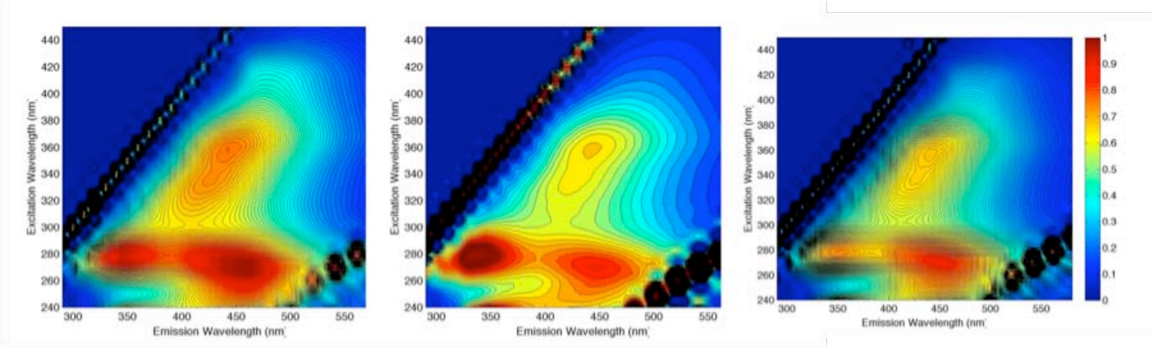


Figure 11. Removal Efficiency of TOrC Attenuation STE Fed Soil Columns.

Calculation of removal efficiencies for some compounds may be complicated due to sample recovery issues. The concentration of naproxen and some flame-retardants were higher than column influent in some cases suggesting that reported STE concentrations were lower than actual. During quantification, there are four isotope labeled internal standards added to each sample to account for losses during sample preparation. However corrections made with these values are compound specific and not advisable unless an isotope labeled sample is available for the compound of interest. A full matrix spike would be necessary to understand the effect that matrix has on these results.

4.3.2 MBR as a Function of Loading Rate

The SBMBR treatment train includes microbial treatment under both oxic and anaerobic conditions. One of the treatment objectives is during oxic phase convert ammonia to nitrate. This is followed by anaerobic phase to reduce nitrate. During this process DOC concentration is also greatly reduced (from approximately 70 mg/L to around 5 mg/L). During infiltration through soil columns there is little change to DOC and nitrate concentration. Slight decrease in nitrate suggests that anaerobic conditions are achieved at some point in during infiltration. The SBMBR treatment effective at removing the readily degradable protein peak of influent septic water. As SBMBR infiltrates through the subsurface there is little change to the composition of DOC (Figure 12).



Membrane Bioreactor Effluent
DOC = 7.5 mg/L

MBR Column Effluent
1.8 cm/hour
DOC = 6.1 mg/L

MBR Column Effluent
2.4 cm/hour
DOC = 11.1 mg/L

Figure 12. 3D Fluorescence EEMs for SBMBR Soil Column Experiments.

The SBMBR treatment is effective at removing many of the TOrC analyzed in this study. The exception is the persistence of chlorinated flame-retardants in SBMBR effluent. These compounds persisted also through soil infiltration. No appreciable trend of attenuation was found.

Once it had been established that many TOrC were completely attenuated during SBMBR treatment the feed line to soil columns was spiked with 5 select compounds; diclofenac, gemfibrozil, ibuprofen, clofibric acid, and naproxen. There was complete removal of each of these compounds for the studied loading rates (0.6, 0.75, 0.9, 1 mL/hour) while administering a spike concentration of 500 ng/L.

4.4 Conclusions

The attenuation of DOC and ammonia in infiltrating STE increases as loading rate decreases. NOM characterization revealed that this decrease in DOC is the readily degradable protein fraction of DOC. Readily degradable TOrC are also attenuated more as loading rate decreases. The removal of ammonia, caffeine, and ibuprofen suggest that at a lower loading rate oxygen diffusion into the system isn’t limited and oxic or partially oxic conditions can be maintained in the subsurface.

SBMBR effluent achieves high enough quality prior to soil infiltration that there is little additional change during soil treatment. This suggests that using these systems very high loading rates can be used decreasing the footprint of the infiltrative surface. However, poorly degradable TOrC persist through SBMBR treatment and are not further removed during soil infiltration. Future work will examine loading rates further decreased to observe whether carbon and nutrient limited infiltrating water may produce favorable conditions for attenuation of TOrC.

5. 0 Conclusions

5.1 Summary of Findings

Developing an understanding the occurrence and fate of TOrC during onsite wastewater treatment is important to ensure effective design of these systems. Onsite wastewater systems are installed in many different types of locations and sizes. The variability in TOrC occurrence in the septic portion of these systems is a function of the various design uses. Concentrations of TOrC reported in the literature are up to two orders of magnitude different. The frequency of detection is inversely related to the size of the sewershed, however the highest average concentration reported have been from single source units. This study measured concentration of a single system serving 400 housing units and found that concentration from one location varied by one order of magnitude. Understanding the variability and shock loads that onsite systems may experience in TOrC loading is imperative to design systems effective at attenuating these compounds.

Advanced above ground treatment, such as SBMBR, can effectively decrease TOrC concentrations often below detection limits. Effluent water achieves a quality comparable to tertiary treated effluent of centralized wastewater treatment plants. However, poorly degradable TOrC may not be removed during SBMBR treatment. The fate and transport of these compounds to ultimate receiving environments is not well understood.

Soil absorption systems offer the final treatment step in most onsite wastewater systems. These systems prove effective at removing most readily degradable TOrC present in STE. The attenuation of DOC, ammonia, and readily degradable TOrC increases as loading rate decreases. The removal of ammonia, caffeine, and ibuprofen suggest that at a lower loading rate oxygen diffusion into the system isn't limited and oxic or partially oxic conditions can be maintained in the subsurface.

SBMBR effluent achieves high enough quality prior to soil infiltration that there is little additional change during soil treatment. This suggests that one advantage to advanced above ground treatment is the use of very high loading rates can decrease the footprint of the infiltrative surface. However, poorly degradable TOrC persist through SBMBR treatment and are not further removed during soil infiltration.

5.2 Recommendations for Future Work

Future work at Colorado School of Mines will continue to investigate the TOrC in natural media filtration systems. Work has begun on developing additional TOrC quantification methods using a recently acquired dual mass spectrometer with inline liquid chromatography (LC-MS-MS). The target analyte list has been developed after methods established by the Southern Nevada Water Authority (Vanderford and Snyder, 2006). In addition to an expanded analyte list, the detection limits of this method are an order of magnitude or greater lower than the GC-MS method used for this work. Sample preparation of LC-MS-MS may also help to minimize the matrix effect of STE.

An additional week of intensive sampling of STE and SBMBR effluent is planned for September 2009. This will provide additional information regarding the diurnal variation in STE. Both GC-MS and LC-MS-MS methods will be used to quantify TOrC in the system.

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