

# Occurrence and Fate of Trace Organic Contaminants in Onsite Wastewater Treatment Systems and Implications for Water Quality Management

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A stylized graphic at the bottom of the page. It features a black silhouette of a mountain range on the left. Below the mountains are several horizontal bands: a thick black band, a blue band, and another thick black band. The top edge of the graphic is jagged, resembling a water surface or a mountain range.

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**OCCURRENCE AND FATE OF TRACE ORGANIC CONTAMINANTS  
IN ONSITE WASTEWATER TREATMENT SYSTEMS  
AND IMPLICATIONS FOR WATER QUALITY MANAGEMENT**

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Technical Completion Report

Colorado Water Institute

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## ABSTRACT

To determine the occurrence and fate of trace organic contaminants such as endocrine-disrupting consumer product chemicals in onsite wastewater treatment systems (OWTS), research was conducted encompassing field monitoring of operating OWTS, along with controlled field experiments and laboratory tests. Trace organic contaminants, including sterols, surfactant metabolites, metal-chelating agents, antimicrobials, and stimulants, were frequently detected in samples of septic tank wastewaters obtained from 30 Colorado OWTS at concentrations ranging over three orders of magnitude. Non-residential wastewaters generally had more compounds at higher concentrations than residential wastewaters, likely due to differences in water- and chemical-using activities at the source.

Conventional onsite treatment utilizing septic tanks and soil infiltration through a sandy loam soil decreased concentrations of many trace organic contaminants by 90% or more. Removal of trace organic contaminants during anaerobic septic tank treatment was typically low (<50%), with removals attributed to sorption to settling solids and anaerobic biotransformation. The majority of treatment occurred during soil infiltration and percolation through a vadose zone, likely through volatilization, sorption to soil organic matter, and aerobic biotransformation. Compounds not removed by these mechanisms can persist during onsite treatment using a conventional septic tank and soil treatment unit (e.g., a drainfield). In addition, concentrations of certain degradation products of some trace organic contaminants can increase during shallow soil treatment, limiting overall removal. Additional aerobic biofilter treatment beyond traditional anaerobic septic tank treatment enhanced removal for many trace organic contaminants. However, soil solution concentrations at the same depth below the soil infiltrative surface were similar regardless of the effluent applied (septic tank effluent vs. biofilter effluent). In addition, increasing the hydraulic loading rate to the soil increased mass removal without adversely affecting treatment capacity.

Even with high removal efficiencies during onsite treatment, some trace organic contaminants persisted through 120 cm of unsaturated soil, indicating their ability to reach shallow ground water. An OWTS recharging shallow ground water with minimal dilution and treatment in the ground water prior to surface water recharge may adversely affect the receiving environment. Under most conditions, however, additional treatment during deep vadose zone and ground water travel will further decrease concentrations, as was found during sampling of Colorado ground waters and surface waters.

**Keywords:** onsite wastewater treatment, trace organic contaminants, endocrine-disrupting compounds, vadose zone, biofilter, ground water quality, wastewater management

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## ACRONYMS AND ABBREVIATIONS

$C_w^{\text{sat}}$  – water solubility

cBOD<sub>5</sub> – 5-day carbonaceous biochemical oxygen demand

cm/d – centimeters per day

CLLE – continuous liquid-liquid extraction

COD – chemical oxygen demand

CSM – Colorado School of Mines

DAF – Dilution Attenuation Factor

DO – dissolved oxygen

DOC – dissolved organic carbon

EDTA – ethylenediaminetetraacetic acid

EPA – Environmental Protection Agency

ESI-HPLC/MS – electrospray ionization high performance liquid chromatography/mass spectrometry

gal/d – gallons per day

gal/ft<sup>2</sup>/d – gallons per square foot per day

GC/MS – gas chromatography / mass spectrometry

HIR – hydraulic infiltration rate

HLR – hydraulic loading rate

HRT – hydraulic residence time

$K_D$  – solid-water partition coefficient or sorption distribution coefficient

$K_H$  – Henry's Law constant

$K_{OC}$  – organic carbon partition coefficient

$K_{OW}$  – octanol-water partition coefficient

km<sup>2</sup> – square kilometers

L/d – liters per day

LTAR – long-term acceptance rate

MBE – membrane bioreactor effluent

MCL – maximum contaminant level

mg/L – milligrams per liter

mL – milliliters

NH<sub>3</sub> – ammonia

NO<sub>3</sub> – nitrate

NP – 4-nonylphenol  
NP1EC – 4-nonylphenolmonoethoxycarboxylate  
NP1EO – 4-nonylphenolmonoethoxylate  
NP2EC – 4-nonylphenoldiethoxycarboxylate  
NP2EO – 4-nonylphenoldiethoxylate  
NP3EC – 4-nonylphenoltriethoxycarboxylate  
NP3EO – 4-nonylphenoltriethoxylate  
NP4EC – 4-nonylphenoltetraethoxycarboxylate  
NP4EO – 4-nonylphenoltetraethoxylate  
NPE – parent 4-nonylphenolethoxylate surfactants  
NPEC – 4-nonylphenolethoxycarboxylate  
NPEO – 4-nonylphenolethoxylate  
NTA – nitrilotriacetic acid  
OP1EO – 4-*tert*-octylphenolmonoethoxylate  
OP2EO – 4-*tert*-octylphenoldiethoxylate  
OP3EO – 4-*tert*-octylphenoltriethoxylate  
OP4EO – 4-*tert*-octylphenoltetraethoxylate  
OP5EO – 4-*tert*-octylphenolpentaethoxylate  
OPEO – 4-*tert*-octylphenolethoxylate  
OWTS – onsite wastewater treatment system(s)  
pK<sub>a</sub> – acid dissociation constant  
RPD – relative percent difference  
RSD – relative standard deviation  
SPE – solid-phase extraction  
STE – septic tank effluent  
SUVA – specific ultraviolet light absorbance  
t<sub>1/2</sub> – half life  
TDS – total dissolved solids  
TFE – textile filter effluent  
TN – total nitrogen  
TOC – total organic carbon  
TP – total phosphorus  
TS – total solids  
TSS – total suspended solids

µg/L – micrograms per liter

USGS – United States Geological Survey

UV<sub>254</sub> – ultraviolet light absorbance at 254 nanometers

VOC- volatile organic compound

WWTP – wastewater treatment plant(s)

∑NPEC – sum of 4-nonylphenolmono-, di-, tri-, and tetra-ethoxycarboxylate

∑NPEO – sum of 4-nonylphenolmono-, di-, tri-, and tetra-ethoxylate

∑OPEO – sum of 4-*tert*-octylphenolmono-, di-, tri-, and tetra-ethoxylate

# **CHAPTER 1**

## **SUMMARIZED FINDINGS OF RESEARCH**

### **1.1 Introduction**

The objective of this research was to improve the current understanding of the occurrence and fate of trace organic contaminants in onsite wastewater treatment systems to aid in minimizing potential adverse effects on ecosystem and human health. Major research findings are summarized in this chapter, followed by a description of the areas of focus presented in this completion report. References are provided where further results and information from the research not presented in this completion report can be found.

### **1.2 Research Context, Purpose, and Scope**

Wastewater originating from urban areas is commonly treated by large centralized wastewater treatment plants (WWTP). A substantial and growing proportion of wastewater in semi-urban and rural regions of the U.S. and in developing countries is treated by decentralized or onsite wastewater treatment systems (OWTS), which often provide a cost-effective, sustainable alternative to WWTP. OWTS receive wastewater from a single source or small number of sources, treat wastewater through onsite unit operations, and discharge the effluent to a local receiving environment such as underlying ground water. The receiving environments to which these systems discharge often provide the water source for the local community or can recharge nearby surface waters, therefore effective removal of contaminants during onsite treatment is important in minimizing risk to ecosystem and human health.

While much is known regarding the treatment of bulk parameters such as biochemical oxygen demand, nutrients, and pathogens in OWTS, the occurrence and fate of trace organic contaminants such as pharmaceuticals and consumer product chemicals is less understood. Adverse effects, some associated with the endocrine system, have been reported in receiving environments of WWTP discharging low levels of trace organic contaminants. The purpose of this research was to enhance the current understanding of the occurrence and fate of trace organic contaminants during onsite wastewater treatment to aid in minimizing potential adverse effects. The specific objectives of this research were to:

- 1) quantify the occurrence of trace organic contaminants in OWTS varying by source (e.g., residential, commercial, institutional),

- 2) assess removal efficiencies of trace organic contaminants during treatment within engineered unit operations (e.g. septic tanks, biofilters, constructed wetlands),
- 3) assess removal efficiencies of trace organic contaminants during soil treatment (e.g. vadose zone soil infiltration), and
- 4) provide guidance for the design and management of OWTS to minimize potential adverse effects from trace organic contaminants.

A reconnaissance field survey of 30 operational systems in Colorado was conducted to quantify the occurrence of trace organic contaminants in OWTS (as affected by wastewater source and treatment type) and in receiving environments. Controlled field-scale experimentation regarding trace organic contaminants was conducted at the Mines Park Test Site on the Colorado School of Mines (CSM) campus in Golden, Colorado to: assess removal efficiencies during treatment within engineered unit operations, quantify daily, weekly, and monthly variations in effluent composition, determine occurrence and fate during vadose zone soil treatment as affected by effluent type and hydraulic loading rate, HLR, and monitor the soil treatment of a pharmaceutical surrogate during a vadose zone tracer test. Correlated laboratory-scale studies were performed to quantify sorption as a removal mechanism for the pharmaceutical surrogate during soil infiltration. Whole system treatment at the Test Site was assessed by integrating engineered treatment and soil treatment data. The resulting information from the field-scale OWTS monitoring along with controlled field-scale and lab-scale experimentation was integrated to provide recommendations for design and management of OWTS regarding trace organic contaminants.

### **1.3 Major Findings**

Trace organic contaminants including surfactant metabolites, metal-chelating agents, antimicrobials, stimulants, and deodorizers were present in septic tank wastewaters from OWTS serving a variety of residential and non-residential sources. Individual compounds were detected in 0 to 100% of wastewater samples in concentrations ranging from  $<0.5 \mu\text{g/L}$  to  $>1000 \mu\text{g/L}$ . The levels and frequency of occurrence depended on the source, likely due to differences in chemical- and water-using activities. For example, convenience store wastewaters primarily originated from public restrooms visited by a large and diverse population. These wastewaters had elevated levels of a hand soap antimicrobial, a toilet bowl deodorant, and 15 different antibiotics and pharmaceuticals as compared to single-family home wastewaters. In general, non-residential wastewaters had more trace organic contaminants at higher concentrations than residential wastewaters. Individual compounds were detected less frequently ( $\leq 25\%$ ) and at lower concentrations (max =  $19 \mu\text{g/L}$ ) in nearby surface waters and ground waters that could be



potential receiving environments. (Note: selected sites were in OWTS-reliant regions but hydrologic connections to specific anthropogenic sources were not attempted as part of this research.)

Temporal variability of trace organic contaminants in tank wastewaters generally decreased with increasing distance from the source (e.g., with increasing hydraulic retention time and level of treatment). Daily and weekly variability was low, indicating that grab samples are representative of wastewater quality regarding trace organic contaminants. Monthly variability was greater, likely due to seasonal fluctuations in water- and chemical-using activities at the source that could affect wastewater composition and site characteristics (e.g., temperature, frequency of maintenance) that could affect treatment efficiencies.

Removal efficiencies of trace organic contaminants within engineered treatment units (i.e. septic tank, biofilter, or constructed wetland) ranged from <1% to >99%. In general, removal efficiencies during septic tank treatment were low (<50%), attributed to hydrophobic sorption to solids with subsequent settling. Therefore, in a conventional onsite system utilizing a septic tank and soil treatment unit, trace organic contaminants could be loaded to the soil at concentrations similar to influent septic tank wastewater concentrations. Additional aerobic biofilter-based treatment beyond the traditional anaerobic tank-based treatment enhanced removal for many trace organic contaminants, likely due to volatilization and aerobic biotransformation. Compounds that were not hydrophobic, volatile, or biodegradable persisted within engineered treatment unit operations. In addition, the concentrations of transformation products often increased as parent compounds degraded.

Greater than or equal to 90% removal (or to less than the reporting level) of trace organic contaminants from septic tank effluent was achieved during 240 cm of sandy loam soil treatment, often within the first 60 cm of soil treatment. High removal efficiencies are likely due to sorption to soil organic matter and biotransformation. In an exception to this finding, concentrations of 4-nonylphenol, a surfactant metabolite, increased during shallow soil treatment, limiting its overall removal (<50% removal). Soil solution concentrations at the same depth from test cells receiving septic tank effluent (STE) or textile filter effluent (TFE) were similar; therefore soil solution concentrations of trace organic contaminants 60 cm below the infiltrative surface and deeper were not affected by effluent type (e.g. STE vs. TFE). Soil solution concentrations at the same depth from test cells receiving a design HLR of 2 cm/d (a typical value based on Colorado regulations) vs. 8 cm/d were similar; therefore soil solution concentrations of trace organic contaminants 60 cm below the infiltrative surface and deeper were not affected by design HLR (e.g. 2 vs. 8 cm/d), with the exception of the metal-chelating agent ethylenediaminetetraacetic acid, EDTA. A higher HLR resulted in higher soil solution EDTA concentrations at the same depth as compared to a system with a lower HLR. In general, percent removal and mass removal of trace organic contaminants after three years of soil treatment was greater in test cells

receiving STE than in those receiving TFE and was greater in test cells receiving a high HLR than in those receiving a typical HLR of the same effluent. The pharmaceutical surrogate Rhodamine WT was retarded (retardation factor,  $R_F = 5.4$  to  $6.6$ ) during vadose zone transport through sandy loam soil due to sorption to soil surfaces as compared to a conservative tracer. Pharmaceuticals such as the quinolones which have similar aromatic structure and ionic functional groups may behave similarly to RWT during soil treatment.

Knowledge of the distribution of water- and chemical-using activities contributing to raw wastewater can provide initial information regarding the types and levels of trace organic contaminants that will be present in OWTS wastewater. A conventional OWTS (e.g. utilizing septic tank and sandy loam soil treatment) can provide good treatment (>90%) of many trace organic contaminants, even though it was not specifically designed to do so. Therefore, the addition of an engineered treatment unit, such as a textile biofilter, is not necessary for high removal of many trace organic contaminants in systems that are designed, installed, and managed properly. Removal of trace organic contaminants during onsite treatment may be optimized by a number of design features, such as: 1) increasing the hydraulic and sludge retention times within a septic tank(s), 2) minimizing solids discharge from the tank, 3) applying effluent to the soil at an appropriate HLR (~2 to 4 cm/d) to maintain both its infiltrative capacity and an active microbial community at the infiltrative surface, and 4) selection of an appropriate soil (e.g. loam) with a high organic carbon content and sufficient structure for air and water movement.

Even with high removal efficiencies, low levels of some trace organic contaminants could reach ground water located 240 cm or less below an OWTS. Under typical conditions in the Front Colorado Range, trace organic contaminant concentrations in OWTS effluent will be further reduced during ground water recharge and transport prior to potential exposure through a supply well or surface water, thereby reducing the risk to ecosystem and human health. A further understanding of the effects and effect levels of individual compounds and mixtures of compounds is needed to fully assess the general risks associated with trace organic contaminants in OWTS under different design and environmental conditions.

#### **1.4 Report Organization**

This report presents background information, methods, results and discussion, and conclusions related to: 1) the occurrence of trace organic contaminants in operational systems in Colorado, 2) fate during engineered treatment in operational systems and at the Mines Park Test Site, 3) fate during soil treatment as affected by effluent type and hydraulic loading rate, and 4) an integration of results to aid in design and management of OWTS regarding trace organic contaminants. In Chapter 2, background information on trace organic contaminants and OWTS is given. Chapter 3 is a summary of the

methodology employed during the field reconnaissance survey and Mines Park Test Site experimentation. In Chapter 4, results from the reconnaissance survey regarding the occurrence of trace organic contaminants in onsite system wastewaters and receiving environments are presented and discussed. Results regarding the fate of trace organic contaminants during engineered treatment as determined in select field sites and at the Mines Park Test Site are presented and discussed in Chapter 5. Results regarding the fate of trace organic contaminants during soil treatment as determined at the Mines Park Test Site are presented and discussed in Chapter 6. An integration of the results and their implications are presented and discussed in Chapter 7. A summary of key findings and conclusions derived from the four major objectives of the study is presented in Chapter 8 along with recommendations for future research.

Additional information regarding this research, including elements that are not included in this report, can be found in Conn (2008). Conn (2008) presents details regarding research methodology including quality assurance/quality control experiments, site descriptions and flow schematics of the 30 Colorado OWTS, results from the field-scale tracer test and correlated laboratory experiments using Rhodamine WT as a pharmaceutical tracer, and historic data on installation and performance evaluations at the Mines Park Test Site. Several journal articles and conference proceedings papers are in preparation or have been published to disseminate the results of the research. References published at the time of this CWI report submission are listed below:

- Conn, K.E. 2008. Occurrence and fate of endocrine-disrupting compounds and other trace organic contaminants during onsite wastewater treatment. Ph.D. Dissertation, Environmental Science & Engineering, Colorado School of Mines, Golden, Colorado.
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## CHAPTER 2 BACKGROUND

Background information regarding trace organic contaminants, OWTS, and design and management considerations is given in this chapter.

### 2.1 Trace Organic Contaminants

Historically, interest and concern regarding organic chemicals in the environment has focused on compounds originating from agricultural or industrial practices, which may be measured in the environment at milligram per liter (mg/L) or higher concentrations, and have traditional adverse toxicological effects such as carcinogenicity. More recently, there has been an emerging interest in organic chemicals present in the environment at trace levels (e.g. microgram per liter,  $\mu\text{g/L}$ , or less) which may elicit non-traditional toxicological endpoints such as adverse effects on the endocrine system. Trace organic contaminants include prescription and non-prescription pharmaceuticals, natural and synthetic hormones, and household consumer product chemicals such as surfactants, fragrances, plasticizers, and flame retardants (Table 1) which are used frequently and washed or excreted into the wastewater system.

**Table 1.** Some classes of trace organic contaminants and example compounds.

<b>Class</b>	<b>Example Compounds</b>
Antimicrobials	triclosan, triclocarban
Flame-retardants	tri (2-chloroethyl) phosphate, tributyl phosphate
Fragrances	menthol, indole
Hormones	17- $\beta$ -estradiol, 17- $\alpha$ -ethynylestradiol, estrone
Metal-chelating agents	ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA)
Pharmaceuticals	acetaminophen, caffeine, sulfamethoxazole
Plasticizers	bisphenol A
Surfactant metabolites	4-nonylphenol (NP), 4-nonylphenolethoxylates (NPEOs), 4-nonylphenolethoxycarboxylates (NPECs)

Numerous studies have shown the occurrence of trace organic contaminants in the influent of WWTP (Heberer 2002 and references within). Since WWTP are designed to remove bulk constituents such as biochemical oxygen demand, suspended solids, and nutrients rather than individual organic

chemicals, these compounds or their degradation products are often not completely removed during treatment and are discharged to the receiving environment, such as a nearby surface water (Barber et al. 2006, Glassmeyer et al. 2005, Kolpin et al. 2002, Barber et al. 2000), where adverse effects can occur. For example, in Boulder, Colorado, various trace organic contaminants have been measured in WWTP effluent being discharged to Boulder Creek. As compared to the upstream population, white sucker fish living downstream of the effluent discharge point have a significantly higher female to male ratio, are present as intersex fish (i.e. fish with both male and female reproductive tissue) in about 10% of the population, and have other abnormalities in gonadal morphology (Vajda et al. 2008, Woodling et al. 2006). Other studies have reported similar endocrine-disrupting effects on other species of fish and a variety of aquatic organisms such as alligators and oysters exposed to trace organic contaminants (Milnes et al. 2006, Nice et al. 2003, Guillette and Gunderson 2001). Potential effects on humans from exposure to trace organic contaminants such as endocrine-disrupting compounds are complex to determine and currently unknown.

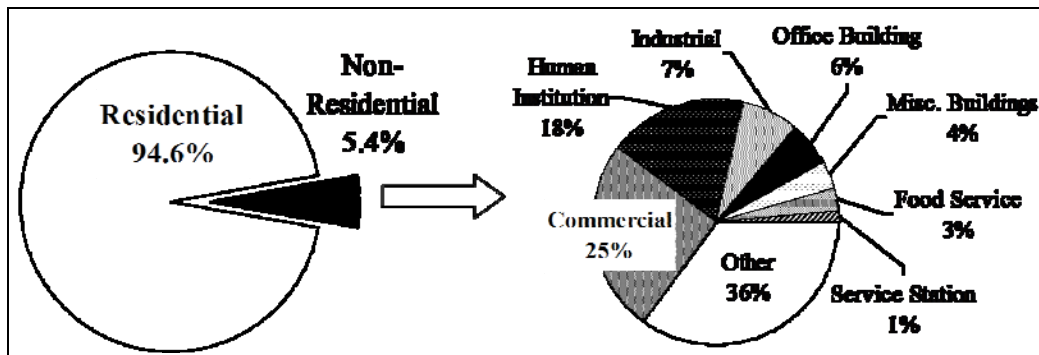
A number of compounds with these endocrine-disrupting properties have been identified including the natural hormone 17- $\beta$ -estradiol, the synthetic hormone 17- $\alpha$ -ethynylestradiol, and the degradation product estrone. Some phenolic consumer product chemicals exhibit less potent endocrine-disrupting effects than the hormones, but may be of equal or greater environmental relevance due to their large production and usage in the world. These include plasticizers such as bisphenol A and the surfactant metabolites 4-nonylphenol (NP), 4-*t*-octylphenol, 4-nonylphenoethoxylates (NPEOs), 4-*t*-octylphenoethoxylates (OPEOs), and 4-nonylphenoethoxycarboxylates (NPECs).

Other adverse effects have been associated with trace organic contaminant occurrence in the environment. The overuse of antimicrobial agents such as triclosan and triclocarban in household products has led to the development of antimicrobial-resistant bacteria, which may reduce the effectiveness of these compounds in critical settings such as hospitals. The majority of ingested prescription and non-prescription pharmaceuticals are excreted unmetabolized and may elicit their designed biological effect in non-target organisms. Other trace organic contaminants, such as the metal-chelating agents ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA), may serve as indicators of anthropogenic impact due to their ubiquitous use and frequent co-occurrence with other consumer product chemicals.

## **2.2 Onsite Wastewater Treatment Systems (OWTS)**

While much research has focused on the occurrence and fate of trace organic contaminants in WWTP and receiving environments, a substantial contribution of trace organic contaminants to the

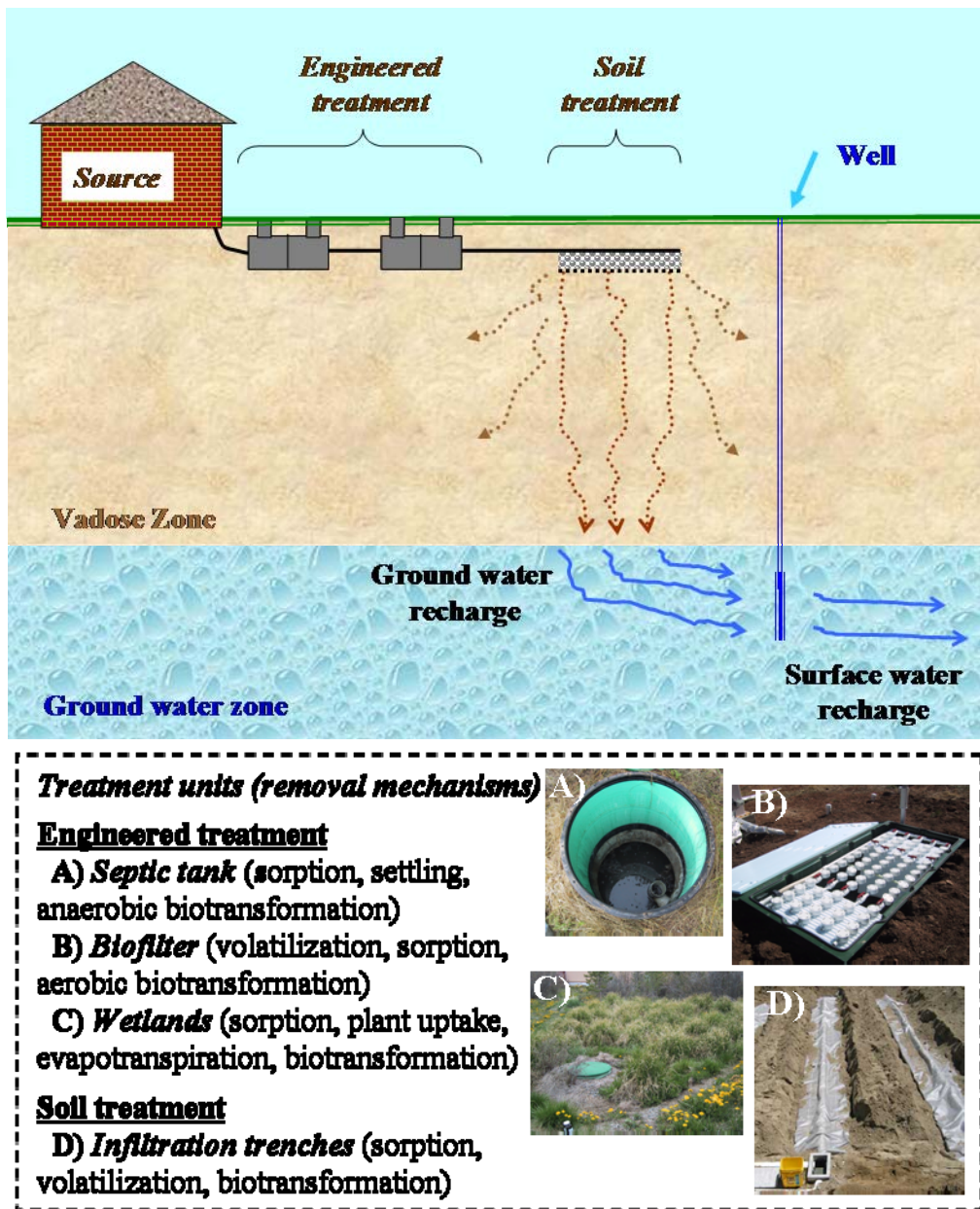
environment may be through the discharge of treated effluent from OWTS. These systems serve over 22 million U.S. homes, businesses and other facilities (Figure 1), and approximately one third of new residential and commercial development, resulting in over 15 billion liters of wastewater that is processed onsite and discharged to the environment every day (Lowe et al. 2006, U.S. Census Bureau 2003, USEPA 2002). In the vast majority of these systems, wastewater from a single source or small number of sources is treated locally within engineered unit operations such as septic tanks followed by soil treatment (Figure 2). In some systems, septic tank effluent, STE, is treated within additional engineered units such as a biofilter or constructed wetland prior to discharge to the soil. The treated effluent from an OWTS may ultimately recharge underlying ground water that supplies water to the local population or nearby surface water, so effective removal of contaminants by OWTS is critical to both ecosystem and human health.



**Figure 1.** Example source distribution of onsite wastewater treatment systems. [Data from Boulder, Colorado provided by Jill Tomaras, Colorado School of Mines.]

### 2.3 Trace Organic Contaminants in OWTS

Much is known regarding the occurrence and treatment of bulk wastewater parameters in OWTS serving various residential and non-residential sources (Crites and Tchobanoglous 1998). In systems that are designed, installed, and managed appropriately, effective removal of many pollutants can be achieved. For example, greater than 90% removal of influent concentrations of oxygen demanding substances, particulate solids, bulk organic carbon, and pathogens can be achieved during onsite treatment, while nutrient removal (e.g. nitrogen and phosphorus species) is more variable (Lowe and Siegrist 2008, Van Cuyk et al. 2001, Crites and Tchobanoglous 1998). Less is known, however, regarding the occurrence and treatment of individual organic contaminants in OWTS.



**Figure 2.** Key components of an onsite wastewater treatment system (top) and relevant removal mechanisms for trace organic contaminants in common treatment units (bottom).

Past research regarding organic chemicals in OWTS focused on Environmental Protection Agency (EPA) – designated “priority pollutants” such as volatile organic compounds, VOCs (Sauer and Tyler 1996, Umari et al. 1995, DeWalle et al. 1985), and detergent-derived surfactants and other consumer product chemicals (Robertson 1994, Nielson et al. 2002) which were measured in STE typically in mg/L concentrations, persisted during septic tank treatment, and were hypothesized to be removed in

the subsurface by volatilization, sorption and biodegradation. Current organic chemical research in OWTS has focused on trace organic contaminants originating from household consumer products. A summary of recent field monitoring studies is given in Table 2. These studies have reported a wide range of concentrations of pharmaceuticals and consumer product chemicals such as sterols, fragrances, plasticizers, flame-retardants and detergent metabolites in STE, from less than 1 µg/L to greater than 1000 µg/L. The studies suggest that concentrations of some trace organic contaminants in STE can be orders of magnitude higher than concentrations in WWTP effluents (Rudel et al. 1998), there can be more temporal variability in STE from non-residential sources than from residential sources (Chalew 2006), and that treatment by an additional engineered unit operation such as a sand filter can reduce effluent concentrations of some compounds (Chalew 2006), while more frequent detections at higher concentrations were reported for other compounds (Zimmerman 2005).

Detections of trace organic contaminants in the subsurface varied by compound, location, and sampling event. No trace organic contaminants were measured above the reporting level in ground water down gradient of OWTS (Hinkle et al. 2005). In other studies (Carrara et al. 2008, Godfrey et al. 2007, Swartz et al. 2006), trace organic contaminants such as carbamazepine, sulfamethoxazole, NP, and 4-nonylphenoldiethoxycarboxylate (NP2EC) were detected at least 20 m down gradient of OWTS. These studies identify a need for a comprehensive assessment of the occurrence of trace organic contaminants in onsite systems from varying sources and an assessment of the fate of these compounds during engineered treatment and soil treatment through controlled experimentation.

## **2.4 Design and Management Considerations**

OWTS are designed to protect human and environmental health by hydraulically processing all of the wastewater generated while treating the wastewater to a level which minimizes adverse effects. Unlike WWTP which are regulated through effluent water quality monitoring prior to discharge to a receiving environment, there is currently no defined effluent of an OWTS that can be easily monitored. Rather than a performance-based design rationale, OWTS are usually prescriptively designed based on conservative flow assumptions and basic soil tests that may or may not accurately describe the future system (Siegrist 2006). Design considerations that can affect the performance of an OWTS include septic tank sizing, use of an additional engineered unit operation (and associated design decisions specific to each treatment technology), HLR to the soil infiltrative surface (which determines the surface area of the field), suitability of the soil, and depth to ground water or other limiting conditions.



**Table 2.** Summary of published monitoring studies of trace organic contaminants in onsite wastewater treatment systems. [STE = septic tank effluent, GW = ground water, SW = surface water, WW = wastewater, NP = 4-nonylphenol, NP1EC = 4-nonylphenolmonoethoxycarboxylate, NP2EC = 4-nonylphenoldiethoxycarboxylate, WWTP = wastewater treatment plant. <RL = less than the reporting level.]

Geographic Location	Experiment Type: Sample Type	Source	Analytes	Major Results	Reference
Ontario, Canada	Monitoring: STE, GW in plume	1 national park, 2 campgrounds	11 pharmaceuticals and triclosan	10/12 detected in GW up to 12 µg/L (ibuprofen); some transported greater than 20 m.	Carrara et al. 2008
Missoula, Montana, U.S.	Monitoring: STE, GW	32 single-family homes, 10 multi-family homes, 1 high school	20 pharmaceuticals and 2 metabolites	STE: 18/22 detected up to 1530 µg/L (acetaminophen); GW: carbamazepine and sulfamethoxazole transported at least 15.3 m downgradient.	Godfrey et al. 2007, Godfrey 2004
Cape Cod, Massachusetts, U.S.	Monitoring: STE, GW in plume	Multi-family residential	14 detergent components, estrogenic compounds, others	STE: ng/L to µg/L concentrations. GW: removal in shallow oxic zone, persistence in deep suboxic-anoxic zone. Production of NP, NP2EC from STE to GW. Transport in GW at least 6 m.	Swartz et al. 2006
North Carolina, U.S.	Monitoring: STE, surfacing effluent, SW	1 high school, 1 office building, several single-family homes, mobile home parks, hotel	caffeine, triclosan	STE: caffeine = 5.4-88 µg/L, triclosan = 0.11-16 µg/L, order of magnitude higher than WWTP effluent. Institutional STE more variable than residential STE. High removal during sand filter treatment. Low concentrations in surfacing effluent. Overland transport during rain event contaminated SW.	Chalew 2006
La Pine, Oregon, U.S.	Monitoring: STE, STE mixed with advanced treatment effluent, vadose zone solution, GW	20 single-family homes, 1 senior center	63 trace organic contaminants and 18 pharmaceuticals	Organics- STE and mixed STE: 45/63 detected up to 1300 µg/L (4-methylphenol), 14 detected in >90% of samples. GW: 8 detections but <RL. Most treatment occurred during vadose zone. Pharmaceuticals (1 site)- STE: 8/18 detected up to 120 µg/L (acetaminophen). GW: 3 detections <0.2 µg/L.	Hinkle et al. 2005
Cape Cod, Massachusetts, U.S.	Monitoring: STE and STE mixed with sand filter effluent	Single-family home	85 trace organic contaminants and pharmaceuticals	STE: 12/85 detected, all <RL or estimated <1 µg/L. STE+sand filter effluent: 28/85 detected up to 6.4 µg/L (acetaminophen)	Zimmerman 2005
Cape Cod, Massachusetts, U.S.	Monitoring: septicage, untreated WW, aerobically-treated WW	Primarily residential (many sources)	20 phenolic compounds	Septage: 19/20 detected up to 1500 µg/L (nonylphenol). Untreated WW: 18/20 detected up to 33 µg/L (nonylphenol). Treated WW: 11/20 detected up to 42 µg/L (NP1EC).	Rudel et al. 1998

For example, to design a conventional OWTS for a 3-bedroom single-family home based on Colorado’s Guidelines on Individual Sewage Disposal Systems (CDPHE 2008), the average daily flow is calculated based on the assumption that there are two people per bedroom and each person produces 284 L (75 gallons) of wastewater per day. The design daily flow, Q, includes a safety factor of 1.5:

$$\begin{aligned} \text{Design daily flow, } Q &= \\ 3 \text{ bedrooms} * 2 \text{ people/bedroom} * 284 \text{ L/person/day} * 1.5 \text{ safety factor} \\ &= 2555 \text{ L/d (675 gal/d)} \end{aligned}$$

The septic tank(s) is sized according to the number of bedrooms, with 3800 L (1000 gal) as the minimum septic tank capacity required. A hydraulic residence time in the septic tank of 1 to 2 days is typical- in Colorado the goal is at least 30 hours. The soil treatment unit usually utilizes native soil that has been deemed suitable based on local regulations. For example, in Colorado, soil with a percolation rate faster than 2.54 cm per hour and slower than 2.54 cm per five minutes as determined by a percolation test is acceptable. The surface area of the field can be determined based on the design daily flow, Q, and a long-term acceptance rate (LTAR), according to the relationship:

$$SA(ft^2) = \frac{Q(gal/d)}{LTAR(gal/ft^2/d)} \quad (2-1)$$

where SA = surface area of the soil infiltration treatment unit in square feet. A maximum LTAR of 0.72 gal/ft<sup>2</sup>/d (~3 cm/d) is allowed for a sandy loam soil in Colorado, resulting in a minimum required field area of 940 ft<sup>2</sup> (~90 m<sup>2</sup>) in the example above. A minimum distance to limiting conditions is often required, which includes ground water, bedrock, surface water, drinking water wells and others. In Colorado, a minimum of 120 cm of unsaturated soil below the infiltrative surface to the high water table is required.

Variances from these requirements are allowed. For example, reductions of up to 50% of the soil treatment unit surface area are allowed in Colorado with use of a gravel-less infiltrative surface, use of a dosing system (rather than flow by gravity), and other engineered variations (CDPHE 2008). A reduction of 50% of the surface area could result in a doubling of the HLR to the soil treatment unit. Use of additional engineered treatment units beyond traditional septic tank treatment may also be considered for use in regions with unacceptable conditions for the installation of an OWTS (e.g. rocky soil, shallow ground water, nearby surface water). No variance is allowed for the minimum distance to ground water of 120 cm in Colorado, though in other states it may be as little as 25 cm or as much as 240 cm.

Once the system has been designed, installed, and is in operation, the property owner is often the primary management entity, and the performance and lifetime of an OWTS depend on the actual site conditions (i.e. heterogeneities within the native soil), appropriate water- and chemical-using practices at the source, and the frequency of solids removal from the septic tank. Failure of an OWTS is most frequently defined as a hydraulic failure as evidenced by effluent backing up into the property or surfacing at the land surface above the tank or field. Because of the lack of effluent monitoring, an OWTS failure is rarely defined by a performance failure even if contamination is occurring in a receiving environment such as ground water. Therefore, to minimize risks to human and environmental health, OWTS must be designed to effectively treat all potential contaminants originating from wastewater. Pathogens, which can cause disease and infection, biochemical oxygen demand and nutrients, which can cause eutrophication in surface waters and adverse effects in humans (e.g. methemoglobinemia) at elevated levels, have historically been the main constituents of concern regarding OWTS effluent quality. However, trace organic contaminants may need to be considered during OWTS design and management to minimize potential risks to exposed organisms.

The effective removal of contaminants during onsite wastewater treatment is critical to ecosystem and human health. While much is known regarding bulk parameters, less is understood about the occurrence, fate, and potential risk of trace organic contaminants in onsite systems. Prior studies of trace organic contaminants in OWTS have primarily monitored select pharmaceuticals and other compounds in a few residential wastewaters and ground water monitoring wells. The goal of this research project was to provide a comprehensive assessment of the occurrence and fate of trace organic contaminants during onsite treatment. The research aimed to quantify the types of consumer product chemicals and their range of expected concentrations in onsite system wastewaters varying by source (i.e. residential, commercial, or institutional). The results also aimed to provide expected removal efficiencies of trace organic contaminants varying by physicochemical properties during conventional tank/soil treatment systems and systems utilizing additional engineered treatment. The information was integrated to provide guidance for design and management of onsite wastewater treatment systems specific to trace organic contaminants to minimize impacts on receiving environments and potential risk to ecosystem and human health.

## **CHAPTER 3**

### **METHODOLOGY**

The methodology employed during this research is summarized in this chapter. To quantify the occurrence of trace organic contaminants in OWTS and receiving environments, a reconnaissance survey of 30 operational systems and 18 receiving environments was conducted. To assess the fate of trace organic contaminants during engineered treatment, a subset of operational systems were sampled, and controlled field-scale experiments were conducted at the Mines Park Test Site in Golden, CO. To assess the fate of trace organic contaminants during soil treatment, monitoring of soil solution from *in-situ* soil test cells was conducted at the Test Site. Additional methodology information has been previously reported (Conn 2008).

#### **3.1 Field Reconnaissance Survey**

##### **3.1.1 Study Design and Site Selection**

The reconnaissance survey was conducted in Summit and Jefferson Counties, Colorado. Summit County is a rapidly growing mountain resort region located approximately 100 km west of Denver with a population in 2000 of 23,548 with 15 persons per km<sup>2</sup> (39 persons per square mile). Jefferson County spans a large region of the Front Range foothills west and south of Denver. In 2000, the population was listed as 527,056 with 264 persons per km<sup>2</sup> (683 persons per square mile). Colorado's population is predicted to increase from 4,168,000 in 2000 to 5,188,000 in 2025 (U.S. Census Bureau 2003) with much of that growth occurring in Summit and Jefferson Counties. Both counties rely heavily on onsite wastewater treatment: in total, there are currently approximately 28,000 OWTS in operation (J. Rada and J. Dale, personal communications, April 13, 2003). The distribution of source types and design types in the sampling regions are similar to those found nationwide. The vast majority (~95%) receive waste from domestic sources, including single- and multi-family homes, while the remaining systems serve commercial and institutional sources. Of the 28,000 systems, approximately 98% have a conventional design consisting of a septic tank or series of tanks that discharge effluent to a soil treatment unit by pump or gravity flow. The remaining 2% of systems currently in use utilize an additional engineered treatment unit such as a filter, aerobic unit, or aquatic system to improve effluent quality before discharge to the soil.

Thirty OWTS, nine water supply wells, and nine surface waters in Summit and Jefferson Counties were selected for inclusion in the reconnaissance survey. Of the 30 OWTS (Table 3), 16 serve residential sources (single- and multi-family homes), with a range of characteristics (e.g. water use from 130 to 2600 L/d). This type of system accounts for >75% of onsite wastewater treatment in the U.S. (Lowe et al. 2006). The other fourteen systems serve non-residential sources (food establishments, convenience stores, retail centers, elementary schools, a church, and veterinary hospitals) with more variable characteristics (e.g. water use from 100 to 13,500 L/d). These non-residential systems were hypothesized to have different, higher-strength wastewater regarding trace organic contaminants as compared to residential systems.

The thirty sites included 22 tank-based treatment units, 7 biofilter-based treatment units, and 1 subsurface-flow constructed wetland (Figure 3). In the tank-based treatment systems, wastewater from the source was treated in one to five septic tanks in series before discharge to the soil treatment unit. In the biofilter-based treatment systems, septic tank wastewater was recirculated through a textile biofilter prior to discharge to the soil treatment unit. All 7 systems included in the study utilized Orenco “Advantex” technology ([www.orenco.com](http://www.orenco.com)), designed for enhanced nitrogen removal by recycling septic tank wastewater on average 1 to 5 times over the biofilter prior to discharge to the soil. In the wetland-based treatment system, septic tank effluent was pumped to a subsurface constructed wetland prior to discharge to the soil. At the beginning of the study all systems had been in operation between one and 41 years (median = 12 years). Estimated hydraulic retention times (HRTs) within engineered unit operations prior to soil application in the 30 systems ranged from 1 to 52 days (median = 7 days), and hydraulic loading rates (HLRs) to the soil ranged from 0.21 to 2.9 cm/d.

From the thirty OWTS, five sites were selected for analysis of additional non-target trace organic contaminants as part of a larger source characterization study conducted by the United States Geological Survey (USGS) Toxic Substances Hydrology Program. The five sites were (Table 3): a multi-family home (Site 16), a restaurant (Site 17), a convenience store (Site 20), an elementary school (Site 26), and a veterinary hospital (Site 29).

A ground water or surface water supply well was located on the same premises as each OWTS. Nine wells were selected at random for sampling in conjunction with the OWTS. Nine tributary surface water sites near the OWTS or in nearby areas utilizing OWTS were additionally selected for sampling. These 18 samples represent a reconnaissance effort to obtain preliminary information on occurrence of trace organic contaminants in receiving environments in Summit and Jefferson Counties.

**Table 3.** Description of the 30 onsite wastewater treatment systems located in Summit and Jefferson Counties, Colorado.

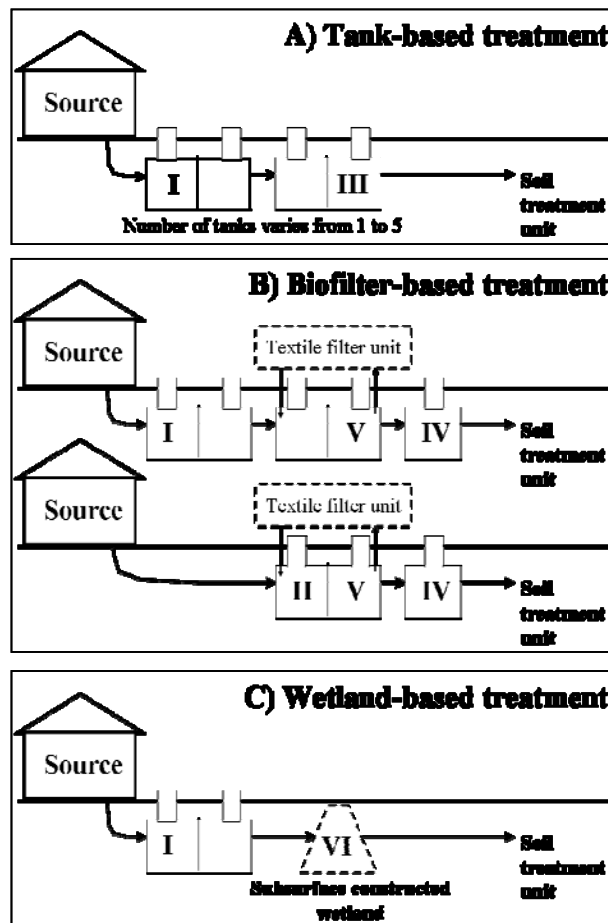
Site ID	Wastewater Source	Avg # Occupants/Day			Average Water Use (L/d) <sup>a</sup>	Treatment Type <sup>b</sup>	Sampling Locations <sup>c</sup>						HRT (d) <sup>d</sup>	HLR (cm/d) <sup>e</sup>	
		Adults	Children	Animals			I	II	III	IV	V	VI			Well
<b>Residential</b>															
1	Single-Family	2	0	0	500 (B)	T			X					10	0.21
2	Single-Family	2	2	0	570 (C)	T			X					9	1.18
3	Single-Family	2	2	0	760 (C)	T	X							5	1.89
4	Single-Family	2	0	0	570 (B)	T			X					6	1.53
5	Single-Family	3	2	0	950 (C)	T			X					3	1.42
6	Single-Family	2	1	0	480 (C)	T	X		X					7	1.44
7	Single-Family	2	0	0	380 (C)	T	X		X				X	7	0.59
8	Single-Family	3	0	0	570 (C)	T	X		X					13	1.35
9	Single-Family	2	0	0	130 (C)	B			X					34	0.35
10	Single-Family	2	0	0	550 (A)	B			X					8	0.82
11	Single-Family	2	4	0	660 (A,B)	B			X					6	0.59
12	Single-Family	2	0	0	280 (A,B)	B			X				X	15	0.63
13	Single-Family	2	2	0	760 (C)	B	X						X	7	1.1
14	Single-Family	2	0	0	570 (B)	W	X						X	22	2.79
15	Multi-Family	5-10	0	0	2120 (B)	T	X							9	0.59
16	Multi-Family	5-10	0	0	2600 (B)	T			X <sup>f</sup>					4	- <sup>g</sup>
<b>Commercial</b>															
17	Restaurant	170	0	0	13500 (B)	T	X		X <sup>f</sup>					4	2.91
18	Restaurant	100	0	0	3230 (A)	B	X		X					7	1.61
19	Bakery	30	0	0	800 (C)	T	X							5	- <sup>g</sup>
20	Convenience Store	1100	0	0	3000 (A,B)	B	X		X <sup>f</sup>					6	1.83
21	Convenience Store	600	0	0	1500 (B)	T			X					2	2.78
22	Retail	125	0	0	2000 (B,C)	T	X						X	4	0.83
23	Retail	80	0	0	1900 (B,C)	T			X					4	2.05
24	Retail	4	0	0	100 (B,C)	T	X							52	- <sup>g</sup>
<b>Institutional</b>															
25	Elementary School	30	150	0	1850 (B)	T	X		X					8	0.55
26	Elementary School	45	300	0	4445 (B)	T	X		X <sup>f</sup>				X	6	0.26
27	Church	150	0	0	1200 (B)	T			X				X	8	0.77
28	Veterinary Hospital	45	40	40	2250 (B,C)	T	X		X					1	- <sup>g</sup>
29	Veterinary Hospital	25	20	20	2000 (B,C)	T	X <sup>f</sup>						X	4	1.49
30	Veterinary Hospital	50	30	30	1200 (B,C)	T			X					6	0.81

Table 3. (Continued)

<sup>a</sup> Based on - A, onsite flow meter; B, personal interviews and system capacity reports; C, literature values for relevant activities (Crites and Tchobanoglous 1998). <sup>b</sup> Treatment type – T, tank-based; B, biofilter-based; W, wetland-based. <sup>c</sup> Sampling locations shown in Figure 3 – I, inlet; II, inlet mixed with filtrate; III, effluent (1 or more tanks); IV, biofilter effluent; V, filtrate recirculation tank; VI, end of subsurface flow constructed wetland; Well, supply well on property was sampled. <sup>d</sup> HRT, nominal engineered treatment hydraulic retention time =  $\left( \frac{\text{Engineered Treatment Units Total Capacity (L)}}{\text{Water Use (L/d)}} \right)$ . <sup>e</sup> HLR, hydraulic

loading rate =  $\left( \frac{\text{Water Use (L/d)}}{\text{Soil Treatment Unit Surface Area (cm}^2\text{)}} \right) \left( \frac{1000 \text{ cm}^3}{1 \text{ L}} \right)$ . <sup>f</sup> Effluent and solids sampled for

additional non-target USGS trace organic contaminant analysis in spring 2004 (see Conn 2008). <sup>g</sup> Information not available.



**Figure 3.** Schematic of sample collection points for onsite systems utilizing A) tank-based treatment, B) biofilter-based treatment, and C) wetland-based treatment. [See Table 3-1 for site descriptions. Locations I and III are anaerobic. Locations II, IV, V, VI are aerobic.]

### 3.1.2 Sample Collection

The thirty OWTS, nine wells, and nine surface waters were sampled twice during August to October 2003 and March to May 2004. A subset of the onsite systems was sampled a third time in October 2005 for bulk wastewater parameters only. At each OWTS, grab samples of wastewater were collected from the clarified layer located at mid-depth (~0.5 m below the liquid surface) at the outlet of each tank using a tank sampler. At some sites, samples were collected at the tank inlet and other locations in the treatment train (specified by roman numerals in Table 3 and Figure 3), resulting in a total of 45 unique sampling locations. In May 2004, settled septic tank solids from the five USGS-selected sites were sampled using a stainless steel bucket. Between sites the tank sampler and bucket were rinsed three times with distilled water, three times with a 50% ethanol / 50% distilled water solution, and five times with distilled water. Well samples were collected after any treatment processes directly from an outside or inside faucet. A grab sample was obtained at each surface water site.

Unfiltered samples were collected in amber glass bottles that had been pre-cleaned with soap, rinsed 3 times with tap water, rinsed 3 times with distilled water, and oven burned at 250 °C for 12 hours. Samples from each location were split into three aliquots: one unpreserved for bulk parameter analysis, one unpreserved for trace organic contaminant analysis, and one preserved with 1% v/v formalin (37% formaldehyde) for trace organic contaminant analysis. In May 2004, additional wastewater aliquots and solids samples were collected for the five USGS-selected sites. Samples were stored at 4 °C until analysis, which generally was performed within 24 hours for bulk wastewater parameters, within 2 weeks for unpreserved trace organic contaminants, and within 1 month for preserved trace organic contaminants. Samples for the USGS study were shipped immediately for analysis by the USGS laboratories.

### 3.1.3 Analytical Procedures

All samples were analyzed for a suite of bulk wastewater parameters (Table 4) by standard methods (APHA 1998, Hach 1998) and 35 target trace organic contaminants (Table 5) using methods modified from methods developed by Dr. Larry Barber at the USGS (Barber et al. 2000). Samples were prepared for analysis for target trace organic contaminants by either a continuous liquid-liquid extraction (CLLE) or an acetyl propanol derivatization method. Twenty nine nonionic trace organic contaminants including 4-nonylphenol (NP), 4-*t*-octylphenol, 4-nonylphenolmonoethoxylate (NP1EO), 4-nonylphenoldiethoxylate (NP2EO), 4-nonylphenoltriethoxylate (NP3EO), 4-nonylphenoltetraethoxylate (NP4EO), 4-*t*-octylphenolmonoethoxylate (OP1EO), 4-*t*-octylphenoldiethoxylate (OP2EO), 4-*t*-



octylphenoltriethoxylate (OP3EO), 4-*t*-octylphenoltetraethoxylate (OP4EO), and 4-*t*-octylphenolpentaethoxylate (OP5EO) were isolated using CLLE. A one-liter unpreserved, unfiltered sample was spiked with surrogate standards (*d*<sub>21</sub>-2,6-di-*t*-butyl-4-methylphenol, *d*<sub>6</sub>-bisphenol A, 4-*n*-nonylphenol, 4-*n*-nonylphenolmonoethoxylate, 4-*n*-nonylphenoldiethoxylate, *d*<sub>4</sub>-17 $\beta$ -estradiol, and *d*<sub>7</sub>-cholesterol), ionic strength was increased by adding 50 g of sodium chloride, and pH was dropped below 2 by adding 3.5 mL of sulfuric acid (25% v/v). Wastewater samples were often diluted 2:1 or more with distilled water to minimize matrix effects. The samples were extracted for 7 hours, during which time 80 mL of distilled methylene chloride was recycled through a microdroplet dispersing frit to improve extraction efficiency. The extract was concentrated under nitrogen gas to 0.5 mL and spiked with an internal standard mix of deuterated polycyclic aromatic hydrocarbons (*d*<sub>4</sub>-1,4-dichlorobenzene, *d*<sub>8</sub>-naphthalene, *d*<sub>10</sub>-acenaphthalene, *d*<sub>10</sub>-phenanthrene, *d*<sub>12</sub>-chrysene, *d*<sub>12</sub>-perylene). The extract was transferred to a GC/MS vial for analysis by capillary column GC/MS.

EDTA, NTA, 4-nonylphenolmonoethoxycarboxylate (NP1EC), 4-nonylphenoldiethoxycarboxylate (NP2EC), 4-nonylphenoltriethoxycarboxylate (NP3EC), and 4-nonylphenoltetraethoxycarboxylate (NP4EC) required derivatization to be analyzed by GC/MS due to their active functional groups and non-volatility. A 100-mL formalin-preserved sample was poured into a 250-mL pear shaped flask that had been pre-cleaned with soap, rinsed three times with tap water, rinsed three times with distilled water, and burned at 500 °C over an 8-hour time period. Wastewater samples were often diluted 2:1 or more with distilled water to minimize matrix effects. The samples were spiked with surrogate standards (*d*<sub>12</sub>-EDTA and 4-*n*-NP2EC) and evaporated to dryness at 90° C for 36 hours. After cooling, two milliliters of formic acid was added and the sample was rotary vacuum evaporated to dryness. The residue was reacted with 2 mL of 1-propanol/acetyl chloride (10% v/v) at 90° C for one hour to form the propyl esters of the analytes. Ten mL of 2% potassium bicarbonate and 2 mL of chloroform were added to the flask and vortex mixed for 30 seconds. After settling, the chloroform layer was removed and passed over a sodium sulfate drying column to remove any residual water. The chloroform extraction from the potassium bicarbonate solution was repeated 3 additional times with 1 mL each, followed by a 1 mL chloroform rinse of the drying column. The chloroform (~5 mL) was evaporated to dryness by nitrogen gas. The residue was re-dissolved in 200  $\mu$ L of toluene and spiked with an injection standard (1-phenylnonane). The extract was transferred to a GC/MS vial for analysis by capillary column GC/MS.

**Table 4.** Summary of bulk wastewater parameters analyzed during the reconnaissance survey. [Abbrev = abbreviation, DL = method detection level, FAU- formazin attenuation units, CFU- colony forming units, “X” indicates that samples were analyzed for indicated parameter. (APHA 1998, HACH 1998)]

Parameter	Abbrev	Unit	DL	Analysis Method	Instrument	Sampling Event		
						Fall 2003	Spring 2004	Fall 2005
Temperature	-	°C	-5	APHA 2550	Thermometer	X	X	X
pH	-	SU	0	APHA 4500-H+ B	Thermo Orion 9106BNWP pH meter	X	X	X
Dissolved oxygen	DO	mg/L	0	APHA 4500-O G	YSI Model 58 Dissolved Oxygen Meter	X	X	X
Specific conductance	-	µS/cm	0	APHA 2510 B	Oakton WD-35607-10 Conductivity Meter	X	X	X
Total solids	TS	mg/L	0	APHA 2540 B	Oven dried at 103 - 105 °	X	X	X
Total suspended solids	TSS	mg/L	0	APHA 2540 D	Oven dried at 103 - 105 °	X	X	X
Total dissolved solids	TDS	mg/L	N/A	Empirically-derived	N/A	X	X	X
Alkalinity	-	mg CaCO <sub>3</sub> /L	0	APHA 2320 B	HACH Digital Titrator	X	X	X
Biochemical oxygen demand	cBOD <sub>5</sub>	mg/L	2	APHA 5210 B	YSI Model 58 Dissolved Oxygen Meter	X	X	X
Total nitrogen	TN	mg N/L	0.5	HACH 10071	HACH DR/4000 U Spectrophotometer	X	X	X
Ammonia	NH <sub>3</sub>	mg N/L	0.4	HACH 2465	HACH DR/4000 U Spec.	X	X	X
Nitrate	NO <sub>3</sub> <sup>-</sup>	mg N/L	0.2	HACH 10020	HACH DR/4000 U Spec.	X	X	X
Total phosphorus	TP	mg P/L	0.02	HACH 8190	HACH DR/4000 U Spec.	X	X	X
Chemical oxygen demand	COD	mg/L	20	HACH 8000	HACH DR/4000 U Spec.	X	X	X
Turbidity	-	FAU	0	HACH 10047	HACH DR/4000 U Spec.	X	X	X
Fecal coliform	-	CFU/100 mL	0	APHA 9222 D	Membrane filtration	X	X	X
Total organic carbon	TOC	mg/L	0.5	APHA 5310 D	O.I. Analytical Model 700 TOC Analyzer	X	X	X
Dissolved organic carbon	DOC	mg/L	0.5	APHA 5310 D	O.I. Analytical Model 700 TOC Analyzer	X	X	X
Ultraviolet absorbance (254 nm)	UV <sub>254</sub>	m	0.005	HACH 5910 B	Spectronics/Unicam Genesys 10UV Spec.	X	X	X
Specific ultraviolet absorbance	SUVA	L/mg-m	N/A	Empirically-derived	N/A	X	X	X

**Table 5.** Summary of target trace organic contaminants analyzed during the reconnaissance survey.  
 [CASRN = Chemical Abstracts Service Registry Number. Method: 1, continuous liquid-liquid extraction;  
 2, acetyl propanol derivatization.  
 NA, not available.]

Compound	CASRN	Use	Method
Bisphenol A	80-05-7	plasticizer	1
2[3]- <i>t</i> -Butyl-4-methoxyphenol	25013-16-5	antioxidant	1
4- <i>t</i> -Butylphenol	98-54-4	antioxidant	1
Caffeine	58-08-2	stimulant	1
Cholesterol	57-88-5	animal steroid	1
Coprostanol	360-68-9	animal fecal steroid	1
1,2-Dichlorobenzene	95-50-1	fumigant	1
1,3-Dichlorobenzene	541-73-1	fumigant	1
1,4-Dichlorobenzene	106-46-7	deodorizer	1
2,6-Di- <i>t</i> -butyl-1,4-benzoquinone	719-22-2	antioxidant byproduct	1
2,6-Di- <i>t</i> -butyl-4-methylphenol	128-37-0	antioxidant	1
2,6-Di- <i>t</i> -butylphenol	128-39-2	antioxidant	1
Ethylenediaminetetraacetic acid	60-00-4	metal complexing agent	2
4-Ethylphenol	123-07-9	plasticizer	1
4-Methylphenol	106-44-5	disinfectant	1
Nitrilotriacetic acid	139-13-9	metal complexing agent	2
4-Nonylphenol	25154-52-3	surfactant metabolite	1
4-Nonylphenoldiethoxycarboxylate	106807-78-7	surfactant metabolite	2
4-Nonylphenoldiethoxylate	NA	surfactant metabolite	1
4-Nonylphenolmonoethoxycarboxylate	3115-49-9	surfactant metabolite	2
4-Nonylphenolmonoethoxylate	9016-45-9	surfactant metabolite	1
4-Nonylphenoltetraethoxycarboxylate	NA	surfactant metabolite	2
4-Nonylphenoltetraethoxylate	NA	surfactant metabolite	1
4-Nonylphenoltriethoxycarboxylate	NA	surfactant metabolite	2
4-Nonylphenoltriethoxylate	NA	surfactant metabolite	1
4- <i>n</i> -Octylphenol	1806-26-4	plasticizer	1
4- <i>t</i> -Octylphenol	140-66-9	surfactant metabolite	1
4- <i>t</i> -Octylphenoldiethoxylate	NA	surfactant metabolite	1
4- <i>t</i> -Octylphenolmonoethoxylate	9036-19-5	surfactant metabolite	1
4- <i>t</i> -Octylphenolpentaethoxylate	NA	surfactant metabolite	1
4- <i>t</i> -Octylphenoltetraethoxylate	NA	surfactant metabolite	1
4- <i>t</i> -Octylphenoltriethoxylate	NA	surfactant metabolite	1
4- <i>t</i> -Pentylphenol	80-46-6	plasticizer	1
4-Propylphenol	645-56-7	plasticizer	1
Triclosan	3380-34-5	antimicrobial	1

Extracts from both sample extraction methods were analyzed by electron impact GC/MS in the full scan and selected ion monitoring (SIM) modes. The general gas chromatography conditions were: Hewlett Packard (HP) 6890 GC; column - HP Ultra II (5% phenylmethyl silicone), 25 m x 0.2 mm, 33  $\mu\text{m}$  film thickness; carrier gas – ultra high purity helium with a linear flow velocity of 27 cm/sec; injection port temperature – 300 °C; initial oven temperature – 40 °C (CLLE), 100 °C (derivatization); split vent open – 0.75 min; ramp rate – 6 °C/minute to 300 °C; hold time – 15 minutes at 300 °C. The mass spectrometer conditions were: HP 5793 Mass Selective Detector; tune with perfluorotributylamine; ionization energy – 70 eV; source temperature – 250 °C; interface temperature 300 °C; full scan – 40 to 550 atomic mass units at 1 scan/second.

Target compound concentrations were calculated based on SIM data using diagnostic ions for each compound. Each compound was identified based on a peak signal to noise ratio of at least 3:1, matching of retention times ( $\pm 0.02$  min) and ion ratios ( $\pm 20\%$ ) determined from analysis of authentic standards. A 7-point standard curve (typically ranging from 0.01 to 50 ng/ $\mu\text{L}$ ) based on the response ratio to an internal standard was used for calculating concentrations. Surrogate standards were added prior to extraction and derivatization to evaluate compound recovery and whole method performance.

Full scan chromatograms were used to identify semi-quantifiable compounds in environmental samples. The largest 50 peaks in each full scan chromatogram of the underivatized extract were integrated using ChemStation software (version D), and each peak's spectral composition was compared against the NIST Mass Spectral Search Program library (Version 1.6d, 1998). A quality value from 0 to 100 (with 100 being a perfect match) was assigned by the software to each potential compound to indicate how well the spectrum matched the spectrum of the peak in the environmental sample. The relative size of each peak was also given (as a percent of the total peak area). The ten largest peaks and/or peaks with a quality value of 90 or greater were recorded, with special note given to those with a large percent area and a high quality value.

The five USGS-selected samples were additionally analyzed by three USGS laboratories for 120 pharmaceuticals, antibiotics, and non-target trace organic contaminants in wastewater and by one of those laboratories for 61 trace organic contaminants on septic tank solids. Prescription and non-prescription pharmaceuticals were analyzed (Cahill et al. 2004) by solid-phase extraction (SPE) and positive electrospray ionization high performance liquid chromatography/mass spectrometry (ESI-HPLC/MS). Filtered water samples were analyzed for antibiotics by SPE using ESI-HPLC/MS (Meyer et al. 2007). Additional trace organic contaminants were isolated from filtered samples by SPE, elution with methylene chloride/diethyl ether, and analysis by full scan GC/MS (Zaugg et al. 2001) using similar protocols (i.e. surrogate standards) as the CLLE method. The non-target trace organic contaminants

determined in wastewater also were measured on tank solids using accelerated solvent extraction with a water/isopropanol solution, SPE cleanup, and analysis by GC/MS (Burkhardt et al. 2005).

### **3.1.4 Quality Assurance**

A field blank was collected on each sampling trip from a lab distilled water source subjected to the same sample processing, handling, and equipment as the environmental samples. A randomly-selected wastewater sample from each sampling trip was collected in triplicate to perform quality control analyses on a duplicate and matrix spike sample. Field blanks, field replicates, lab blanks, lab replicates, and field and laboratory duplicate matrix spikes comprised approximately 40% of the analyses conducted with each set of environmental samples. Each method incorporated surrogate standards to evaluate method performance for individual samples. Additional quality assurance included solvent and reagent blanks and replicate GC/MS injections. Environmental concentrations within three times the average values observed in the blank were reported as less than the reporting level.

## **3.2 Mines Park Test Site Experimentation**

In 1998 the Mines Park Test Site was established on the Colorado School of Mines (CSM) campus in Golden, Colorado, to enable controlled field experimentation to enhance the quantitative understanding of OWTS design and performance (Small Flows 2008a). At the site, wastewater from an 8-unit apartment complex is diverted and managed onsite using above-ground pilot-scale unit operations and below-ground soil treatment units with associated sensors and monitoring devices. Experimentation relevant to this research, which includes a vadose zone tracer test and various characterization sampling experiments, utilized a treatment train designed to investigate effects on soil treatment due to differences in engineered pre-treatment technologies. The treatment train (Figure 4, sampling locations numbered in red) included septic tanks, a textile biofilter, a membrane bioreactor, and 18 soil infiltration test cells (of which 12 were outfitted with sampling devices) which began receiving effluent in April 2004. A soil test cell receiving tap water from a companion study was included for comparison purposes. A wealth of data is available from completed and on-going studies regarding site assessment, installation of unit operations, and characterization of the wastewater and the treatment efficiencies of the unit processes for a suite of chemical and microbial wastewater parameters (Lowe and Siegrist 2008, Walsh 2006, Van Cuyk et al. 2005, Siegrist et al. 2004, Dimick 2005, Tackett 2004, Lowe and Siegrist 2002). Characterization of the site specific to this research project is summarized below.

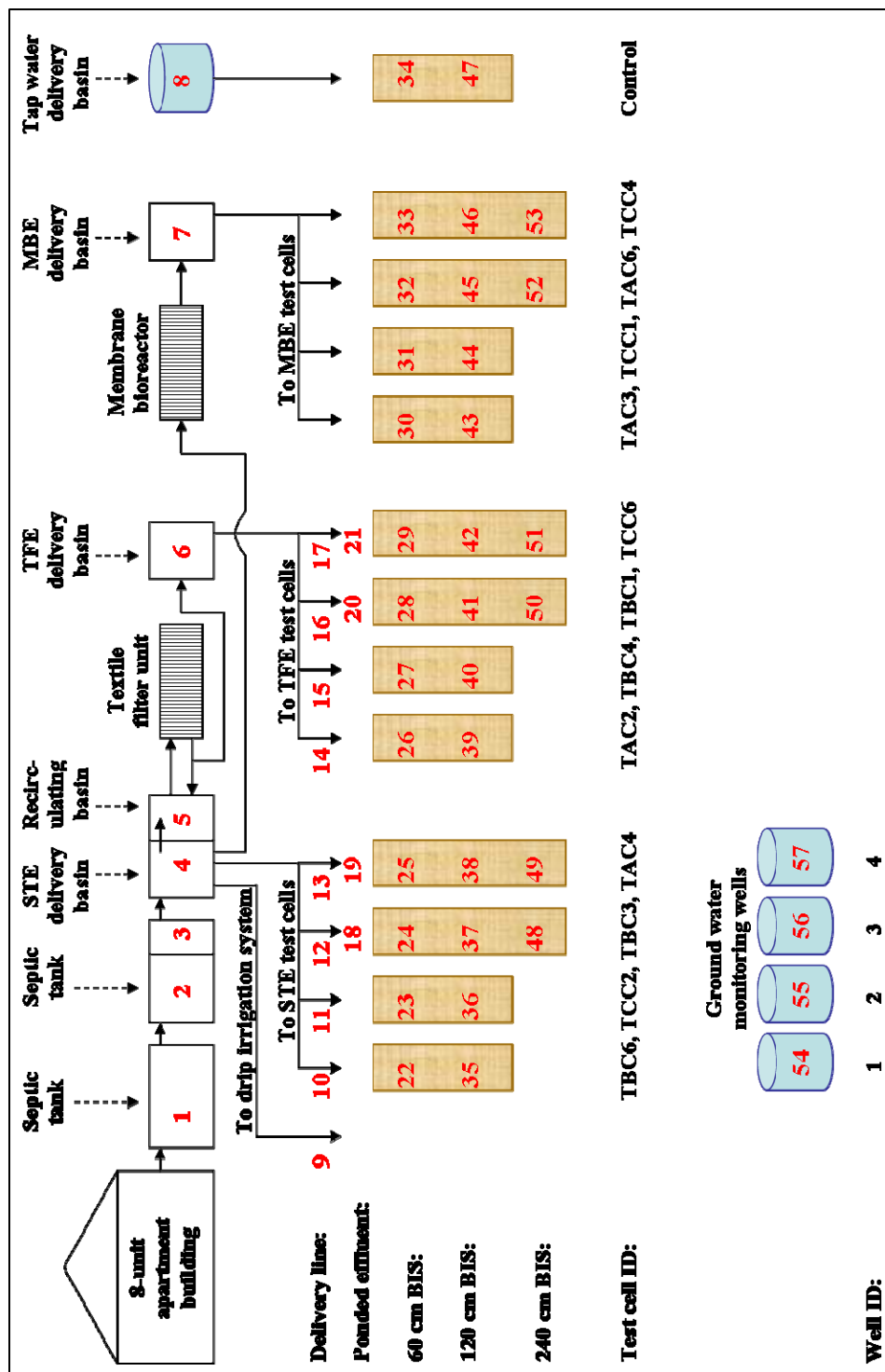


Figure 4. Schematic of Mines Park Test Site unit operations utilized during this research. [Red numbers indicate sampling locations. BIS = below infiltrative surface. Test cell ID, see Table 6.]

### **3.2.1 Site Description**

#### **3.2.1.1 Natural Resource Characterization**

The Test Site is located in the Rocky Mountain Front Range foothills in Golden, Colorado approximately 1820 m above sea level. Typical temperatures range between 0.5 °C in the winter and 26 °C in the summer. The average annual precipitation is 45 cm. The soils at the Test Site are Ascalon sandy loam (fine-loamy, mixed, mesic Aridic Arugiustolls) with the parent materials generally derived from igneous and metamorphic rocks of the mountains and sedimentary rocks of the foothills (USDA 1983). A site evaluation (Lowe and Siegrist 2002) determined that the particle size distribution ranged from 59 to 69% sand, 13 to 17% silt, and 18 to 24% clay, dry weight %. Total organic matter ranged from 1.0% (dry wt. %) at 60 cm to 0.5% at 2.6 m below ground surface. The soil moisture content ranged from 6.4 to 7.1% (dry wt. %). Cation exchange capacity ranged between 11.3 and 15.0 meq/100 g dry soil and was relatively constant across the site. The soil pH was 6.4. Ground water was present in two of seven shallow boreholes around the site at 2.88 and 4.38 m below ground surface.

#### **3.2.1.2 Site Design**

The unit operations utilized during this research (Figure 4) have been previously described (Van Cuyk et al. 2005) and relevant design characteristics are summarized here. Raw wastewater from the 8-unit apartment building is first treated by two 5700 L (1500 gal) septic tanks in series, each with an average hydraulic residence time of 2 days. The first tank is single-chambered and the second tank is double-chambered. Effluent from the second chamber of the second tank is pumped approximately 160 m uphill to the 2840 L (750 gal) septic tank effluent (STE) delivery basin at the Test Site. Approximately 1500 to 2500 L of effluent per day are delivered to the STE delivery basin to meet demand from all activities at the site, resulting in a typical hydraulic residence time in the STE delivery basin of less than 2 days.

From the STE delivery basin, STE is delivered by pump to six of the 18 soil test cells and serves as the influent for the textile filter unit and the membrane bioreactor. The textile filter unit is an Orenco Systems, Inc. AdvanTex AX20 unit, of which 75% (approximately 1.4 m<sup>2</sup>) of the total textile pod area receives effluent. Approximately 250 L/d of STE is pumped from the delivery basin to the 2870 L (750 gal) recirculation basin. A pump delivers effluent from the recirculation basin through a distribution network to the top of the hanging textile sheets. Effluent percolates through the filter sheets, collects at the bottom of the pod, and returns to the recirculation basin by gravity flow. An air vent is present to

allow passive air flow through the textile filter unit. STE is delivered to the filter unit at a rate of 26 L/min for 30 seconds every 13 minutes, resulting in a recirculation ratio of approximately 3:1. The return pipe is outfitted with a splitter valve to redirect, when the recirculation basin is full, excess textile filter effluent (TFE) to the 340 L (90 gal) TFE delivery basin. TFE is delivered by pump from the TFE delivery basin to six of the 18 soil test cells. The hydraulic residence time in the TFE delivery basin is approximately 2.5 days. The hydraulic residence time within engineered units is approximately 5 days prior to application to the STE soil test cells and approximately 13 days prior to application to the TFE soil test cells.

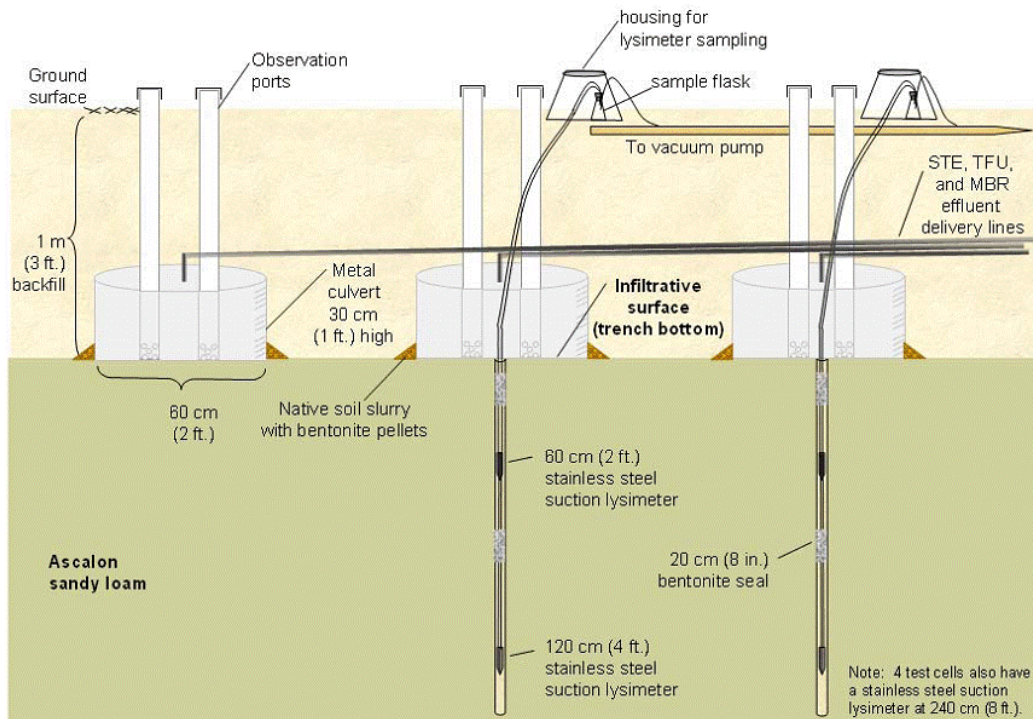
While the HomeSpring membrane bioreactor (Zenon Environmental Corporation, Canada) was in operation (see Section 3.2.1.3), it processed STE from the STE delivery basin using a suspended growth biological reactor. Membrane bioreactor effluent (MBE) was delivered by pump to six of the 18 soil test cells from the 190 L (50 gal) MBE delivery basin.

Eighteen *in situ* soil infiltration test cells were utilized to mimic a typical soil infiltration treatment unit in an OWTS. The infiltrative surface of each test cell is approximately 1 m below ground surface, below which is intact native soil (Figure 5). The infiltrative surface area of each test cell is approximately 2900 cm<sup>2</sup>, as defined by a steel culvert section (60 cm in diameter, 30 cm high) pressed a few centimeters into the infiltrative surface and covered with plywood. The areas around and above the test cells were backfilled to the ground surface. Three observation ports installed in each test cell allow access to the infiltrative surface from the ground surface for determination of infiltration rates, observation of effluent ponding heights, and access for future soil coring events.

Effluent is delivered to the open infiltrative surface of each test cell from a delivery manifold. The three effluent types (STE, TFE, MBE) were designed to be delivered at two HLRs (2 and 8 cm/d) in triplicate (Table 6). The delivery method is a 90 second dose once an hour over 16 hours each day. Approximately 360 mL (2 cm/d) and 1450 mL (8 cm/d) are delivered during each dose, resulting in 5.8 L (2 cm/d) and 23.3 L (8 cm/d) of total volume per day applied to each test cell.

Twelve of the 18 test cells were outfitted with microporous stainless steel suction lysimeters (Model SW-074, Soil Measurement Systems, Tucson, Arizona) at 60 cm, 120 cm, and (in the 6 cells initially loaded at 8 cm/d) 240 cm below the infiltrative surface. By applying a vacuum to the lysimeter apparatus, soil solution around each lysimeter was collected through the 0.2 µm nominal pore size of the lysimeter and associated tubing into a sampling flask at the ground surface. A similar test cell (“Control”, see Figure 4 and Table 6) located in a nearby trench was useful for comparison purposes. Since May 2003, tap water from an on-site holding tank was delivered to the soil infiltrative surface at a HLR of 4 cm/d, applied at a continuous rate of 22 mL/min over 16 hours each day.





**Figure 5.** Schematic of soil test cell installation. [from Van Cuyk et al. 2005]

**Table 6.** Description of the soil test cells. [Event = sampling event in which test cell was utilized, T = tracer test (2004-2005), C = characterization (2007); “-“ = no lysimeter installed. 8,2 = HLR was reduced from 8 cm/d to 2 cm/d on 10/29/04.]

ID	Effluent applied	Design HLR (cm/d)	Lysimeter location			Event
			60 cm	120 cm	240 cm	
TAC1	STE	2	-	-	-	none
TAC2	TFE	2	X	X	-	T, C
TAC3	MBE	2	X	X	-	T
TAC4	STE	8	X	X	X	T, C
TAC5	TFE	8	-	-	-	none
TAC6	MBE	8	X	X	X	T
TBC1	TFE	8,2	X	X	X	T, C
TBC2	MBE	8	-	-	-	none
TBC3	STE	8,2	X	X	X	T, C
TBC4	TFE	2	X	X	-	T, C
TBC5	MBE	2	-	-	-	none
TBC6	STE	2	X	X	-	T, C
TCC1	MBE	2	X	X	-	T
TCC2	STE	2	X	X	-	T, C
TCC3	TFE	2	-	-	-	none
TCC4	MBE	8	X	X	X	T
TCC5	STE	8	-	-	-	none
TCC6	TFE	8	X	X	X	T, C
Control	Water	4	X	X	-	T, C

Ground water quality was assessed through four monitoring wells (Figure 4) installed at the site along the assumed ground water flow path (generally southeast). Monitoring well 1 is located within a companion set of soil test cells, with an average depth below the ground surface to water of 6.3 m. Well 2 is located approximately 8 to 24 m southeast of the soil test cells, and the depth to water averages 4.3 m. Well 3 is located approximately 15 to 25 m east of the test cells, and the depth to water averages 3.9 m. Well 4 is located approximately 30 to 45 m southeast of the test cells, and the depth to water averages 3.8 m.

### **3.2.1.3 Operationally-Induced Changes**

In February 2004, delivery of tap water to the 18 soil test cells began. Baseline values for hydraulic performance were collected, including HLRs and infiltration rates. The baseline infiltration rates of the 18 soil test cells generally ranged from 39 to 96 cm/d, with a few cells as low as 23 cm/d or as high as 158 cm/d. Approximately three weeks after tap water delivery began, a tracer test was conducted (Conn 2008). On April 6, 2004, delivery of the three types of effluent (STE, TFE, MBE) to the soil test cells began. Periodic monitoring of hydraulic conditions (infiltration rates at 6 months, 2 years, and 3 years, weekly HLRs, and weekly ponding heights above the infiltrative surface) and wastewater and effluent characterization have been conducted by a team of researchers since operation began (Dimick 2006, Van Cuyk et al. 2005).

Within six months of operation, two test cells with low baseline infiltration rates (e.g. ~ 25 cm/d) receiving 8 cm/d of effluent (TBC1 and TBC3) had become ponded to the maximum height above the infiltrative surface. The HLR was reduced to 2 cm/d on October 29, 2004 and has remained at that rate since. Therefore, the four STE and four TFE soil test cells outfitted with lysimeters have triplicate conditions of a 2 cm/d HLR and a single condition of an 8 cm/d HLR.

The membrane bioreactor was in operation from April 2004 to May 2005, after which time a surrogate effluent was delivered to the six MBE soil test cells through November 2005. At that time, tracer test sampling ceased and nothing has been applied to the MBE soil test cells since. A summary of relevant hydraulic conditions over time in the 13 lysimeter-equipped soil test cells is given in Table 7. Infiltration rates in test cells initially loaded at 2 cm/d remained sufficiently high to infiltrate all volume applied. Infiltration rates decreased over time in test cells initially loaded at the higher loading rate (8 cm/d) to less than the actual HLR, resulting in surface ponding and an actual infiltrated volume of less than the applied volume. The estimated actual cumulative volume of effluent infiltrated into each test cell (Table 7) is useful for mass removal calculations during the tracer test (which ended November 2005) and during the characterization studies (conducted around 3 years of operation, April 2007).

**Table 7.** Summary of hydraulic changes in Mines Park lysimeter-equipped soil test cells during three years of operation. [All values are cumulative. HLR = hydraulic loading rate, HIR = hydraulic infiltration rate. Design = design rates and volumes. C Design = design rates and volumes for control cell. \* Control cell began operation 11 months prior to test cells: Baseline IR (3/03), 1 year IR (7/05), 53 month IR (10/07). NA = not applicable, s = same value as HLR (for HIR) or loaded effluent (for infiltrated effluent).]

Test Cell	Effluent applied	Design HLR (cm/d)	Infiltration Rate (cm/d)				HLR (cm/d)	At end of tracer test (11/05):		At start of characterization (4/07):			
			Baseline (4/04)	6 month (10/04)	2 year (4/06)	3 year (4/07)		HLR (cm/d)	Loaded effluent (L)	HIR (cm/d)	Infiltrated effluent (L)	HLR (cm/d)	Loaded effluent (L)
TBC6	STE	2	95.9	29.5	>100	49.3	1.47	2,530	s	1.04	3,330	s	s
TCC2	STE	2	64.2	24	4.1	9.9	1.46	2,511	s	1.39	4,433	s	s
TBC3	STE	8, 2	25.3	0.9	0.51	0.36	3.01	5,174	2.21	2.83	9,027	1.39	4,420
TAC4	STE	8	63.7	7.5	0.78	0.62	5.54	9,511	5.23	5.58	17,774	3.24	10,313
TAC2	TFU	2	61.4	65.5	>100	52.8	2.06	3,527	s	2.08	6,642	s	s
TBC4	TFU	2	79.4	48.8	>100	24.8	2.41	4,137	s	2.5	7,964	s	s
TBC1	TFU	8, 2	25.2	0.7	0.34	0.29	5.8	9,947	2.86	4.49	14,297	1.7	5,399
TCC6	TFU	8	70.6	22.1	0.49	0.92	8.9	15,281	s	7.75	24,704	5.46	17,374
TAC3	MBR	2	38.8	66.1	NA	NA	1.54	2,637	s	NA	NA	NA	NA
TCC1	MBR	2	60	37	NA	NA	1.42	2,440	s	NA	NA	NA	NA
TAC6	MBR	8	157.9	76.1	NA	NA	6.81	11,679	s	NA	NA	NA	NA
TCC4	MBR	8	70	10.9	NA	NA	7.01	12,036	s	NA	NA	NA	NA
<i>Design</i>	-	2	NA	NA	NA	NA	2	3,462	s	2	6,430	s	s
<i>Design</i>	-	8	NA	NA	NA	NA	8	13,717	s	8	25,474	s	s
<i>Control*</i>	Water	4	52.14	59.88	20.85	NA	4.75	16,037	s	3.06	24,381	s	s
<i>C Design</i>	-	4	NA	NA	NA	NA	4	12,640	s	4	30,562	s	s

### 3.2.2 Study Design

Experiments were conducted between December 2006 and December 2007 at the Test Site to: 1) quantify the fate and variability of trace organic contaminants during treatment within a textile biofilter as compared to septic tank treatment alone, and 2) evaluate the fate of trace organic contaminants during soil treatment as affected by effluent type and HLR.

A subset of the target compounds from the reconnaissance survey was selected for further study at the Mines Park Test Site: caffeine, EDTA, NTA, NP, NP1EO, NP1EC, and triclosan. These compounds were commonly identified in operational OWTS wastewaters at measurable concentrations, had high recoveries through the lysimeter apparatus used at the Test Site, spanned a range of physicochemical properties and, therefore, had varying hypothesized behaviors during onsite treatment, and/or had known or potential adverse ecological effects.

To assess fate during engineered treatment, grab samples of nine tank or ponded effluents (locations 1, 2, 3, 4, 5, 6, 9, 19, and 21 – see Figure 4) were collected once a day (at 12:00) for seven consecutive days (11/30 – 12/6/2007). An aliquot of the daily sample from each location was also combined into a composite sample. The daily and composite samples were analyzed for target trace organic contaminants (Section 3.2.4). The average concentrations at each location were compared to assess removal during septic tank and textile biofilter treatment. Variability in trace organic contaminant concentrations in OWTS effluents over time was also assessed during this sampling effort. Weekly variability was evaluated by comparing individual concentrations to each other and to the composite sample at each location. To assess daily variability, grab samples of three tank effluents (locations 1, 4, and 6 – see Figure 4) were collected four times in one day (08:00, 12:00, 16:00, and 20:00 on 12/3/2007). To assess monthly variability, grab samples of seven effluents (locations 1, 2, 3, 4, 5, 6, and 9 – see Figure 4) were collected 9 to 13 times over 7 months (May through December 2007). Results were also used to quantify typical effluent compositions applied to the soil test cells.

A second major sampling effort was conducted between December 2006 and December 2007 to assess fate during soil treatment. Sampling and analysis of conventional parameters and trace organic contaminants in soil solution was conducted utilizing nine soil test cells outfitted with lysimeters (4 receiving STE, 4 receiving TFE, 1 receiving tap water). Soil solution at 60 cm, 120 cm, and 240 cm (i.e. 22 unique soil solution locations) were sampled two to three times over one year. Composition was compared with effluent composition to assess soil treatment efficiency of bulk parameters and trace organic contaminants as affected by effluent type, HLR, and depth.

### 3.2.3 Sample Collection

The sampling protocol was consistent throughout the characterization experiments at the Mines Park Test Site. Grab samples of wastewater were collected from the clarified layer located at mid-depth (~0.5 m below the liquid surface) at the outlet of each tank (locations 1 through 8, see Figure 4) using a tank sampler. Location 9 was collected at the end of the pressured drip irrigation system pipe network. A 90-second dose was collected through the delivery line tubing (locations 10 through 17) at the delivery apparatus (see Van Cuyk et al. 2005). Pondered effluent (locations 18 through 21) was collected through an observation port using a tank sampler. Soil solution (locations 22 through 53) was collected through the lysimeter apparatus after purging the system of at least 30 mL of solution (which required less than 1 day to over 3 days of purging time). Collection of a sufficient volume of soil solution varied between test cells and depths, ranging from less than one day to over one week, and, in some locations, no volume was able to be collected. To minimize sample degradation during extended sampling, collection flasks were chilled to 4 °C in the field using cold packs. A silicon stopper connected the tubing to the collection flask. Ground water samples were collected through the monitoring wells (locations 54 through 57) using dedicated Teflon tubing after purging the well with at least 3 pore volumes.

Unfiltered samples were collected in amber glass bottles that had been pre-cleaned with soap, rinsed 3 times with tap water, rinsed 3 times with distilled water, and burned at 250 °C for 12 hours. Samples from each location were split into up to four aliquots: one unpreserved for bulk parameter analysis, one unpreserved for trace organic contaminant analysis, one preserved with 1% v/v formalin (37% formaldehyde) for trace organic contaminant analysis, and one unpreserved for USGS non-target compound analysis. Samples were stored at 4 °C until analysis which generally was performed within 24 h for bulk wastewater parameters, within 1 week for unpreserved trace organic contaminants, and within 1 month for preserved trace organic contaminants. A subset of samples analyzed for antibiotics were immediately shipped to the USGS laboratory.

### 3.2.4 Analytical Procedures

Bulk parameters were analyzed following the same procedures as described in Section 3.1.3. In addition, a subset of samples was acidified for analysis of major ions and trace metals by inductively coupled plasma atom emission spectrometry utilizing a Perkin-Elmer Optima 3000 as per manufacturer's specifications. Target trace organic contaminants were analyzed using two extraction methods- a solid-phase extraction (SPE) and an acetyl propanol derivatization. The derivatization method has been described in Section 3.1.3. Caffeine, NP, NP1EO, and triclosan were isolated using SPE. SPE is

preferable over CLLE because less solvent is used, smaller sample volumes can be processed, and fewer emulsions are generated (Thurman and Mills 1998), though filtration may be necessary for particulate-laden samples (i.e. raw wastewater). A 50 mL unpreserved, unfiltered sample was spiked with surrogate standards (*d*<sub>9</sub>-caffeine, 4-*n*-nonylphenol, 4-*n*-NP1EO) and passed through a pre-conditioned cartridge (Waters tC18<sup>+</sup>, conditioned with dichloromethane, methanol, and distilled water) at a rate of approximately 5 mL/min. Cartridges were rinsed with a 20% methanol / 80% distilled water solution to elute interfering polar compounds. Target compounds were eluted with dichloromethane into anhydrous sodium sulfate, and passed over a sodium sulfate drying column to remove any residual water. The extract was concentrated under nitrogen gas to 0.2 mL and transferred to a GC/MS vial for analysis by capillary column GC/MS. Quantification by GC/MS has been described in Section 3.1.3.

A subset of tank effluent and soil solution samples were analyzed for a suite of antibiotics including sulfamethoxazole by Mike Meyer at the USGS Environmental Geochemistry Group in Lawrence, Kansas using the methods described in Section 3.1.3 (Meyer et al. 2007).

### **3.2.5 Quality Assurance**

On each day of sampling at the Mines Park Test Site, a randomly-selected sample was collected in duplicate to perform quality control analyses. Most often field duplicate samples were tank effluents, but lysimeter samples were also used when there was sufficient volume. Every set of 12 samples run simultaneously through the SPE vacuum apparatus included one laboratory blank, one laboratory duplicate, and one or both of a distilled water matrix spike and environmental matrix spike. Laboratory blanks, replicates, and matrix spike samples comprised approximately 20% of derivatization analyses. Compounds were quantified from surrogate standards when they were commercially available. Additional quality assurance included solvent and reagent blanks and GC/MS replicate injections.

## CHAPTER 4

### OCCURRENCE IN OWTS AND RECEIVING ENVIRONMENTS

Results from the reconnaissance field survey regarding the occurrence of bulk parameters and trace organic contaminants in OWTS and receiving environments are presented and discussed.

#### 4.1 Quality Assurance

The wastewater matrix from onsite treatment systems is very concentrated and complex, and presents an analytical chemistry challenge. Within a given suite of trace organic contaminants, measured concentrations of individual compounds in a single analysis can vary by 2 to 5 orders of magnitude. Likewise, concentrations of trace organic contaminants between seemingly similar samples (i.e. single family residence, single tank systems) can differ by orders of magnitude. In this study, distilled water matrix spike recoveries averaged 119% (n=26 compounds, 2 analyses; relative standard deviation, RSD=37%). Wastewater sample matrix CLLE spike recoveries averaged 78% (n=25 compounds, 5 analyses; RSD=43%), with the exception of caffeine and 4-methylphenol, which had erratic recoveries due to high matrix concentrations. For the derivatization method, recoveries averaged 97% (n=6 compounds, 3 analyses; RSD=34%). Surrogate standard recoveries averaged 88% (n=90 analyses; RSD=55%) for *d*<sub>6</sub>-bisphenol A and 79% (n=90 analyses; RSD=29%) for 4-*n*-NP2EC. Field and laboratory CLLE replicate analysis had an average relative percent difference (RPD) of 54% (n=29 compounds, 15 analyses; RSD=46%). Field and laboratory replicate analysis for the derivatization method had an average RPD of 22% (n=6 compounds, 12 analyses; RSD=35%). The percent difference between field and laboratory duplicate samples (n varied from 1 to 15) averaged less than 25% for bulk parameters, with the exception of turbidity (46%, field duplicate n=1). TDS values averaged 185 mg/L in the blank samples, indicating that additional rinsing of the filter paper is necessary (which was implemented in future studies). TDS values in environmental samples in this study are likely lower than reported due to this error.

Reporting levels for target compounds in the fall 2003 sampling were 0.5 µg/L, with the exception of NP-derived compounds, which were 2.0 µg/L due to the isomeric side chain. The reporting levels conservatively accounted for matrix limitations, and are 3 times the average concentration of any compounds detected in field or laboratory blanks. Reporting levels for NP1EC, NP2EC, EDTA, and caffeine in the spring 2004 sampling increased to 6.0, 5.0, 4.0, and 1.0 µg/L respectively to account for blank contamination. Concentrations of bisphenol A in quality control samples were erratic, and results

are excluded. Therefore, results are presented for 24 target compounds, where  $\sum\text{NPEO} = \text{NP1EO} + \text{NP2EO} + \text{NP3EO} + \text{NP4EO}$ ,  $\sum\text{NPEC} = \text{NP1EC} + \text{NP2EC} + \text{NP3EC} + \text{NP4EC}$ , and  $\sum\text{OPEO} = \text{OP1EO} + \text{OP2EO} + \text{OP3EO} + \text{OP4EO} + \text{OP5EO}$ .

Quality assurance for non-target compounds was performed at each USGS laboratory according to specific protocols. Final data received at CSM had passed quality assurance and control requirements, or had been flagged and noted (e.g. when a value exceeded the standard curve or had been estimated due to analytical difficulty).

## 4.2 Occurrence in OWTS

### 4.2.1 Bulk Parameters and Target Trace Organic Contaminants

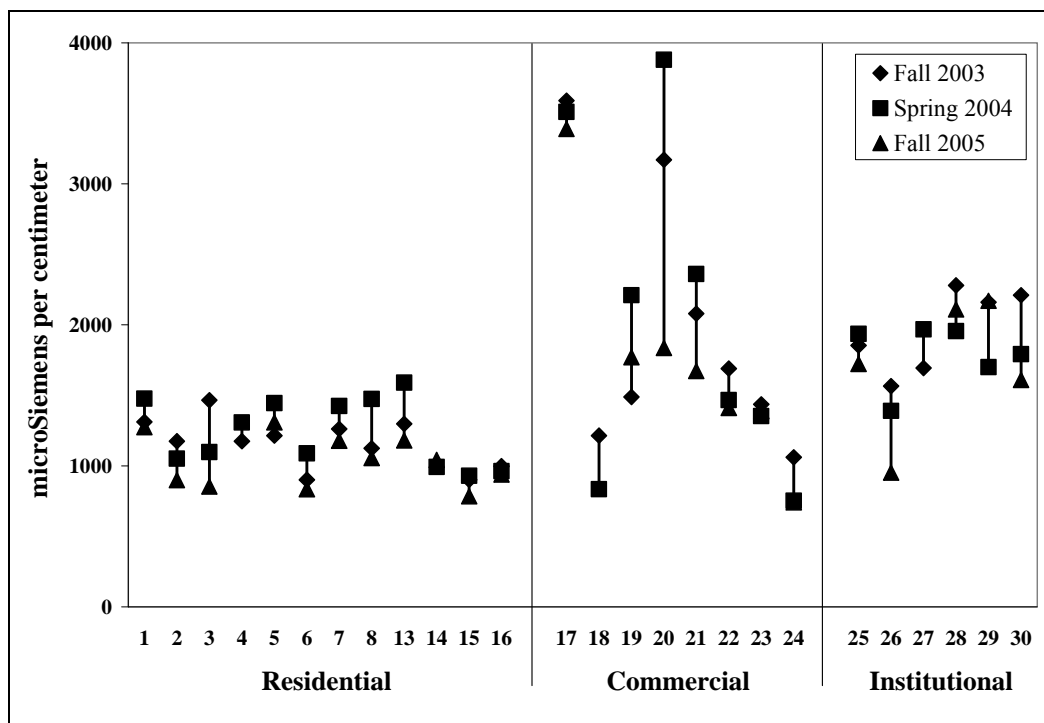
Septic tank wastewater (Locations I or III, see Table 3 and Figure 3) from 26 OWTS was compared for bulk parameters and trace organic contaminants. Analysis of bulk parameters revealed a wide range of compositions (Table 8) expected in systems treating wastewater from a wide variety of sources (i.e. single-family homes, restaurants, medical facilities). Water temperature ranged from 5 °C to 30 °C, with the warmest temperatures measured in wastewater from a restaurant (site 17). pH values were typically from 6.5 to 7.5, with the exception of two sites. Wastewater from a bakery (site 19) had pH values ranging from 4.8 to 5.1 and wastewater from a veterinary hospital (site 30) had pH values ranging from 7.9 to 8.7. Alkalinity ranged from 120 to 660 mg-CaCO<sub>3</sub>/L in wastewaters from all sources except from the bakery (20 to 100 mg-CaCO<sub>3</sub>/L) and the restaurant, site 17 (480 to 750 mg-CaCO<sub>3</sub>/L).

Within the 26 OWTS compared, residential septic tank wastewater was relatively constant spatially (between different sites) and temporally (at the same site over time) regarding bulk parameters. Values of bulk parameters were similar to typical literature values for residential wastewater (Crites and Tchobanoglous 1998), such as an average cBOD<sub>5</sub> of 290 mg/L and an average ammonia concentration of 65 mg-N/L. Non-residential septic tank wastewater showed higher spatial and temporal variability, often with higher levels of bulk parameters than residential septic tank wastewater. For example, specific conductance ranged from 780 to 1600 μS/cm in residential septic tank wastewater and from 740 to 3900 μS/cm in non-residential wastewater (Figure 6), with maximum values in some food establishments (sites 17 and 19), convenience stores (sites 20 and 21), and veterinary hospitals (sites 28, 29 and 30). Ammonia was also more variable and often higher in non-residential sources (4.0 to 210 mg-N/L) as compared to residential sources (38 to 99 mg-N/L), with maximum concentrations in wastewater from convenience stores (sites 20 and 21) and institutional sources such as schools, churches, and veterinary hospitals (sites 25, 26, 27 and 28).



**Table 8.** Summary of combined fall 2003, spring 2004, and fall 2005 results for bulk parameter composition of septic tank wastewater. [Septic tank wastewater (Location I or III, Figure 3 and Table 3) was compared for 26 sites. Each site was sampled one to three times. n = number of samples.]

Parameter	Units	Residential Wastewater				Non-Residential Wastewater					
		Minimum	Maximum	Average	Median	n	Minimum	Maximum	Average	Median	n
Water Temperature	°C	5	23	13	13	33	9	30	16	17	38
Specific Conductance	µS	780	1600	1200	1200	34	740	3900	1890	1700	40
pH	S.U.	6.51	8.40	7.14	7.14	35	4.92	8.69	6.80	6.78	40
Alkalinity	mg CaCO <sub>3</sub> /L	240	550	380	380	35	20	750	390	410	40
Dissolved Oxygen	mg/L	0.51	2.23	1.18	1.12	23	0.39	3.08	1.40	1.23	26
Total Dissolved Solids	mg/L	360	890	560	600	34	420	3500	1100	830	40
Biochemical Oxygen Demand	mg/L	150	500	290	260	25	80	1200	430	320	27
Chemical Oxygen Demand	mg/L	290	5700	3000	3500	10	320	16500	5400	4200	12
Total Nitrogen	mg-N/L	38	150	87	84	23	6	190	100	92	25
Nitrate	mg-N/L	0.5	14	2.8	1.5	23	<0.5	9.5	1.9	1.4	24
Ammonia	mg-N/L	38	99	65	63	23	4.0	210	99	87	26
Total Phosphorus	mg-P/L	7.5	34	14	13	23	1.7	37	17	16	26
Turbidity	FAU	86	1900	360	190	11	99	660	320	250	12
Fecal Coliforms	CFU/100 mL	6.00E+04	1.80E+06	6.21E+05	6.30E+05	11	1.50E+05	3.34E+07	4.19E+06	6.75E+05	12
Total Organic Carbon	mg/L	21	87	41	40	20	33	340	100	89	25
Dissolved Organic Carbon	mg/L	20	97	39	34	20	21	230	87	77	25
Specific UV Absorbance	L/mg-m	0.82	2.7	1.5	1.4	20	0.61	4.2	2.0	2.1	24



**Figure 6.** Specific conductance of 26 septic tank wastewaters in Colorado. [Numbers on x-axis refer to Site ID. Data is from Location I or III. See Table 3 and Figure 3.]

Nineteen of the 24 target trace organic contaminants were detected in one or more samples from residential septic tank wastewater at concentrations ranging from <0.5 to 4500  $\mu\text{g/L}$  (Table 9). Caffeine, coprostanol, cholesterol, and 4-methylphenol had concentrations exceeding the highest calibration standard (denoted as estimated concentration, “E”). Six compounds were detected in all of the anaerobic residential samples: caffeine, coprostanol, cholesterol, EDTA, 4-methylphenol, and ©NPEC. Five additional compounds had median concentrations above the reporting level: 4-ethylphenol, NTA, NP, ©NPEO, and triclosan. The remaining 8 compounds that were detected occurred less frequently and at lower concentrations. Concentrations of several compounds were similar to previously reported results in septic tank wastewater: caffeine (<0.5 to 320  $\mu\text{g/L}$ ; Godfrey 2004, Hinkle et al. 2005, Swartz et al. 2006), triclosan (<1 to 5  $\mu\text{g/L}$ ; Hinkle et al. 2005), and NP (<26 to E210  $\mu\text{g/L}$ ; Rudel et al. 1998, Hinkle et al. 2005, Swartz et al. 2006). One of the multi-family residential tank-based systems (site 16) was analyzed by the USGS for non-target compounds. Elevated levels of acetaminophen (45  $\mu\text{g/L}$ ), 1,7-dimethylxanthine (56  $\mu\text{g/L}$ ), and tetracycline (20  $\mu\text{g/L}$ ) were detected in the wastewater, as well as 19 other non-target compounds, including methyl salicylate (1.6  $\mu\text{g/L}$ ), erythromycin (0.137  $\mu\text{g/L}$ ), carbamazepine (0.0048  $\mu\text{g/L}$ ), and anthraquinone (1.1  $\mu\text{g/L}$ ).

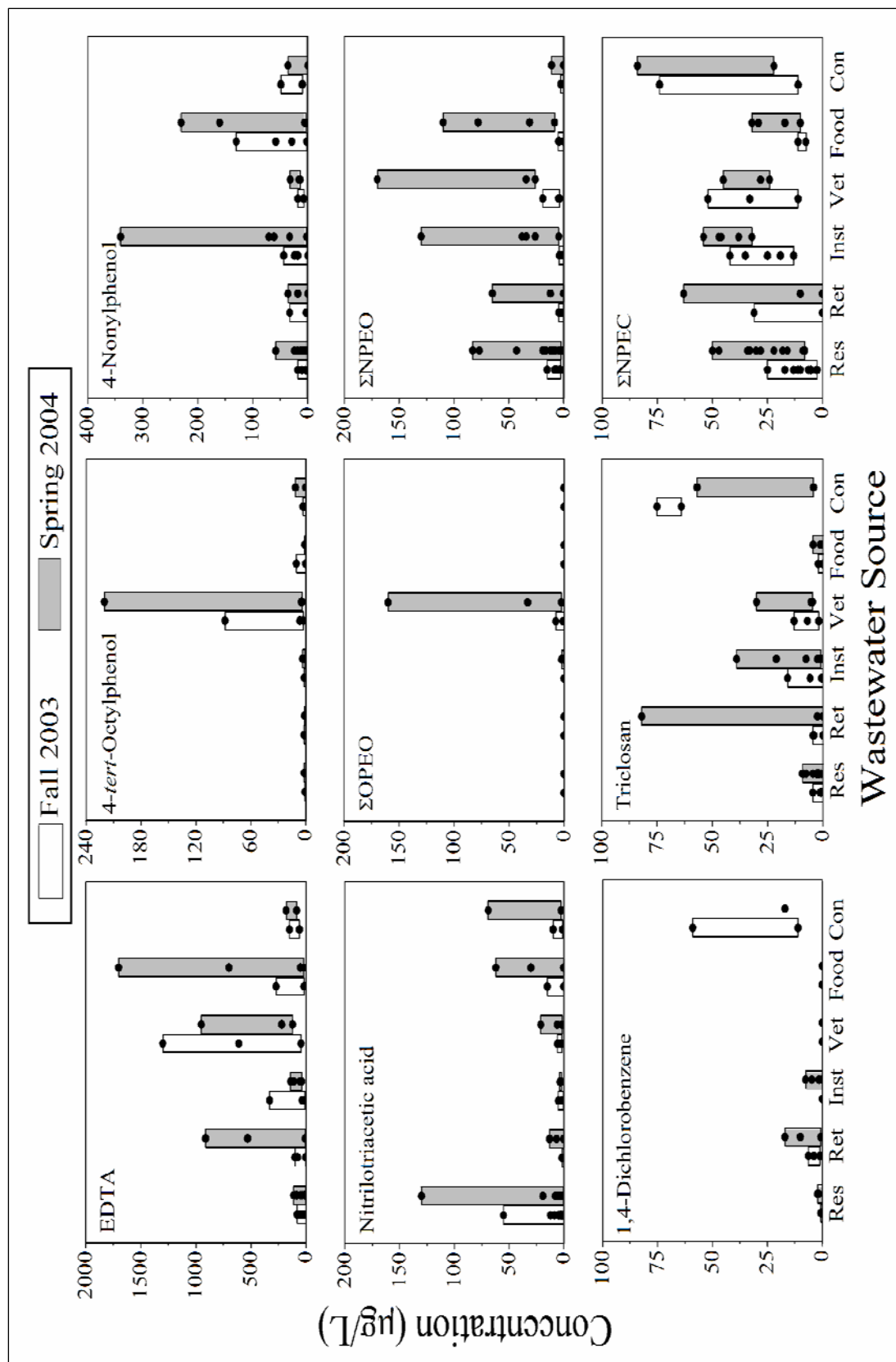
**Table 9.** Summary of combined fall 2003 and spring 2004 results for target trace organic contaminants in septic tank wastewater. [Residential n = 30, Non-residential n = 34. RL = reporting level, increased to 1.0 (caffeine), 4.0 (EDTA), and 6.0 ( $\Sigma$ NPEC)  $\mu\text{g/L}$  during spring 2004. Frequency of detection = number of samples with concentrations greater than RL/total number of samples (percent detection given in parentheses). For compounds with median concentrations <RL, median concentrations of detections are given in parentheses. Concentrations exceeded maximum value of standard curve for caffeine (25/87), cholesterol (72/90), coprostanol (74/90), and 4-methylphenol (61/77), and values are estimated as indicated by “E”.]

Target Compounds	RL ( $\mu\text{g/L}$ )	Residential			Non-residential		
		Frequency of Detection (%)	Max ( $\mu\text{g/L}$ )	Median ( $\mu\text{g/L}$ )	Frequency of Detection (%)	Max ( $\mu\text{g/L}$ )	Median ( $\mu\text{g/L}$ )
2[3]- <i>t</i> -Butyl-4-methoxyphenol	0.5	2/29 (7)	1.2	<RL (1.0)	2/34 (6)	1.1	<RL (0.89)
4- <i>t</i> -Butylphenol	0.5	6/29 (21)	9.6	<RL (1.0)	11/34 (32)	6.4	<RL (1.1)
Caffeine	0.5	30/30 (100)	E450	15	34/34 (100)	E9300	E110
Cholesterol	0.5	30/30 (100)	E700	E71	34/34 (100)	E2200	E89
Coprostanol	0.5	30/30 (100)	E2800	E90	34/34 (100)	E7100	E190
1,2-Dichlorobenzene	0.5	0/30 (0)	<RL	<RL	0/34 (0)	<RL	<RL
1,3-Dichlorobenzene	0.5	0/30 (0)	<RL	<RL	0/34 (0)	<RL	<RL
1,4-Dichlorobenzene	0.5	4/30 (13)	2.1	<RL (1.2)	12/34 (35)	59	<RL (7.0)
2,6-Di- <i>t</i> -butyl-1,4-benzoquinone	0.5	4/29 (14)	3.1	<RL (2.3)	5/34 (15)	2.6	<RL (1.6)
2,6-Di- <i>t</i> -butyl-4-methylphenol	0.5	9/30 (30)	1.1	<RL (0.77)	10/34 (29)	12	<RL (1.7)
2,6-Di- <i>t</i> -butylphenol	0.5	0/29 (0)	<RL	<RL	0/34 (0)	<RL	<RL
Ethylenediaminetetraacetic acid	0.5	30/30 (100)	110	29	32/32 (100)	1700	100
4-Ethylphenol	0.5	16/28 (57)	7.5	1.2	22/34 (65)	15	1.4
4-Methylphenol	0.5	30/30 (100)	E4500	E260	33/34 (97)	E4500	E570
Nitritotriacetic acid	0.5	25/30 (83)	130	2.1	26/32 (81)	69	2.5
NP	2	19/30 (63)	58	4.4	30/34 (88)	340	19
$\Sigma$ NPEC	2.0	30/30 (100)	50	17	29/32 (91)	320	30
$\Sigma$ NPEO	2	21/30 (70)	83	4.3	26/33 (79)	170	4.8
4- <i>n</i> -Octylphenol	0.5	1/30 (3)	0.57	<RL (0.57)	4/33 (12)	3	<RL (2.0)
4- <i>t</i> -Octylphenol	0.5	6/30 (20)	1.6	<RL (0.76)	21/34 (62)	220	1
$\Sigma$ OPEO	0.5	0/30 (0)	<RL	<RL	6/33 (18)	160	<RL (4.9)
4-Propylphenol	0.5	11/28 (39)	4	<RL (2.1)	13/34 (38)	2.6	<RL (1.0)
4- <i>t</i> -Pentylphenol	0.5	0/29 (0)	<RL	<RL	2/34 (6)	0.66	<RL (0.60)
Triclosan	0.5	17/30 (57)	9.3	0.83	26/33 (79)	82	4.2

Non-residential sources had similar occurrences of trace organic contaminants as the residential systems. Twelve compounds had median concentrations above the reporting level - the same 11 observed in residential systems plus 4-*t*-octylphenol. Median concentrations for 7 of the 12 compounds were greater ( $p < 0.05$ , Mann-Whitney U-test) in non-residential than in residential systems (Table 9). Although median concentrations were below reporting levels, 1,4-dichlorobenzene and ©OPEO were detected in the non-residential systems at maximum concentrations of 59 and 160 µg/L, but were infrequently detected in residential systems. USGS analysis of non-target compounds in wastewater identified 1,7-dimethylxanthine (21-49 µg/L), cimetidine (0.28-12 µg/L), ciprofloxacin (0.036-0.593 µg/L), cotinine (0.92-3.9 µg/L), norfloxacin (0.039-0.11 µg/L), ofloxacin (0.018-2.31 µg/L), and trimethoprim (0.005-0.229 µg/L) in all 4 non-residential systems. The results suggest that non-residential sources have unique compositions regarding trace organic contaminants, with higher concentrations and more compounds than in residential systems.

Variability in occurrence and concentrations of trace organic contaminants and bulk parameters in the OWTS studied was likely due to differences in water- and chemical-using activities at the source contributing to the wastewater (Figure 7). Typical water use for a residential source is 30% toilets, 30% dish and clothes washing, 20% bathing, 10% faucets, and 10% miscellaneous (Crites and Tchobanoglous 1998), resulting in a dilute wastewater composition composed of a mix of human waste, kitchen waste, and consumer product chemicals. Biogenic (coprostanol) and anthropogenic compounds (EDTA and ©NPEC) were detected in all of the residential systems.

In contrast to residential systems, retail centers discharge wastewater from multiple sources to the OWTS. Commercial effluent composition can vary over time as changes in business practices affect water and chemical use. For example, differences in EDTA and triclosan concentrations in one of the retail centers between the fall 2003 and spring 2004 samplings may be explained by the re-opening of a restaurant during the winter of 2003. Compound occurrence in institutional sources also was variable, and can be attributed to changes in activities. The fall 2003 school samples were collected during summer vacation while the spring 2004 sample was collected while school was in session. The spring samples had greater concentrations of caffeine, coprostanol, and triclosan.



**Figure 7.** Distribution of select trace organic contaminants in septic tank wastewaters as a function of wastewater source. [Res, residential (n=15); Ret, retail (n=3); Inst, human institution - schools and church (n=5); Vet, veterinary hospital (n=4); Food, food establishment (n=4); Con, convenience store (n=2); upper limit of box = maximum concentration, lower limit = minimum concentration.]

Water use at convenience stores differs from residential sources, and most of the wastewater entering onsite treatment systems originates in public restrooms and sinks. This difference in water use is reflected in the results for the two convenience stores (Figure 7), which had high concentrations of nitrogen as ammonia (fecal matter), triclosan (hand soaps), 1,4-dichlorobenzene (urinal deodorant), and ©NPEC (cleaning products). Proportional use of cleaning products is more intensive in commercial than in residential activities. The elevated concentrations (E2500-E5800 µg/L) of caffeine in convenience stores can be explained by inputs from both human excretion and disposal of unconsumed caffeinated beverages. For example, approximately 3 pots of coffee (2.5 L per pot) poured down the drain each day would result in wastewater concentrations in the range of those observed (assuming 500 mg/L caffeine and water consumption of 1500 L/day). The convenience store wastewater composition also reflects the large and diverse population (up to 1000 people/d) visiting the stores. The highest concentrations of 15 pharmaceuticals and antibiotics (analyzed by the USGS), including cimetidine and ranitidine (antacids), ofloxacin and sulfamethoxazole (antibiotics), and gemfibrozil (antihyperlipidemic), were detected in the convenience store wastewater.

Veterinary hospitals use a high proportion of their water in washing and disinfecting practices, resulting in a different trace organic contaminant distribution than the other sites. In addition to NP, ©NPEO, and ©NPEC, the nonionic surfactant metabolites 4-*t*-octylphenol and ©OPEO were detected in all samples from veterinary hospitals, but only 48% (4-*t*-octylphenol) and 2% (©OPEO) of the other sites. Concentrations of both compounds in wastewater from one veterinary hospital were 20 times the concentrations in other sources.

Wastewater from food establishments had high concentrations of NP and ©NPEO. Concentrations of ©NPEO were higher (paired *t*-test,  $p < 0.0001$ ) during the spring than fall. Possible factors contributing to this variability include seasonal variations and inherent variability within these systems due to chemical and water fluxes associated with intensive, time-regulated business practices. The results suggest that wastewater from other institutional sources, such as human medical facilities, also will have compositions that differ from residential wastewater. Knowledge of the source, water use, and chemical use activities contributing to wastewater flow should be considered during onsite treatment system design and operation to ensure proper treatment.

#### **4.2.2 Semi-Quantifiable Compounds**

The target compounds may represent only a fraction of the total organic carbon (TOC) in a wastewater. TOC, which ranged from 21 to 340 mg/L in septic tank wastewater (Table 8), is an aggregate measure of proteins, carbohydrates, oils and fats, and urea in addition to synthetic organic

molecules (Crites and Tchobanoglous 1998). Full scan chromatograms of wastewaters were assessed to identify the concentrations of target compounds relative to other organic compounds contributing to the TOC in septic tank wastewater. Table 10 shows the distribution of the 20 largest peaks in five representative wastewaters (Figure 8) as three categories: fatty acids, sterols, and consumer product chemicals. Regardless of wastewater source, 7 to 14 of the 20 largest peaks in all five septic tank wastewater samples were fatty acids, such as octadecanoic acid and benzenecetic acid, while 0 to 4 peaks were identified as sterols, such as cholesterol and coprostanol, and 2 to 11 peaks were identified as consumer product chemicals, such as surfactants and stimulants.

**Table 10.** Distribution of the 20 largest chromatographic peaks in five onsite system wastewaters and the consumer product chemicals identified as one of the 50 largest peaks. [FA- fatty acids; ST- sterol; CP- consumer product chemicals. Unidentifiable peaks: multi-family home=1, convenience store=3, restaurant=2, veterinary hospital=1.]

Source, Site ID	# in Largest 20 Peaks			Consumer Product Chemicals Identified as one of the Largest 50 Chromatographic Peaks (Rank)
	FA	ST	CP	
Multi-family home, 16	11	2	6	4-Methylphenol (4), fragrances (5,9,16,27,40,44,48), surfactant amine (13), caffeine (18), cyclic octaatomic sulfur (36), 5-methyl-1H-benzotriazole (39)
Elementary school, 26	14	4	2	4-Methylphenol (8), chloroxylenol (18), fragrances (25,28), 5-methyl-1H-benzotriazole (27), caffeine (42), ibuprofen (50)
Convenience store, 20	12	2	3	Caffeine (9), 4-methylphenol (11), surfactant amine (19), fragrance (37)
Restaurant, 17	14	0	4	Cyclic octaatomic sulfur (4), 4-methylphenol (7), caffeine (10), 5-methyl-1H-benzotriazole (18), NP (23), chloroxylenol (28), 4- <i>t</i> -octylphenol (36)
Veterinary hospital, 29	7	1	11	Surfactant amines (1,4,6,16,18), 4-methylphenol (2), fragrances (7,13,15,19,22,23,26,28,32,44,47), caffeine (16), methyl salicylate (37), methylparaben (38), octylphenolethoxylate (46)

The results suggest that the majority of organic carbon present in a septic tank wastewater is from fatty acids, likely originating from human and food waste. While consumer product chemicals typically comprise a small fraction of TOC in a sample (here: 0.1 to 7 wt. % of the TOC), they may represent the largest risk regarding exposure to receiving environments. A number of consumer product chemicals were semi-quantitatively identified in the 5 representative wastewaters (Table 10), some of which were identified during target compound analysis (e.g. caffeine and 4-methylphenol) as well as additional compounds. Cleaning product chemicals such as surfactant amines, NP, 4-*t*-octylphenol, and octylphenolethoxylate occurred frequently in veterinary hospital, restaurant, multi-family home, and convenience store wastewaters. Various fragrances were commonly detected, and were most frequent in the veterinary hospital and multi-family home wastewaters. An antimicrobial agent, chloroxylenol, used in treatment shampoos and antiseptic soaps and lotions, was identified in elementary school and

restaurant wastewaters. Methylparaben is a preservative and fungicide often used in deodorants and shampoos and was found in the veterinary hospital wastewater. The anticorrosive compound 5-methyl-1H-benzotriazole was found in multi-family home, elementary school, and restaurant wastewaters. The analgesic ibuprofen was identified in the elementary school. The source of elemental sulfur (cyclic octatomic sulfur) is unknown and hypothesized to be present in wastewater from the oxidation of hydrogen sulfide by anaerobic microbes. The results indicate that a number of trace organic contaminants not quantified as target compounds are also present in septic tank wastewaters from residential and non-residential sources.

### **4.3 Occurrence in Receiving Environments**

OWTS effluent is assimilated by the receiving environment, which may be local ground water or surface water. Ancillary samples from 9 supply wells (8 ground water sources and 1 surface water source) and 9 surface waters in OWTS-reliant regions in Colorado were analyzed for bulk parameters and trace organic contaminants. The water supply at site 27 was not being used as a drinking water source at the time of the study due to known contamination of chloride and potential contamination by other analytes. Specific conductance ranged from 6900 to 9400  $\mu\text{S}/\text{cm}$  and TDS values were over 6000 mg/L at this site (Table 11). The water supply at a restaurant (site 17) also had elevated levels of specific conductance (3000  $\mu\text{S}/\text{cm}$ ) and TDS (2100 to 2300 mg/L) as compared to the other sites (specific conductance = 220 to 1100  $\mu\text{S}/\text{cm}$ , TDS = 170 to 710 mg/L). The restaurant water was treated by filtration and chlorination prior to use. Oxygen demand and nutrient levels were typically near or below the reporting level in all receiving water samples. Total organic carbon values averaged less than 4 mg/L. The dissolved oxygen concentrations in surface waters ranged from 5.99 to 8.79 mg/L, indicating well aerated waters. The results indicate minimal anthropogenic impact as revealed by bulk parameters in the surface waters and supply wells sampled in this study.



**Table 11.** Summary of combined fall 2003 and spring 2004 results for bulk parameter composition of receiving environments. [Nine supply wells and nine surface waters were sampled. n = number of samples. NM = not measured.]

Parameter	Units	Supply Well				Surface Water					
		Minimum	Maximum	Average	Median	n	Minimum	Maximum	Average	Median	n
Water Temperature	C	8	22	17	17	15	6	20	11	9.5	18
Specific Conductance	µS	220	9400	1700	620	18	54	800	230	170	18
pH	S.U.	5.24	8.69	7.36	7.38	18	6.45	8.53	7.97	8.06	18
Alkalinity	mg CaCO <sub>3</sub> /L	8	230	110	100	18	12	100	48	42	18
Dissolved Oxygen	mg/L	1.7	6.7	3.9	4.1	8	6.0	8.8	7.1	6.8	9
Total Dissolved Solids	mg/L	170	6500	1200	490	18	0	340	130	130	18
Biochemical Oxygen Demand	mg/L	<5	6	<5	<5	9	<5	<10	<5	<5	9
Chemical Oxygen Demand	mg/L	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
Total Nitrogen	mg-N/L	<0.5	1.7	1.1	1.0	8	<0.5	2.9	1.2	0.8	9
Nitrate	mg-N/L	<0.2	1.2	0.5	0.3	9	<0.2	0.5	0.3	0.2	9
Ammonia	mg-N/L	<0.4	0.7	<0.4	<0.4	9	<0.4	0.4	<0.4	<0.4	9
Total Phosphorus	mg-P/L	0.06	0.34	0.18	0.13	9	0.05	0.18	0.11	0.09	9
Turbidity	FAU	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
Fecal Coliforms	CFU / 100 mL	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
Total Organic Carbon	mg/L	0.3	7.5	2.2	1.3	16	0.9	9.7	3.6	3.8	16
Dissolved Organic Carbon	mg/L	0.5	7.9	2.2	1.4	16	0.9	8.1	3.8	3.9	16
Specific UV Absorbance	L/mg-m	0.1	4.7	1.9	1.5	18	0.3	3.7	2.2	2.6	16

Target and semi-quantifiable trace organic contaminants were detected infrequently at low concentrations in receiving environments as compared to septic tank wastewaters. In the nine surface waters sampled in the study, only 1 of the 24 target trace organic contaminants, coprostanol, was identified (Table 12). The surface water sites are located in regions which rely on OWTS for wastewater treatment, but are not directly impacted by wastewater from municipal wastewater treatment plant discharge. Instead, treated OWTS effluent percolates through the soil until it reaches the water table and recharges the ground water which may, in turn, recharge the local surface water. Surface water may also be impacted by runoff from agriculture and development. Eight target compounds were detected in supply wells at concentrations from the reporting level to 19  $\mu\text{g/L}$  (Table 12). These included caffeine, cholesterol, coprostanol, 2,6-di-*t*-butyl-1,4-benzoquinone, EDTA, 4-methylphenol, NP, and  $\Sigma\text{NPEC}$ . Seven of the eight compounds were detected in only one of the two sampling events at a specific location. However, one well serving a veterinary hospital had elevated concentrations of EDTA during both sampling events (11 and 19  $\mu\text{g/L}$ ) as well as low levels of caffeine, coprostanol, cholesterol, and 2,6-di-*t*-butyl-1,4-benzoquinone during one sampling event. Two barbiturates commonly used for veterinary anesthesia and/or euthanasia, pentobarbital and secobarbital, were semi-quantitatively identified in the same well. The barbiturates were not identified in the wastewater on the same property. In a residential well, EDTA and the endocrine disruptor  $\Sigma\text{NPEC}$  were both identified. The disinfectant and herbicide 2,4,6-trichlorophenol was semi-quantitatively identified in a sample from an elementary school drinking water source.

Eight of the sites are drinking water wells located up gradient on the same property as an OWTS included in the study. In the OWTS-reliant developments, contamination of these wells could indicate regional impacts to the ground water from treated effluent recharge. Conversely, contamination may originate from the supply infrastructure (i.e. pumps, pipes, faucets, etc.) since the samples were collected at the point of use (i.e. indoor or outdoor faucet). These limited results represent an ancillary effort and further sampling should be conducted to assess the occurrence of trace organic contaminants in receiving waters.

**Table 12.** Summary of combined fall 2003 and spring 2004 results for trace organic contaminants in receiving environments. [RL = reporting level, increased to 1.0 (caffeine, 4.0 (EDTA), and 6.0 ( $\Sigma$ NPEC)  $\mu$ g/L in spring 2004. Frequency of detection = number of samples with concentrations greater than RL/total number of samples (percent detection given in parentheses). For compounds with median concentrations <RL, median concentrations of detections are given in parentheses.]

Target Compounds	RL ( $\mu$ g/L)	Ground water			Surface water		
		Frequency of Detection (%)	Max ( $\mu$ g/L)	Median ( $\mu$ g/L)	Frequency of Detection (%)	Max ( $\mu$ g/L)	Median ( $\mu$ g/L)
2[3]- <i>t</i> -Butyl-4-methoxyphenol	0.5	0/18 (0)	<RL	<RL	0/17 (0)	<RL	<RL
4- <i>t</i> -Butylphenol	0.5	0/18 (0)	<RL	<RL	0/17 (0)	<RL	<RL
Caffeine	0.5	2/18 (11)	1.6	<RL (1.1)	0/17 (0)	<RL	<RL
Cholesterol	0.5	4/18 (22)	3.5	<RL (1.7)	0/17 (0)	<RL	<RL
Coprostanol	0.5	4/20 (25)	10	<RL (3.4)	1/17 (6)	0.51	<RL (0.51)
1,2-Dichlorobenzene	0.5	0/18 (0)	<RL	<RL	0/17 (0)	<RL	<RL
1,3-Dichlorobenzene	0.5	0/18 (0)	<RL	<RL	0/17 (0)	<RL	<RL
1,4-Dichlorobenzene	0.5	0/18 (0)	<RL	<RL	0/17 (0)	<RL	<RL
2,6-Di- <i>t</i> -butyl-1,4-benzoquinone	0.5	3/18 (17)	1.8	<RL (0.88)	0/17 (0)	<RL	<RL
2,6-Di- <i>t</i> -butyl-4-methylphenol	0.5	0/18 (0)	<RL	<RL	0/17 (0)	<RL	<RL
2,6-Di- <i>t</i> -butylphenol	0.5	0/18 (0)	<RL	<RL	0/17 (0)	<RL	<RL
Ethylenediaminetetraacetic acid	0.5	4/18 (22)	19	<RL (8.9)	0/18 (0)	<RL	<RL
4-Ethylphenol	0.5	0/18 (0)	<RL	<RL	0/17 (0)	<RL	<RL
4-Methylphenol	0.5	1/18 (6)	0.53	<RL (0.53)	0/17 (0)	<RL	<RL
Nitrilotriacetic acid	0.5	0/18 (0)	<RL	<RL	0/18 (0)	<RL	<RL
NP	2	1/18 (6)	3.0	<RL (3.0)	0/17 (0)	<RL	<RL
$\Sigma$ NPEC	2.0	1/18 (6)	2.4	<RL (2.4)	0/18 (0)	<RL	<RL
$\Sigma$ NPEO	2	0/18 (0)	<RL	<RL	0/17 (0)	<RL	<RL
4- <i>n</i> -Octylphenol	0.5	0/18 (0)	<RL	<RL	0/17 (0)	<RL	<RL
4- <i>t</i> -Octylphenol	0.5	0/18 (0)	<RL	<RL	0/17 (0)	<RL	<RL
$\Sigma$ OPEO	0.5	0/18 (0)	<RL	<RL	0/17 (0)	<RL	<RL
4-Propylphenol	0.5	0/18 (0)	<RL	<RL	0/17 (0)	<RL	<RL
4- <i>t</i> -Pentylphenol	0.5	0/18 (0)	<RL	<RL	0/17 (0)	<RL	<RL
Triclosan	0.5	0/18 (0)	<RL	<RL	0/17 (0)	<RL	<RL

## **CHAPTER 5**

### **FATE DURING ENGINEERED TREATMENT**

Although the nature of the source is a primary factor contributing to wastewater composition (Chapter 4), the type of engineered treatment also contributes to variability of occurrence and concentration of bulk parameters and trace organic contaminants in onsite systems. Chapter 5 presents results from the reconnaissance survey and experiments conducted at the Mines Park Test Site regarding fate during treatment within engineered unit operations.

#### **5.1 Operational Field Systems**

At a subset of the 30 OWTS included in the reconnaissance survey (Chapter 4), additional wastewater samples within downstream unit operations were collected to assess removal of bulk parameters and trace organic contaminants during engineered treatment. The most common treatment system is a tank or series of tanks for settling of solids, sorption, and anaerobic biotransformation prior to discharge to an aerobic soil treatment unit (Figure 3A). At 7 of the sites, wastewater from the anaerobic tank was recirculated through aerobic textile-media biofilters (Figure 3B), which enhance treatment through additional sorption, volatilization, and aerobic biotransformation. One system used a subsurface-flow constructed wetland (mixed anaerobic/aerobic environment) for additional treatment (Figure 3C). Wetlands have the potential for additional removal by rhizosphere interactions. Estimated removals were calculated as the difference between influent concentrations (Figure 3, location I) and effluent concentrations (Figure 3, locations III, IV, or VI) and were compared for the three treatment types. The tank- and biofilter-based systems with paired influent and effluent samples had similar HRTs (4 to 13 d), and the wetland-based system had a HRT of 22 d (Table 3). Grab samples of influent and effluent wastewaters were collected at the same time, and variation in chemical use over the HRTs of the systems adds uncertainty to the removal results.

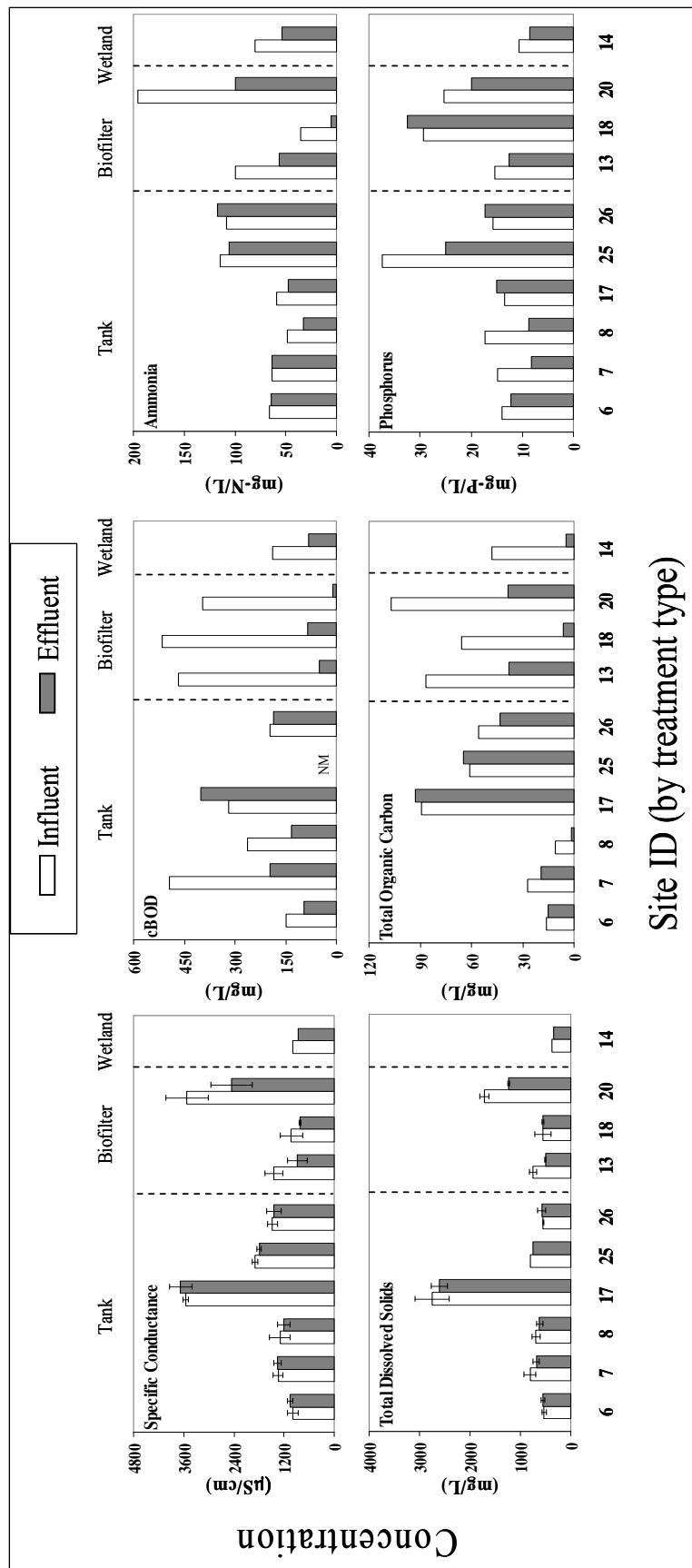
##### **5.1.1 Bulk Parameters**

While grab samples have their limitations, results for specific conductance and TDS (Figure 8) show reproducibility between sampling events and between influent and effluent wastewater in anaerobic tank-based systems. The average apparent removal of specific conductance observed in the biofilter-based ( $30 \pm 9\%$  removal) and wetland-based (13% removal) systems compared to the tank-based systems

( $0.9 \pm 5\%$  removal) reflects their increased hydraulic complexity. Average phosphorus removal (Figure 8) was less than or equal to 20% for all three types of engineered treatment units (tank =  $20 \pm 27\%$ , biofilter =  $10 \pm 18\%$ , wetland = 19% removal). Low removal is typical in engineered treatment units that are not specifically designed for phosphorus removal (e.g. by inorganic sorption or precipitation).

Engineered treatment units such as recirculating textile biofilters and constructed wetlands can provide enhanced treatment beyond that of a conventional septic tank for many bulk wastewater parameters such as cBOD, TOC, and ammonia (Figure 8). Removal of cBOD during tank-based systems was variable (removal =  $23 \pm 35\%$ ), while biofilter-based systems had high and consistent removal (removal =  $90 \pm 7\%$ ). Similarly, average apparent removal of TOC during biofilter treatment was  $70 \pm 18\%$ , while septic tank treatment alone was lower and more variable (removal =  $22 \pm 34\%$ ). The single wetland-based system appeared to provide treatment intermediate between tank- and biofilter-based systems for cBOD (removal = 56%) and high removal of TOC (removal = 90%).

Ammonia concentrations ranged from 4 to 200 mg-N/L in anaerobic wastewaters and 0.1 to 100 mg-N/L in aerobic wastewaters. Nitrate concentrations were low in all wastewaters, ranging from 0.1 to 14 mg-N/L and 0.1 to 4.5 mg-N/L in anaerobic and aerobic wastewaters, respectively. The occurrence of relatively high concentrations of nitrate (e.g. 14 mg-N/L) in some anaerobic wastewaters and ammonia (e.g. 100 mg-N/L) in some aerobic wastewaters suggests these wastewaters have high inputs of all nitrogen species and/or may have limiting conditions for complete conversion from one species to another. Fate of nitrogen species during biofilter treatment provides evidence for conversion and removal of nitrogen. Average removal of ammonia-N was  $59 \pm 23\%$ , while nitrate-N concentrations increased slightly from influent to effluent (average increase = 2 mg-N/L), and total nitrogen removal averaged  $48 \pm 11\%$ . As expected, in systems employing septic tank treatment alone, removal of ammonia-N was low ( $9 \pm 15\%$ ), nitrate-N concentrations were similar between influent and effluent (average decrease of 1.4 mg-N/L), and total nitrogen removal was low and variable (removal =  $18 \pm 23\%$ ). The single wetland-based system appeared to provide treatment intermediate between tank- and biofilter-based systems for ammonia (removal = 33%).

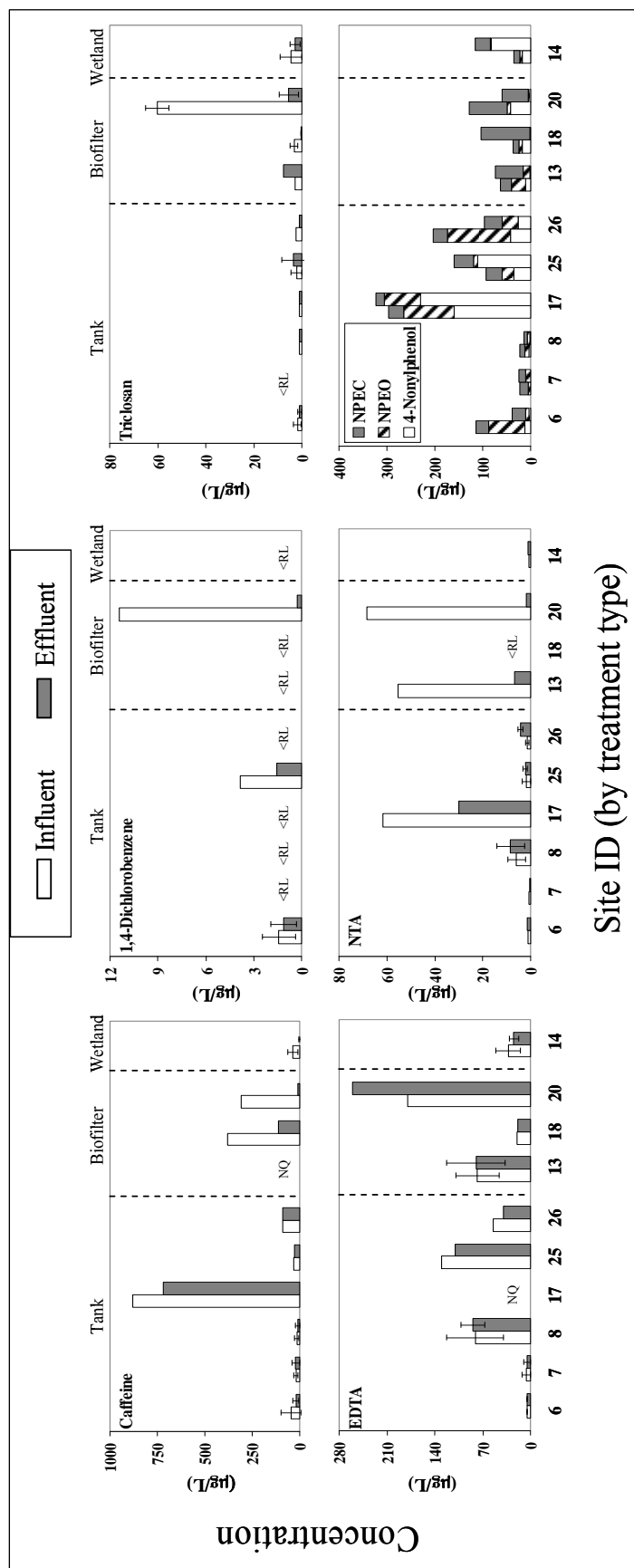


**Figure 8.** Comparison of influent and effluent concentrations of bulk parameters for three engineered treatment types. [Influent = location I; effluent = location III (tank), location IV (biofilter), and location VI (wetland); sites 6, 7, 8, 13, and 14 are single-family homes; sites 17 and 18 are food establishments; site 20 is a convenience store; sites 25 and 26 are schools; see Table 3 and Figure 3 for sample locations and site descriptions; cBOD = carbonaceous biochemical oxygen demand; data with error bars are average concentration of fall 2003 and spring 2004 samples; error bars represent relative percent difference (RPD) between fall 2003 and spring 2004 sample; data without error bars represent a single sampling event; NM = not measured.]

### 5.1.2 Trace Organic Contaminants

Biofilter-based systems also had greater removal efficiencies for many trace organic contaminants than tank-based systems (Figure 9), though removal varied based on physicochemical properties and removal mechanisms employed within the treatment units. For example, caffeine is aerobically biotransformed, which may explain its enhanced removal during textile biofilter ( $84 \pm 19\%$  removal) and constructed wetland ( $95\%$  removal) treatment as compared to septic tank treatment alone ( $18 \pm 23\%$  removal). Biofilter treatment resulted in a  $98\%$  reduction in 1,4-dichlorobenzene as compared to  $40 \pm 26\%$  removal in tank-based treatment. Volatilization may be an effective removal mechanism during biofilter treatment for compounds with large Henry's Law constants ( $K_H$ ) due to increased air-water exchange and enhanced turbulence. The two-film theory of volatilization was used to describe the loss of trace organic contaminants across the air/water boundary layer (Schwarzenbach et al. 2003, Keefe et al. 2004). Volatile organic compounds (VOCs) such as 1,4-dichlorobenzene ( $K_H = 2.40 \text{ atm-L/mol}$ , Keefe et al. 2004), have estimated volatilization half-lives ( $t_{1/2}$ ) on the order of 4 days in tank-based systems, which is similar to the HRTs (Table 3). Earlier studies on the fate of VOCs during tank-based treatment indicated little removal (DeWalle et al. 1980). In contrast, the estimated biofilter-based volatilization  $t_{1/2}$  for 1,4-dichlorobenzene was  $<12 \text{ h}$ . Other VOCs also could be effectively removed during biofilter-based treatment. In contrast, nonvolatile compounds such as triclosan ( $K_H = 5 \times 10^{-4} \text{ atm-L/mol}$ , Lindström et al. 2002) have estimated volatilization  $t_{1/2}$  of  $>22 \text{ d}$  in biofilter-based systems and  $>1 \text{ yr}$  in tank-based systems, which is much longer than the HRTs.

Removal of nonvolatile trace organic contaminants during engineered treatment can occur by biotransformation and sorption. Sorption of trace organic contaminants to solids with subsequent removal by sedimentation or filtration are effective removal mechanisms in tank- and biofilter-based systems for compounds with large octanol/water partition coefficients ( $K_{ow}$ ) such as triclosan ( $\log K_{ow} = 4.35$ , Lindström et al. 2002) and NP ( $\log K_{ow} = 4.70$ , Barber et al. 1988). Removal of triclosan in tank- and wetland-based systems (tank =  $38 \pm 22\%$  removal; wetland =  $39\%$  removal) may be attributed to sorption. In filter-based systems, additional triclosan removal ( $92 \pm 1\%$ ) can be attributed to aerobic biotransformation (Lindström et al. 2002) and filtration of particulates containing sorbed triclosan.



**Figure 9.** Comparison of influent and effluent concentrations of trace organic contaminants for three engineered treatment types. [Influent = location I; effluent = location III (tank), location IV (biofilter), and location VI (wetland)]; sites 6, 7, 8, 13, 14 are single-family homes; sites 17 and 18 are food establishments; site 20 is a convenience store; sites 25 and 26 are schools; see Table 3-1 and Figure 3-1 for sample locations and site descriptions; EDTA = ethylenediaminetetraacetic acid; NPEO = 4-nonylphenolmonoethoxyethylate through 4-nonylphenoltetraethoxyethylate; NPEC = 4-nonylphenolmonoethoxyethylate through 4-nonylphenoltetraethoxyethylate; data with error bars are average concentration of fall 2003 and spring 2004 samples; error bars represent relative percent difference (RPD) between fall 2003 and spring 2004 sample; data without error bars represent a single sampling event; NQ = not quantifiable; <RL = less than the reporting level.]



Theoretical distribution coefficients ( $K_D = \text{solids concentration/water concentration}$ ) were calculated for triclosan ( $K_D = 1200 \text{ L/kg}$ ) and NP ( $K_D = 2500 \text{ L/kg}$ ) based on (Chiou 2002)

$$K_D = 0.512 f_{oc} (K_{ow})^{0.904} \quad (5-1)$$

where  $f_{oc}$  is the fraction of organic carbon in the solids (kg organic carbon/kg solids) and is estimated at 0.27 for septic tank solids (Parnaudeau et al. 2004). Analysis of trace organic contaminants in the tank solids (Conn 2008) indicated orders of magnitude greater concentrations than in the wastewater for triclosan (maximum = 19,000  $\mu\text{g/kg}$ ) and NP (maximum = 1,800,000  $\mu\text{g/kg}$ ). The measured  $K_D$  values ranged from 1200 to 9500 L/kg for triclosan and 3,100 to 82,000 L/kg for NP. In contrast, 4-methylphenol, which is less hydrophobic ( $\log K_{ow} = 1.93$ , Schwarzenbach et al. 2003), had a calculated  $K_D$  of 8 L/kg and measured  $K_D$  values of 1 to 110 L/kg. Measured  $K_D$  values in onsite treatment systems will vary as a function of the liquid/solid ratio, solids characteristics, and source water composition.

The fate of the metal-chelating agents EDTA and NTA illustrate the role of biotransformation during onsite treatment because EDTA is resistant to sorption and biotransformation whereas NTA is resistant to sorption but is readily biotransformed under aerobic conditions (Alder et al. 1990). Removal of EDTA was negligible in both tank-and biofilter-based systems (Figure 9, tank =  $12 \pm 12\%$  removal, biofilter =  $-6 \pm 8\%$  removal). The apparent negative removal in biofilter-based systems is likely due to increased hydraulic complexity and deviation from the assumption of uniform mixing, as also was observed for specific conductance. Removal of NTA in tank-based systems was negligible ( $-8 \pm 42\%$  removal), whereas removal in biofilter-based systems was  $76 \pm 29\%$ . Selective removal of NTA relative to EDTA in the biofilter based systems is attributed to aerobic biotransformation.

The ultimate fate of trace organic contaminants is complicated by the production of metabolites as parent compounds are transformed. For example, the metabolites NP,  $\Sigma\text{NPEO}$ , and  $\Sigma\text{NPEC}$  are formed by biotransformation of the parent nonylphenolethoxylate (NPE) surfactants which have 10 to 20 ethoxylate units (Ahel et al. 1994). Over 95% of the wastewater samples had detectable NPE degradation products, with concentrations ranging from 2 to 500  $\mu\text{g/L}$ . Although the parent NPE compounds were not measured in this study, they contribute 80% of the total NPE in primary WWTP effluent (Ahel et al. 1994) which is similar to anaerobic tank effluent. In the anaerobic tank-based systems, the ratio of NP:  $\Sigma\text{NPEO}$ :  $\Sigma\text{NPEC}$  (1.0:1.5:3.0) was relatively constant between influent and effluent (Figure 9), suggesting little transformation during tank residence. Aerobic biofilter-treatment shifted the NP:  $\Sigma\text{NPEO}$ :  $\Sigma\text{NPEC}$  ratio (1.0:0.7:30) to a predominance of  $\Sigma\text{NPEC}$  in the effluent. Both  $\Sigma\text{NPEC}$  and  $\Sigma\text{NPEO}$  are intermediates that continue to degrade to form NP, which in turn sorbs to biosolids. Because

of the greater water solubility of the acidic  $\Sigma$ NPEC compounds relative to NP, they are the predominant NPE degradates in the aerobic effluents. Apparent production of NP in the wetland system may be due to conversion from  $\Sigma$ NPEC and  $\Sigma$ NPEO in the mixed redox environment.

## **5.2 Mines Park Test Site**

To confirm the results of the field sampling effort, controlled field-scale experiments examining the fate of trace organic contaminants during treatment in engineered unit operations at the Mines Park Test Site were conducted, and are presented and discussed here. First, quality assurance results for all Mines Park sampling (i.e. engineered treatment and vadose zone sampling) for bulk parameters and trace organic contaminants are presented, followed by results and discussion of temporal variability within the engineered units at the Test Site.

### **5.2.1 Quality Assurance and Temporal Variability**

Bulk parameters were not measured above the reporting level in any field and laboratory distilled water samples. The percent difference between laboratory duplicate samples (n varied between 1 and 26) averaged less than 25% for all parameters (pH, DOC, UV<sub>254</sub>, COD, TN, NO<sub>3</sub><sup>-</sup>, TP, BOD, TS, and TSS) except for ammonia (average difference = 31%).

Use of SPE and surrogate compounds for quantification improved method performance as compared to the CLLE method. For the seven compounds that were the focus of the Mines Park experimentation (caffeine, EDTA, NP, NP1EC, NP2EC, NTA, and triclosan), average distilled water matrix spike recoveries ranged from 72 to 107% (n=8 to 12). Average environmental sample matrix spike recoveries ranged from 93 to 114% (n=8 to 14), with the exception of NP1EC (138%, n=4). Average percent difference between field replicates and laboratory replicates ranged from 5 to 56% and 5 to 25%, respectively. Reporting levels were 0.02 µg/L for NTA, 0.1 µg/L for EDTA, 0.2 µg/L for caffeine and triclosan, 1 µg/L for NP1EC and NP1EO due to the isomeric side chain, and 2 µg/L for NP due to consistent blank contamination, which may be inherently present in the multi-use laboratory.

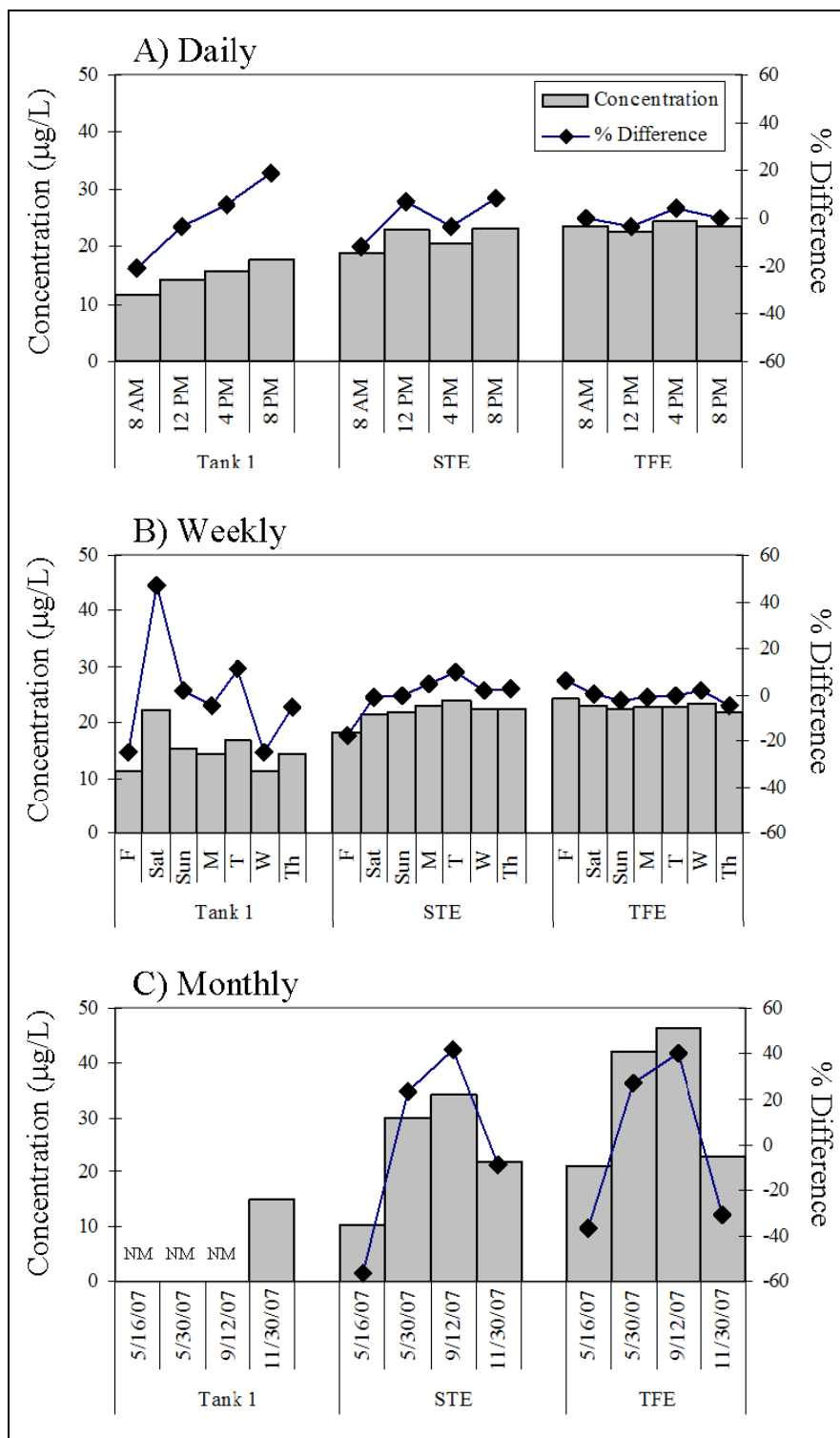
The variability of bulk parameters during engineered treatment at the Mines Park Test Site has been previously investigated (Lowe et al. 2008, Small Flows 2008b, Rothe 2006, Van Cuyk et al. 2005) and results suggest that a grab sample is representative of effluent quality regarding bulk wastewater parameters. Long-term average values for bulk parameters in locations 1, 3, 4 and 6 (Table 13) show some variability as expected due to changes in source and site characteristics over five years of operation.

However, average values of wastewater from locations 1, 3, and 4 are within typical concentration ranges for residential STE (Lowe et al. 2006, Crites and Tchobanoglous 1998).

**Table 13.** Long-term average and variability of bulk parameters in Mines Park engineered treatment unit effluents. [AVG, average value; RSD, relative standard deviation = standard deviation / average \* 100; N = number of samples. See Table 4 for parameter descriptions and units.]

Sample location: Figure 4 ID Reference:	Tank 1 1 Lowe et al. 2008			Tank 2 compartment 2 3 Lowe et al. 2008			STE 4 Small Flows 2008b			TFE 6 Small Flows 2008b		
	AVG	RSD	N	AVG	RSD	N	AVG	RSD	N	AVG	RSD	N
TS	440	24	5	420	26	4	430	76	126	360	28	80
TSS	74	35	5	51	31	4	43	80	87	6	96	40
pH	7.13	2	6	7.32	2	5	7.20	3	155	6.30	17	97
Alkalinity	230	22	6	220	26	5	260	21	151	75	105	81
Turbidity	240	33	5	260	43	5	140	41	69	15	92	67
TP	20	37	2	18	24	2	24	34	147	21	26	90
COD	370	39	5	350	18	5	260	41	151	45	59	94
BOD	230	36	4	1880	42	4	160	53	106	14	78	67
TN	58	18	5	52	33	5	60	44	147	36	37	95
NO <sub>3</sub> <sup>-</sup>	0.2	141	2	0.2	141	2	1.8	74	149	16	47	93
NH <sub>3</sub>	53	28	5	50	25	5	55	31	143	16	100	91
DOC	NM	NM	NM	NM	NM	NM	38	43	34	11	46	13

In general, the temporal variability of trace organic contaminants in engineered treatment unit effluents is greatest in the first treatment unit (e.g. location 1) and decreases in downstream effluents (Figure 10). For example, the RSD (%) between four samples collected throughout one day for target trace organic contaminants ranged from 9 to 38% in wastewater from the first septic tank (location 1), 5 to 20% in STE (location 4), and < 1 to 10% in TFE (location 6). Samples collected over one week showed a similar trend of decreasing variability with increasing distance from the source. For example, the RSD of EDTA concentrations in seven consecutive daily samples ranged from 13 to 25% in locations 1, 2 and 3, and ranged from 3 and 8% in all locations further downstream (locations 4, 5, 6, 9, 19, and 21). Concentrations in daily grab samples differed from concentrations in the weekly composite sample by an average of 17%, indicating that a grab sample is fairly representative of effluent quality regarding trace organic contaminants. Overall, the daily and weekly RSD values were less than 30% (except in location 1: RSD < 40%), suggesting relatively consistent effluent quality regarding trace organic contaminants within these time periods.



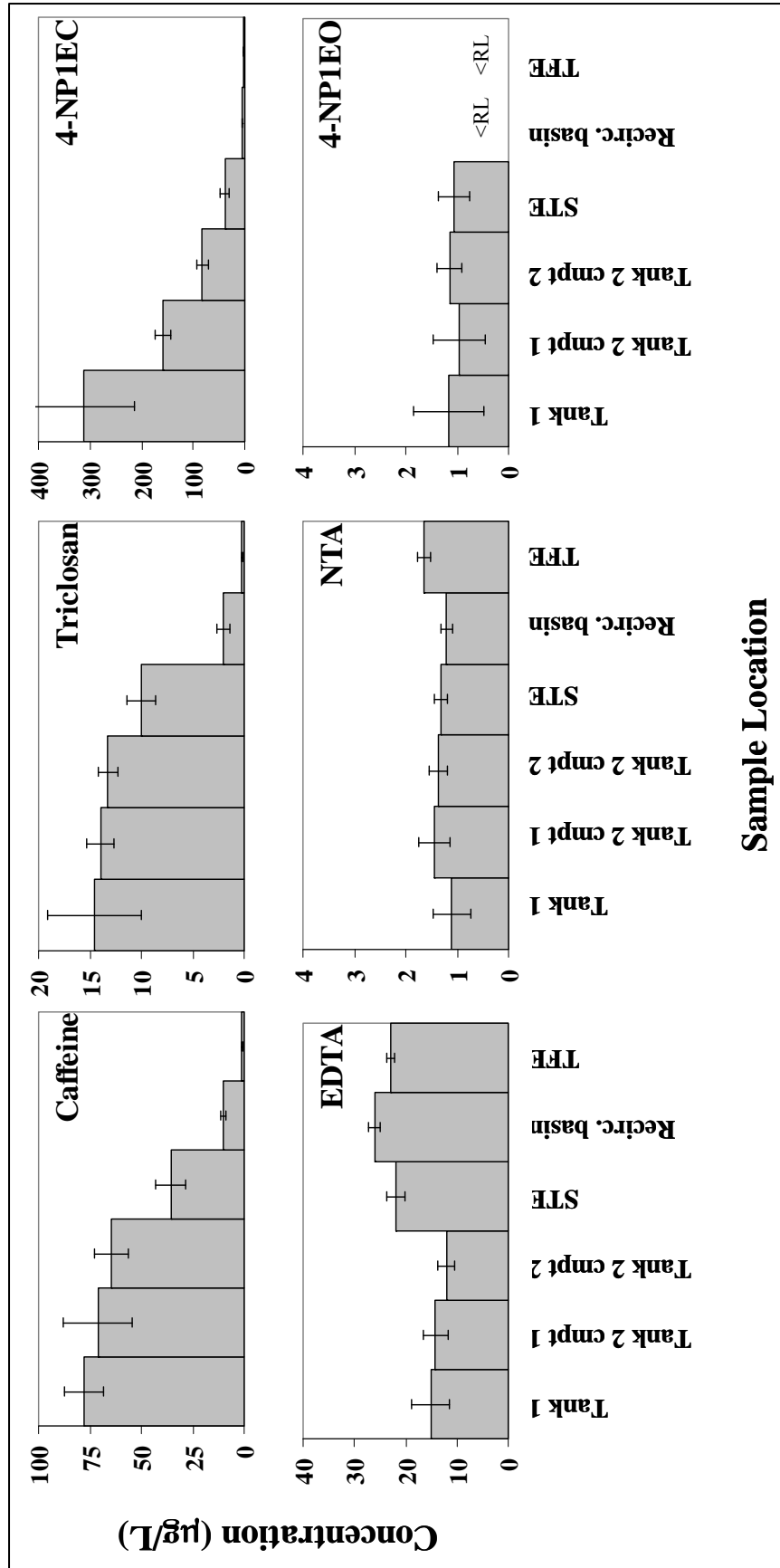
**Figure 10.** Daily (A), weekly (B), and monthly (C) variability of EDTA wastewater concentrations in three tanks at the Mines Park Test Site. [% Difference = percent difference from average during each experiment. NM = not measured.]

Greater variability was observed between samples collected over seven months for all compounds at all sample locations (RSD = 8 to >100%, Figure 10). This is likely due to a combination of varying source activities over time, changes in treatment efficiencies due to climatic differences, and analytical variability. Different water- and chemical-using activities are expected at the Mines Park apartment complex during school months as compared to summer and winter vacation months. Lower temperatures in the winter may affect treatment efficiencies (i.e. volatilization and biotransformation) of trace organic contaminants and of bulk parameters that may impact the treatment efficiency of trace organic contaminants. Also, there is increased variability between samples analyzed at different times in the lab due to factors such as varying lots of extraction cartridges, different standard curves, and varying GC/MS conditions.

### **5.2.2 Fate during Engineered Treatment**

The fate of bulk parameters during treatment within engineered unit operations at the Mines Park Test Site has been previously investigated (Lowe et al. 2008, Small Flows 2008b, Rothe 2006, Van Cuyk et al. 2005) and results are summarized here. Treatment of bulk parameters (Small Flows 2008b) was negligible (<5%) during tank-based treatment (i.e. between locations 1 and 4) for alkalinity, TS, TP, TN,  $\text{NO}_3^-$ , and  $\text{NH}_3$ , while some removal of TSS, turbidity, cBOD, and COD occurred (removal = 28 to 42%). Treatment within the textile biofilter unit produced a higher quality effluent than STE regarding cBOD, COD, DOC, and TN, while phosphorus was unchanged (Van Cuyk et al. 2005). These results are similar to findings from the reconnaissance survey.

The fate of trace organic contaminants during treatment within engineered unit operations varied by physicochemical properties such as hydrophobicity, volatility, and aerobic biodegradability of the target compounds. The fate of caffeine and triclosan during engineered treatment at the Mines Park Test Site (Figure 11) was similar to observations during the reconnaissance survey. Seventeen percent removal of caffeine was observed during tank-based treatment at the Test Site (e.g. between locations 1 and 3, see Figure 4), which is similar to removal during the reconnaissance survey (average removal =  $18 \pm 23\%$ ). Caffeine concentrations were reduced to near the reporting level (97% removal) during biofilter treatment at the site (e.g. between locations 4 and 6), which compares to removal during the reconnaissance survey ( $84 \pm 19\%$ ). Enhanced removal during biofilter treatment is attributed to aerobic biotransformation.



**Figure 11.** Concentrations of trace organic contaminants during engineered treatment at the Mines Park Test Site. [4-NP1EC = 4-nonylphenolmonoethoxycarboxylate; EDTA = ethylenediaminetetraacetic acid; NTA = nitrotriacetic acid; 4-NP1EO = 4-nonylphenolmonoethoxycarboxylate; Error bars =  $\pm 1$  standard deviation of seven samples collected on consecutive days; <RL = less than the reporting level. cmpt = compartment; STE = septic tank effluent; Recirc. = Recirculation; TFE = textile filter effluent.]

Nine percent of triclosan was removed during tank-based treatment at the site (vs.  $38 \pm 22\%$  during the reconnaissance survey) likely due to sorption to settling solids, while 98% removal was observed during biofilter treatment (vs.  $92 \pm 18\%$  during the reconnaissance survey). Enhanced removal during biofilter treatment is attributed to additional sorption to filtered particulate matter and aerobic biotransformation.

Concentrations of the metal-chelating agent, NTA, were low – around  $1 \mu\text{g/L}$  during the week-long experiment– in all tank effluents at the site (Figure 11). NTA is a common ingredient in laundry detergents. Wastewater originating from clothes washing activities is a minor contribution to the Mines Park wastewater flow because there are no laundry facilities within the apartment complex. As compared to the reconnaissance survey in which higher concentrations of NTA ( $\sim 60 \mu\text{g/L}$ ) were reduced by  $76 \pm 29\%$ , no apparent removal of NTA was observed during biofilter treatment at the Test Site. The low concentrations in the Mines Park wastewater may be insufficient to support a microbial community capable of preferentially degrading NTA.

The other metal-chelating agent EDTA persisted during treatment in engineered unit operations at the Test Site at concentrations similar to influent concentrations (Figure 11), which agrees with observations from the reconnaissance survey ( $<15\%$  removal during tank and biofilter treatment). Previous research has reported similar findings regarding EDTA persistence during municipal wastewater treatment (Alder et al. 1990). EDTA is not expected to be removed during engineered treatment by volatilization ( $K_H = 7.69 \times 10^{-13} \text{ atm-L/mol}$ ) or sorption ( $\log K_{ow} = -3.86$ ).

Quantification of NPE metabolites at the Mines Park Test Site focused on NP, NP1EO, and NP1EC which are the predominant metabolites in wastewater (Ahel et al. 1994). The distribution of NPE metabolites during engineered treatment of the Mines Park wastewater during the 7-day experiment differed from the typical distribution observed during the reconnaissance survey. In the reconnaissance survey, anaerobic domestic wastewater was typically comprised of relatively low levels (e.g. average  $< 20 \mu\text{g/L}$ ) of each of the three metabolite groups (NP,  $\Sigma\text{NPEO}$ , and  $\Sigma\text{NPEC}$ ). During aerobic biofilter treatment, concentrations of  $\Sigma\text{NPEO}$  were reduced to near or below the reporting level, concentrations of  $\Sigma\text{NPEC}$  increased by 2-fold or greater, and changes in NP concentrations varied by site and sampling date. These results are consistent with published literature (Ahel et al. 1994) reporting the accumulation of the acidic metabolite  $\Sigma\text{NPEC}$  under aerobic conditions.

In Mines Park anaerobic septic tank wastewater (location 1), NP and NP1EO concentrations ( $<5 \mu\text{g/L}$ ) were similar to or lower than typical concentrations found during the reconnaissance survey while NP1EC concentrations in the first tank exceeded  $300 \mu\text{g/L}$ , which is more than six times higher than the maximum value reported in any anaerobic wastewater, residential or non-residential, during the reconnaissance survey. NP1EC concentrations remained elevated in the second tank (location 3) at an

average concentration of 160 µg/L, which is more than 50 times higher than NP1EC concentrations measured in the same location during the 2003-2004 reconnaissance survey (concentrations were less than 3 µg/L). NPEs typically originate in domestic wastewater from household cleaning and personal care products such as laundry detergent, which comprise approximately 15% of NPE production (Huntsman et al. 2006). Since there are no laundry facilities in the apartment complex, NPE metabolite concentrations are expected to be lower than typical values, as was observed for NP and NP1EO. The remaining 85% of NPE production is used in high-strength industrial and institutional cleaning products and applications. A few possible explanations for the very high NP1EC concentrations are given:

1) A carpet cleaning service was observed servicing one or more of the units in the Mines Park apartment building during the week-long sampling experiment. The cleaning product may have contained NP1EC or parent NPEs which were degraded and transformed during the aerobic cleaning process. The wastewater was then discharged to the OWTS, resulting in the high observed concentrations of NP1EC in the septic tank wastewater. However, NP1EC concentrations were consistently elevated during all seven days of the experiment, which does not correspond to a single mid-week cleaning event. Also, elevated concentrations of other NPE metabolites are expected, but concentrations of NP and NP1EO were low throughout the experiment.

2) A change in source habits occurred within the 6 months prior to the sampling event, as evidenced by very elevated concentrations of fats, oil, and grease in the septic tank wastewater (Lowe et al. 2008) and the necessity to scour the pipe from the apartment complex to the first septic tank on three occasions between November 2007 and July 2008 (as compared to no scouring events between 1998 and 2007). A specialized product containing NP1EC as the primary ingredient (rather than NPEs) may be in concomitant use with high grease production at the apartment complex. Listing of individual surfactant compounds is not required on ingredient labels of consumer product chemicals and manufacturing and usage information regarding NP1EC is difficult to acquire. However, use of NP1EC as the primary ingredient in an oil soluble corrosion inhibitor for use with circulating oils, compressor oils, fuels, gear oils, greases, hydraulic fluids, industrial lubricants, and metal working fluids has been reported (Ciba-Geigy 2008), suggesting that there may be other previously unreported sources of NP1EC.

The elevated NP1EC concentrations provide another line of evidence for the sensitivity of OWTS to the specific chemical- and water-using activities at the source. Research is underway to investigate potential correlations between water-using activities (i.e. toilet flushes, hand washes) and product occurrence (i.e. laundry detergent, antibacterial soap) and raw wastewater and septic tank wastewater concentrations of trace organic contaminants (Lowe et al. 2008).

During engineered treatment, aqueous concentrations of NP were consistently low - within three times the reporting level (< 6 µg/L) - indicating negligible removal and/or accumulation in the aqueous



phase during anaerobic or aerobic engineered treatment. NP1EO concentrations were low – around 1 µg/L – in the four septic tank effluents, and decreased to concentrations below the reporting level during biofilter treatment. This is consistent with studies reporting efficient elimination of NPEOs during aerobic treatment (Ahel et al. 1994).

NP1EC concentrations decreased in a step-wise fashion during treatment within engineered unit operations (Figure 11). Approximate removal during tank-based treatment was 74%, and removal from STE during biofilter treatment was 92%, resulting in an overall NP1EC removal of 99% during treatment within engineered unit operations at the Mines Park Test Site (from over 300 µg/L in location 1 to less than 3 µg/L in location 6: TFE). NP1EC removal during treatment within the Mines Park engineered unit operations is attributed to anaerobic and aerobic transformation to NP (Ahel et al. 1994, Maguire 1999) with subsequent sorption to septic tank solids. NP concentrations on Mines Park septic tank solids measured in 2004 were estimated near 55,000 µg/kg. On a molar basis, concentrations of NP sorbed to solids (250 µmol/kg) greatly exceeded even the highest NP1EC wastewater concentrations (6 µmol/L), suggesting that the overall removal of NPE surfactants is limited by the mineralization of NP sorbed to septic tank solids.

### **5.3 Loading to the Soil Treatment Unit**

Some trace organic contaminants in the wastewaters (1,4-dichlorobenzene, caffeine, triclosan) are removed during treatment within onsite engineered unit operations, but others (EDTA,  $\Sigma$ NPEC) may be released to soil treatment units at concentrations similar to the influent or as degradation products resistant to further removal. During the reconnaissance survey, loading to the soil treatment units (mg/m<sup>2</sup>/d) in operational systems was calculated from effluent concentrations and individual system HLRs (Table 3). The maximum combined NP,  $\Sigma$ NPEO, and  $\Sigma$ NPEC loading was 10 mg/m<sup>2</sup>/d (restaurant, single-family home), and the maximum EDTA loading was 20 mg/m<sup>2</sup>/d (restaurant). A convenience store had the highest loading of 1,4-dichlorobenzene (1.6 mg/m<sup>2</sup>/d) and triclosan (2.0 mg/m<sup>2</sup>/d), which were 10 times higher than the other systems. Soil treatment unit loading in biofilter-based systems was orders of magnitude lower than tank-based systems with similar sources.

While knowledge of the wastewater source may identify effluents with potentially high trace organic contaminant concentrations, chemical loading also depends on HLRs. High concentration effluents dispersed at low HLRs can have less chemical loading to the soil treatment unit than low concentration effluents dispersed at high HLRs. For example, effluents from veterinary hospitals had higher concentrations of NPE-derived compounds than effluents from single-family homes. However, a

single-family home had a higher  $\Sigma$ NPEC loading (0.7 mg/m<sup>2</sup>/d) than a veterinary hospital (0.4 mg/m<sup>2</sup>/d) due to the greater HLR in the residential (2.8 cm/d) than the veterinary (0.81 cm/d) sources.

The range of target compound concentrations measured in STE, TFE, and tap water from the delivery basins at the Mines Park Test Site is given in Table 14. This provides insight into typical concentrations of trace organic contaminants that have been applied to the soil infiltration test cells during the three years of operation. Using the average effluent concentration (or the RL if the average was <RL) and design HLRs, chemical loading rates (mg/m<sup>2</sup>/d) to test cells receiving STE (Table 15) and TFE (Table 16) were calculated. At a typical HLR (2 cm/d), each soil test cell (surface area ~ 2900 cm<sup>2</sup>) receiving STE from this multi-family residence is being loaded each year with approximately 61 mg of caffeine, 17 mg of triclosan, 48 mg of EDTA, 8.8 mg of NTA, and 144 mg of NPE surfactant metabolites (NP + NP1EO + NP1EC) as well as other non-quantified trace organic contaminants. Soil receiving TFE from this multi-family residence at a typical HLR is being loaded each year with much lower concentrations of caffeine (1.3 mg), triclosan, ( $\leq$ 0.43 mg), and NPE metabolites ( $\leq$ 24 mg), while mass loadings of EDTA (76 mg) and NTA (9.6 mg) are similar. Annual mass loadings of caffeine, triclosan, and NPE metabolites in TFE loaded at a 4-fold higher HLR are still less than or similar to STE mass loadings at a typical HLR.

Total mass loading during the three years of operation to each test cell (Tables 15 and 16) was calculated based on average tank effluent concentrations (Table 14 or the RL if the average was <RL) and the estimated total infiltrated volume of effluent at each test cell (Table 7).

**Table 14.** Range of trace organic contaminant concentrations ( $\mu$ g/L) in effluent applied to the soil infiltration test cells at the Mines Park Test Site. [10 to 13 samples of septic tank effluent (STE) and textile filter effluent (TFE) and 2 to 4 samples of tap water were collected from the delivery basins between May and December 2007; <RL = less than the reporting level; Min = minimum; Max = maximum; Avg = average, 1/2 RL used for values <RL to calculate average.]

Analyte	RL ( $\mu$ g/L)	STE ( $\mu$ g/L)			TFE ( $\mu$ g/L)			Tap Water ( $\mu$ g/L)		
		Min	Max	Avg	Min	Max	Avg	Min	Max	Avg
Caffeine	0.2	20	44	28	<RL	1.2	0.60	<RL	<RL	<RL
Triclosan	0.2	5.0	14	8.0	<RL	0.31	<RL	<RL	<RL	<RL
EDTA	0.1	8.2	37	22	23	48	35	0.91	6.3	3.0
NTA	0.02	1.5	6.4	4.1	1.8	6.6	4.5	0.04	0.13	0.09
NP1EC	1	23	84	58	3.0	12	8.3	1.7	4.8	2.9
NP1EO	1	<RL	5.6	2.0	<RL	<RL	<RL	<RL	<RL	<RL
NP	2	2.4	11	4.3	<RL	2.9	<RL	<RL	<RL	<RL

In contrast to WWTP, which receive raw wastewater whose composition is relatively constant (due to dilution from many sources) and produce effluents whose composition is relatively constant, OWTS effluent composition is subject to variation due to a number of factors. Differences in consumer product use, proportion of water use activities contributing to the wastewater flow, number of occupants, and volume of wastewater, all can fluctuate over time and between households and businesses. Effluents applied to the soil treatment unit may contain trace organic contaminants at concentrations similar to, less than, or greater than influent concentrations. Treatment of trace organic contaminants during travel through the vadose zone is critical in minimizing adverse effects in receiving environments.

**Table 15.** Mass loading (mg) of target trace organic contaminants in residential septic tank effluent (STE) to Mines Park soil test cells at design and actual infiltration rates. [HIR = hydraulic infiltration rate; See Tables 6 and 7 for test cell information.]

Analyte	Daily mass loading rate to test cell (mg/m <sup>2</sup> /d) at design HIR		Yearly mass loaded to test cell (mg) at design HIR		Estimated total mass loaded to test cell (mg) after 3 years of operation at actual HIR			
	2 cm/d	8 cm/d	2 cm/d	8 cm/d	TBC6	TCC2	TBC3	TAC4
Caffeine	0.57	2.3	61	240	94	130	130	290
Triclosan	0.16	0.64	17	68	27	35	35	82
EDTA	0.45	1.8	48	190	74	99	98	230
NTA	0.08	0.33	8.8	35	14	18	18	42
NP1EC	1.2	4.6	130	490	190	260	260	600
NP1EO	0.04	0.16	4.4	17	6.8	9.1	9.0	21
NP	0.09	0.34	9.3	37	14	19	19	44

**Table 16.** Mass loading (mg) of target trace organic contaminants in residential textile filter effluent (TFE) to Mines Park soil test cells at design and actual infiltrated volumes. [HIR = hydraulic infiltration rate; See Tables 6 and 7 for test cell information. \* The RL was used as the average effluent concentration, therefore actual values are less than or equal to these reported values.]

Analyte	Daily mass loading rate to test cell (mg/m <sup>2</sup> /d) at design HIR		Yearly mass loaded to test cell (mg) at design HIR		Estimated total mass loaded to test cell (mg) after 3 years of operation at actual HIR			
	2 cm/d	8 cm/d	2 cm/d	8 cm/d	TAC2	TBC4	TBC1	TCC6
Caffeine	0.01	0.05	1.3	5.1	4.0	4.8	3.2	10
Triclosan *	0.004	0.02	0.43	1.7	1.3	1.6	1.1	3.5
EDTA	0.71	2.8	76	300	240	280	190	610
NTA	0.09	0.36	9.6	38	30	35	24	77
NP1EC	0.17	0.67	18	71	55	66	45	150
NP1EO *	0.02	0.08	2.1	8.5	6.6	8.0	5.4	17
NP *	0.04	0.16	4.3	17	13	16	11	35

## **CHAPTER 6**

### **FATE DURING SOIL TREATMENT**

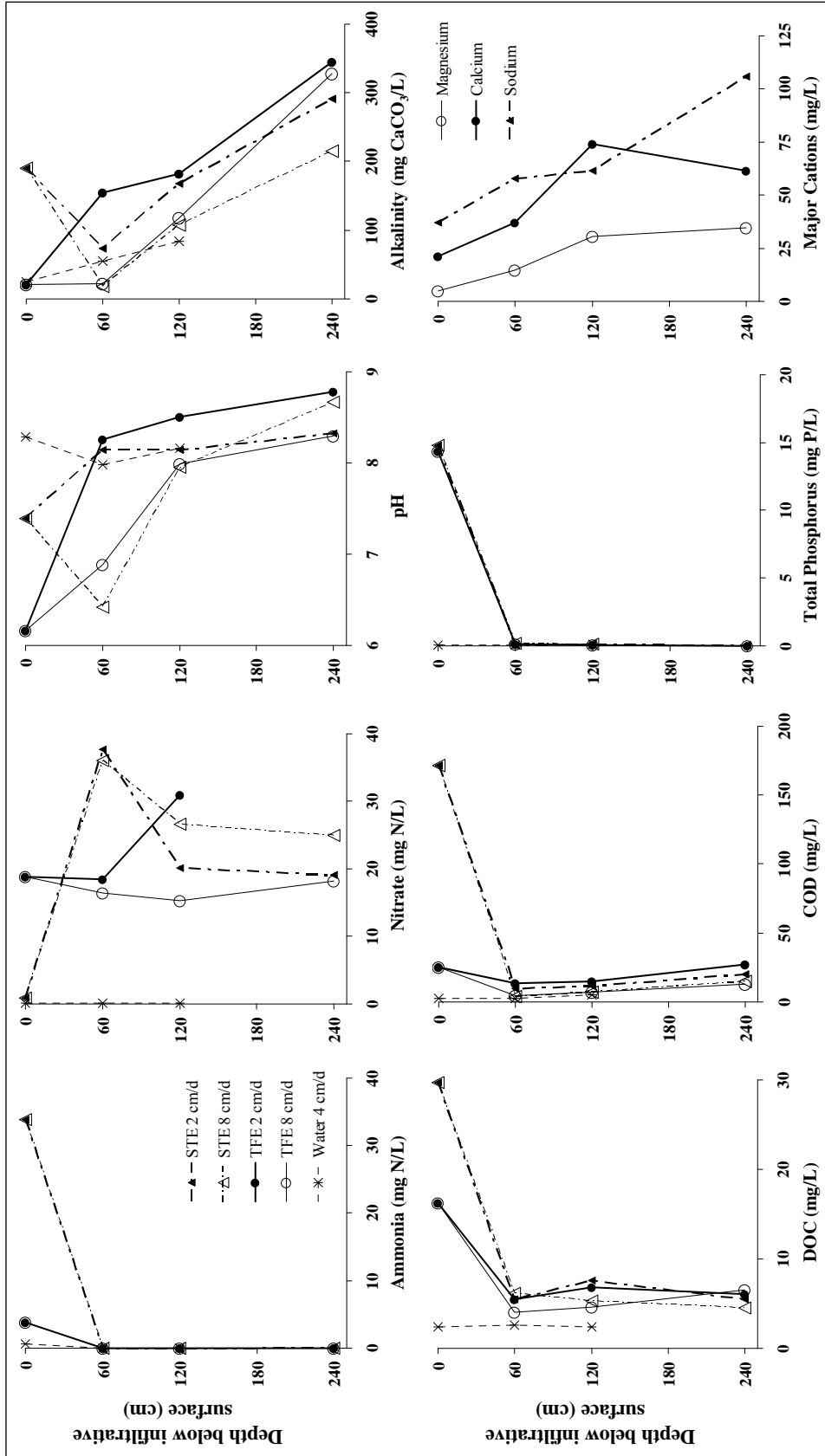
Results from experiments conducted at the Mines Park Test Site to assess the fate of bulk parameters and target trace organic contaminants during soil treatment as affected by effluent type and hydraulic loading rate are presented and discussed.

#### **6.1 Occurrence and Fate in Soil Solution**

##### **6.1.1 Bulk Parameters**

The absence of ammonia and presence of nitrate (Figure 12) in the soil solution suggests that nitrification is occurring in the vadose zone. Ammonia concentrations were below the reporting level at all depths for both effluent types at both HLRs. Nitrate concentrations increased from near zero in STE to almost 40 mg-N/L at 60 cm below the infiltrative surface, and remained elevated (~20 mg-N/L) through 240 cm of soil. Nitrate concentrations in soil solution in TFE cells at all depths were similar to input concentrations (15-20 mg-N/L). At shallow depths (e.g. 60 cm below the infiltrative surface), TFE soil solution nitrate concentrations were about half the concentration of their STE counterparts. At deeper depths (e.g. 240 cm), concentrations of nitrate were similar (~20 mg-N/L) regardless of the hydraulic loading rate or effluent type.

Further evidence of nitrification is provided by changes in pH and alkalinity in soil solution. The nitrification process produces acid and consumes alkalinity. In the high HLR test cells (for both effluent types), alkalinity has been depleted and the pH has decreased to less than 7.0 at 60 cm below the infiltrative surface (vs. background soil solution pH > 8.0). In the low HLR test cells, the pH is near background levels, suggesting that the alkalinity present is sufficient to buffer the soil system from acid-producing nitrification reactions. With depth, the alkalinity increases and the pH becomes slightly alkaline (similar to background soil solution), with corresponding increases in concentrations of major cations (Figure 12) such as sodium, calcium, and magnesium (40 to 100 mg Na/L, 20 to 80 mg Ca/L, 5 to 35 mg Mg/L) while levels of trace metals remain low (i.e. <0.05 mg/L each of Fe, Al, Zn and <0.5 mg Ni/L). DOC, COD, and total phosphorus are removed from soil solution during the first 60 cm of soil treatment regardless of effluent type and hydraulic loading rate (Figure 12). Concentrations of DOC are ~5 mg/L in soil solution, COD remains near background levels (<20 mg/L) at all depths, and concentrations of total phosphorus are less than 0.3 mg phosphate as P/L in soil solution.



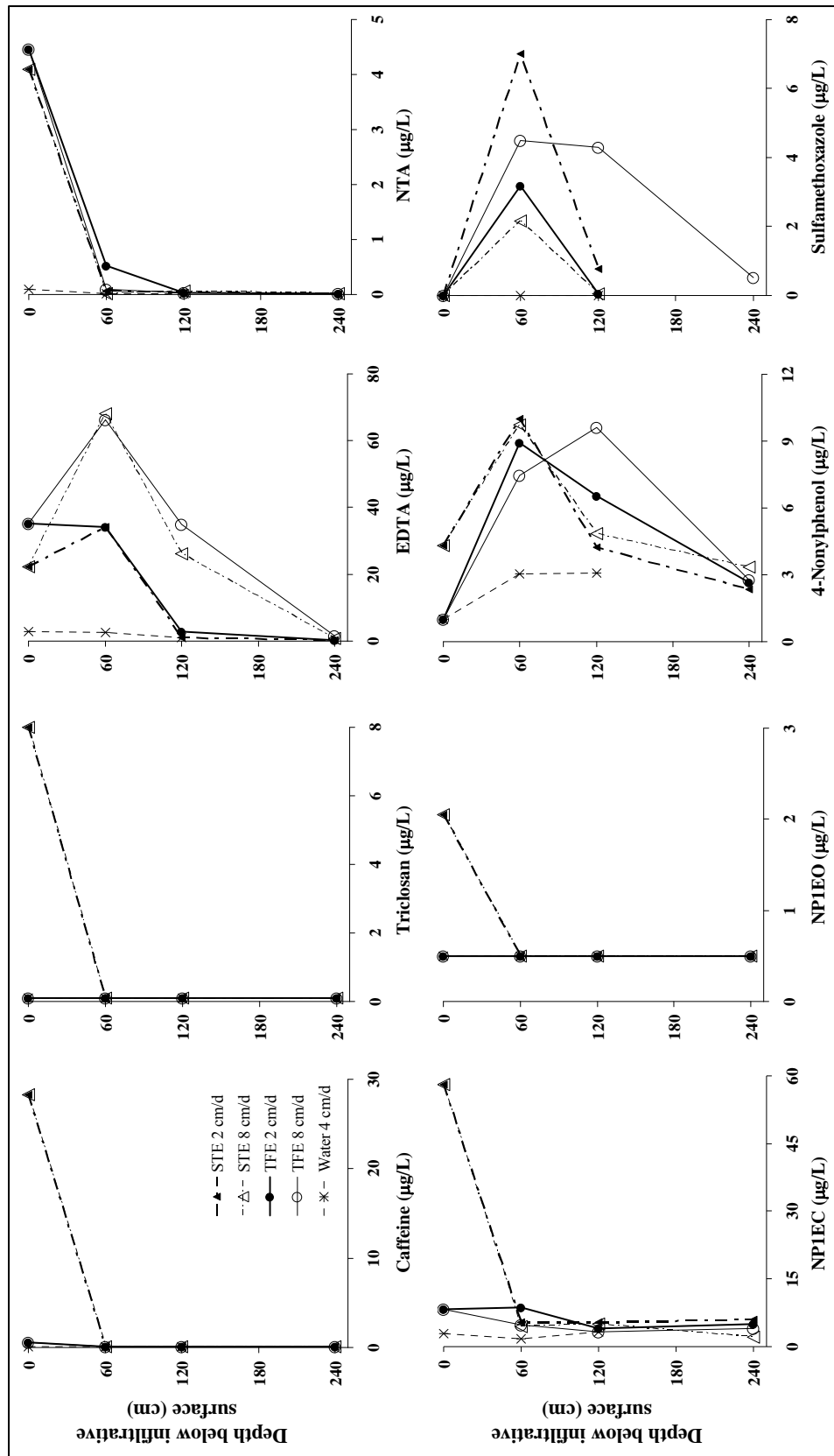
**Figure 12.** Depth profile of bulk parameters in Mines Park soil test cells. [0 cm = average tank effluent concentration. For visualization purposes, values that are less than the method detection level, DL (see Table 4), are shown as 1/2DL and lines connect the data points with depth. 2 cm/d data points represent the average from three test cells each sampled two to three times. 8 cm/d data points represent the average from one test cell sampled two to three times. Major cations: each data point represents the average of both effluent types (STE and TFE) and both hydraulic loading rates (2 and 8 cm/d).]

## 6.1.2 Trace Organic Contaminants

After three years of effluent application to the soil test cells, the occurrence and fate of target compounds in soil solution differed between compounds (Figure 13). In general, soil treatment through 240 cm of sandy loam soil provided greater than 90% removal of many of the target trace organic contaminants from applied effluent; often this treatment was achieved within the first 60 cm of soil. In the following sections, comparisons are made between test cells designed to receive effluent at a HLR of either 2 cm/d or 8 cm/d. At the start of the characterization studies (e.g. after three years of operation), the actual cumulative hydraulic infiltration rate (HIR) ranged from 1.04 to 1.39 cm/d and 1.70 to 2.50 cm/d for STE and TFE cells, respectively, designed to receive 2 cm/d. The HIR of the design 8 cm/d test cells were 3.24 cm/d (STE) and 5.46 cm/d (TFE). Therefore, the high loading rate test cells had processed 2.2 and 3.2 times more effluent than the test cells receiving a “typical” loading rate of effluent. See Section 3.2.1.3 for additional information regarding hydraulic performance as affected by operation and effluent application.

### 6.1.2.1 Caffeine

Caffeine was removed to below the reporting level (0.2 µg/L) in soil solution within the first 60 cm of soil regardless of effluent type and hydraulic loading rate (Figure 13). Other studies have reported removal of caffeine during soil treatment of wastewater effluent to below the reporting level or to low ng/L concentrations (Godfrey et al. 2007, Swartz et al. 2006, Hinkle et al. 2005, Drewes et al. 2003a, Seiler et al. 1999, Cordy et al. 2004). This removal is likely due to biotransformation (Topp et al. 2006) rather than volatilization ( $K_H = 3.58 \times 10^{-8}$  atm/L-mol, see Table 17) or sorption to soil ( $C_w^{sat} = 21,600$  mg/L,  $\log K_{ow} = -0.07$ ), though caffeine has been measured on soil irrigated with reclaimed water (Kinney et al. 2006). Greater than 99% removal of caffeine has been reported during biological treatment in WWTP (Thomas and Foster 2005, Buerge et al. 2003). Topp et al. (2006) found no residual caffeine in an agricultural sandy loam soil microcosm after 2 days, and recovered 60% of added caffeine as CO<sub>2</sub> within 32 d. Greater mineralization occurred with soils amended with 5% biosolids. The results from this study agree with published literature indicating that caffeine is rapidly removed from wastewater effluent during soil treatment likely through aerobic biotransformation.



**Figure 13.** Depth profile of trace organic contaminants in Mines Park soil test cells. [0 cm = average tank effluent concentration. For visualization purposes, values that are less than the reporting level, RL (see Section 5.2.1), are shown as 1/2RL and lines connect the data points with depth. 2 cm/d data points represent the average from three test cells each sampled two to three times. 8 cm/d data points represent the average from one test cell sampled two to three times. Sulfamethoxazole data for 2 cm/d are from one of three test cells for each effluent type (the compound was not detected in the other test cells).]

**Table 17.** Summary of relevant physicochemical properties of target compounds. [CASRN = Chemical Abstracts Service Registry Number; MW = molecular weight; pK<sub>a</sub> = acid dissociation constant; C<sub>w</sub><sup>sat</sup> = water solubility, K<sub>ow</sub> = octanol-water partition coefficient; K<sub>H</sub> = Henry's law constant. Values determined at 25 °C unless otherwise noted. Source: SRC 2008, except <sup>a</sup> Muller and Schlatter 1998, <sup>b</sup> Ahel and Giger 1993a, <sup>c</sup> Ahel and Giger 1993b. nr = not reported (estimated value).]

Analyte	CASRN	MW (g/mol)	pK <sub>a</sub>	C <sub>w</sub> <sup>sat</sup> (mg/L)	log K <sub>ow</sub>	K <sub>H</sub> (atm·L/mol)
Caffeine	58-08-2	194.19	10.4	21,600	-0.07	3.58E-08
Triclosan	3380-34-5	289.55	7.9	10 (20°C)	4.76	4.99E-06
EDTA	60-00-4	292.25	0.26	1000	-3.86	5.77E-13
NTA	139-13-9	191.14	3.03	59,100	-3.81	1.30E-07
NP	104-40-5	220.36	10.3 <sup>a</sup>	6.35 <sup>b</sup> , 7	4.48 <sup>c</sup> , 5.76	3.40E-02
NP1EO	104-35-8	264.41	nr (<10.3)	3.37 <sup>b</sup>	4.17 <sup>c</sup>	nr (<3.4E-02)
NP1EC	3115-49-9	278.39	nr (~3.3-4)	2.2	5.8	1.79E-04

Mean travel times within the first 60 cm of soil in the Mines Park test cells ranged from an average of 22 d (8 cm/d HLR) to an average of 32 d (2 cm/d HLR), as determined by a temporal method of moments analysis of bromide transport during a tracer test (Conn 2008). The monitoring data does not permit the determination of a removal rate constant. First-order kinetics is often assumed for the attenuation of organic compounds. However, the validity of this assumption has been questioned for trace organic contaminants in the environment at low µg/L or ng/L levels in the presence of mg/L levels of organic matter measured as BOD or DOC. If one assumes zero-order rate kinetics, in which the attenuation rate is not affected by the concentration of the trace organic contaminant, the apparent zero-order attenuation rate constant, k<sub>app</sub> (µg/L-d), for caffeine during the first 60 cm of soil was calculated based on the equation:

$$k_{app} = \frac{C_0 - C}{t} \quad (6-1)$$

to range between 1.06 and 1.55 µg/L-d in soils receiving STE and between 0.028 and 0.050 µg/L-d in soil receiving TFE, based on average initial STE and TFE concentrations (C<sub>0</sub>) of 28 µg/L and 0.60 µg/L, respectively, and two final concentrations (C) of 0.2 µg/L (the RL) and 0.002 µg/L (1/100 of the RL) chosen to bound the range of expected caffeine soil solution concentrations. These apparent attenuation rate constants are likely conservative since the majority of caffeine may actually be removed, likely via aerobic biotransformation, within a much shorter time while the effluent is in contact with the organic-rich biofilm at and just below the infiltrative surface. Caffeine may have degraded to 1,7-dimethylxanthine, which was not measured here but is a primary degradation product of caffeine (Swartz



et al. 2006), before potential ultimate mineralization during the long residence time in the vadose zone (Topp et al. 2006).

### 6.1.2.2 Triclosan

Similar to caffeine, triclosan was removed from soil solution to concentrations below the reporting level (0.2 µg/L) within 60 cm of soil in the Mines Park soil test cells regardless of effluent type or hydraulic loading rate (Figure 13). In previous studies, triclosan was not detected above the reporting level in soil solution 30 cm below the infiltrative surface (Hinkle et al. 2005) and was sporadically detected at low levels (ng/L) in ground water downgradient of an OWTS (Carrara et al. 2008).

Volatilization of triclosan is assumed to be negligible given its low Henry's law constant ( $K_H = 4.99 \times 10^{-6}$  atm/L-mol). Sorption to soil organic matter and biotransformation are the likely removal mechanisms during onsite wastewater soil treatment. Numerous studies have reported overall removal of triclosan in WWTP ranging from 58 to >99%, with anywhere from 7 to 50% of that removal attributed to sorption and the rest attributed to biotransformation (Heidler and Halden 2007, Thomas and Foster 2005, Bester 2003, McAvoy et al. 2002, Singer et al. 2002). Orvos et al. (2002) reported equilibrium sorption of triclosan to deactivated WWTP sludge ( $f_{oc} = 0.45$ ) within 8 hours during batch sorption experiments. The data were well fitted to a Freundlich isotherm ( $\log K_F = 4.33$ ,  $n_F = 0.997$ ) with a log of the organic carbon sorption coefficient ( $\log K_{oc}$ ) of 4.68. The biodegradation half life of triclosan on a loam soil ( $f_{oc} = 0.013$ ) was 18 days under aerobic conditions and negligible through the 70 day experiments under anaerobic conditions (Ying et al. 2007), indicating that triclosan sorbed to soil is available for aerobic biotransformation.

At the Mines Park Test Site, the fraction of triclosan present in the neutral (protonated) form,  $f_{HA}$ , in STE is 0.76 and in TFE is 0.98, based on the relationship between pH and  $pK_a$  (Schwarzenbach et al. 2003):

$$f_{HA} = \left(1 + 10^{(pH - pK_a)}\right)^{-1} \quad (6-2)$$

where the average pH in STE is 7.39 and in TFE is 6.17 and the  $pK_a$  of triclosan is 7.9 (Table 17). This is the fraction available to undergo hydrophobic sorption to soil organic matter. Based on the relationship between the equilibrium concentration of an analyte on soil,  $C_s$ , and in the aqueous phase,  $C_w$  (Schwarzenbach et al. 2003):

$$\frac{C_S}{C_W} = K_{OC} f_{OC} f_{HA} \quad (6-3)$$

greater than 99% of triclosan in effluent applied to the soil infiltrative surface at Mines Park is expected to be present sorbed to the soil, assuming equilibrium conditions,  $K_{oc} = 47,863$  (Orvos et al. 2002), and  $f_{oc}$  of the infiltrative surface soil = 0.0275 (McKinley 2008). Effective removal of triclosan within 60 cm of soil is likely achieved by a combination of sorption to soil and aerobic biodegradation of this sorbed triclosan.

### 6.1.2.3 NTA and EDTA

The two metal-chelating agents, NTA and EDTA, showed different behavior during soil treatment at the Mines Park Test Site (Figure 13). NTA, applied at average concentrations between 4 and 5 µg/L, was reduced to less than 0.1 µg/L within the first 60 cm of soil in all test cells (with the exception of one test cell receiving 2 cm/d of TFE in which average NTA concentrations 60 cm BIS were 1.1 µg/L). EDTA was applied to the soil test cells at average concentrations of 22 µg/L (STE) and 35 µg/L (TFE). Average concentrations of EDTA in soil solution from test cells receiving 2 cm/d of either effluent were 34 µg/L (60 cm BIS), 1.0 to 2.8 µg/L (120 cm BIS), and 0.20 to 0.34 µg/L (240 cm BIS). Average concentrations of EDTA in soil solution from test cells receiving 8 cm/d of either effluent were 66 to 68 µg/L (60 cm BIS), 26 to 35 µg/L (120 cm BIS), and 0.72 to 1.4 µg/L (240 cm BIS). EDTA was measured in tap water in the Test Site delivery basin at an average concentration of 3.0 µg/L and in the soil (2.6 µg/L 60 cm BIS and 0.93 µg/L 120 cm BIS) in the test cell receiving tap water at 4 cm/d.

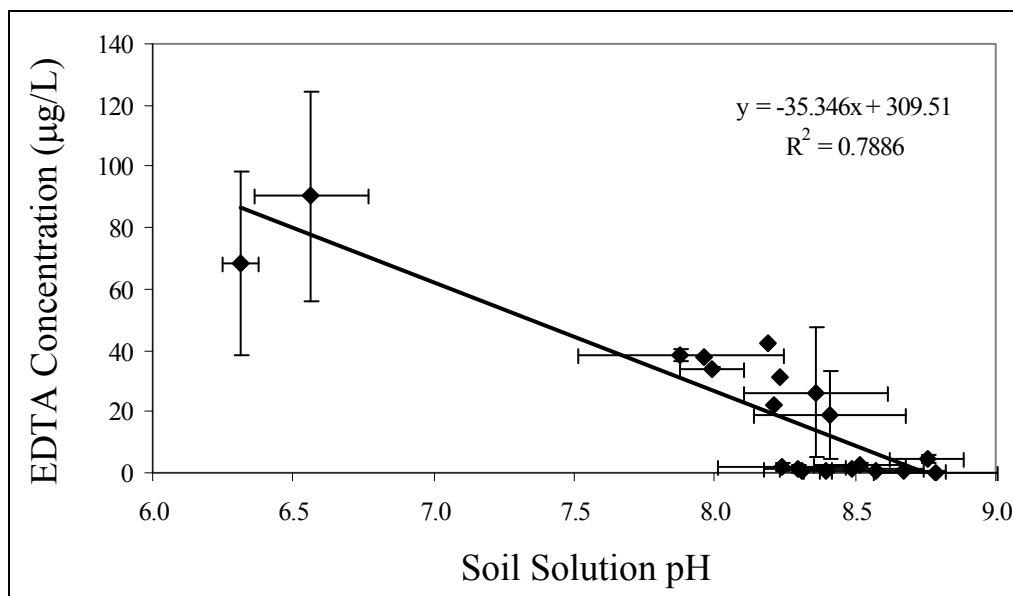
In a study with similar influent concentrations as those in the Mines Park effluent, NTA was reduced from an average of 4 µg/L in chlorinated secondary effluent to 0.4 to 2.1 µg/L (56 to 90%) within 3 m of soil at a soil aquifer treatment site, and to 0.1 to 0.5 µg/L (90 to 98%) by 38 m of unsaturated soil below the infiltrative surface (Yoo et al. 2006). NTA removal during soil treatment is likely by biotransformation rather than volatilization ( $K_H = 1.30 \times 10^{-7}$  atm-L/mol) or sorption ( $C_w^{sat} = 59,100$  mg/L,  $\log K_{ow} = -3.81$ ). The biodegradation half life of NTA in STE (2 mg/L) added to aerobic OWTS soils was less than 3 days in batch laboratory experiments (Shimp et al. 1994). An apparent zero-order attenuation rate constant,  $k_{app}$  (Equation 6-1), of NTA in the Mines Park test cells ranged from 0.115 to 0.182 µg/L-d, assuming travel times to 60 cm ranging from 22 to 32 days, average influent concentrations ranging from 3.7 µg/L (STE) to 4.0 µg/L (TFE), and 60 cm soil solution concentrations ranging from 0.02 µg/L (the RL) to 0.0002 µg/L (1/100 of the RL).

Previous research has reported similar findings regarding EDTA persistence relative to NTA during soil treatment (Yoo et al. 2006, Drewes et al. 2003b, Ding et al. 1999, Nowack et al. 1997). For example, NTA concentrations were reduced by up to 90% during 3 meters of soil transport at a soil aquifer treatment site, but EDTA was present at that depth in similar or higher concentrations than the input concentration (27  $\mu\text{g/L}$ ), and was measured at concentrations around 5  $\mu\text{g/L}$  (80 to 84% removal) in soil solution 38 meters below the infiltrative surface (Yoo et al. 2006). EDTA is not expected to be removed during soil treatment by volatilization ( $K_H = 5.77 \times 10^{-13} \text{ atm-L/mol}$ ) or sorption ( $\log K_{ow} = -3.86$ ). The biodegradability of EDTA strongly depends on pH. No degradation of EDTA was found during activated sludge treatment at pH = 7; however, within one month of increasing the pH to 8.0 to 9.0, EDTA concentrations were consistently reduced to less than the reporting level (Van Ginkel et al. 1997).

This enhanced biodegradability in alkaline solutions may be related to pH effects on EDTA-metal complex formation. At acidic pH values, EDTA forms strong complexes with transition metals such as iron (the log of the stability constant of Fe(III)-EDTA,  $\log K_{\text{Fe-EDTA}}$ , is 25.0 at an ionic strength of 0.1 M, Martell and Smith 1974). At higher pH values, Fe(III) hydroxide precipitates can form, allowing alkaline metals with lower stability constants to form complexes with EDTA (e.g.  $\log K_{\text{Ca-EDTA}} = 10.61$ ,  $\log K_{\text{Mg-EDTA}} = 8.83$ , Martell and Smith 1974). In a slightly alkaline surface water (pH = 8.05 to 8.55) where calcium and sodium were the dominant cations (Xue et al. 1995), only a small fraction of EDTA was complexed with iron, while the majority was complexed with calcium. An EDTA-degrading microorganism has been identified (Nörtemann 1999) that can transport EDTA into its cell when it is complexed with calcium or magnesium but not when it is complexed with iron(III), zinc, copper(II), cobalt(II), or nickel (Henneken et al. 1995, Klüner et al. 1998).

In the effluent and soil solution at Mines Park, sodium, calcium, and magnesium are the dominant cations (40 to 100 mg Na/L, 20 to 80 mg Ca/L, 5 to 35 mg Mg/L) while there are very low levels of transition metals (i.e. <0.05 mg/L of Fe, Al, and Zn, <0.5 mg/L Ni). As the pH increases to greater than 8.0 and the concentrations of the major cations increase with depth below the infiltrative surface (Figure 12), EDTA complexes with alkaline earth metals such as calcium and magnesium may dominate over complexes with iron, which is hypothesized to increase the biodegradability of EDTA. A decrease in EDTA concentrations in soil solution co-occurs with an increase in pH (Figure 14), as well as an increase in major cation concentrations and increasing depth BIS. All soil solution samples with pH > 8.41 had EDTA concentrations < 5% of the average input concentration. All soil solution samples with pH < 8.19 had EDTA concentrations > 95% of the average input concentration. Soil solution samples with pH values between 8.19 and 8.41 varied in concentration from < 5 to > 95% of the average input concentration. Due to the large number of known and potential co-varying characteristics in the Mines

Park vadose zone (e.g. EDTA concentration, pH, depth, cation concentration, water content, redox conditions, organic carbon content, microbial biomass, etc.), the pH-dependent biodegradation of EDTA is a hypothesis to explain the EDTA behavior at the Test Site that is supported and strengthened by results from previous studies. The behavior of EDTA in the Mines Park test cells highlights the interconnectedness of the organic and inorganic realms in the vadose zone, and emphasizes the need to understand all fractions, including organic and inorganic soil-solution interactions and soil physics, when assessing an environmental system.



**Figure 14.** EDTA concentration versus pH in Mines Park soil solution. [Error bars =  $\pm 1$  standard deviation based on three samples from each lysimeter. No error bar = less than three samples collected.]

#### 6.1.2.4 Nonylphenol Surfactant Metabolites

NP1EO, measured in STE at concentrations around 2 µg/L and <RL in TFE, was never measured above the reporting level (1 µg/L) in soil solution regardless of effluent type, HLR, or depth below the infiltrative surface (Figure 13). Concentrations of NP1EC, averaging 58 µg/L in STE and 8 µg/L in TFE, ranged between 3 and 8 µg/L in soil solution 60 cm BIS regardless of effluent type and HLR, with the exception of one test cell with concentrations between 10 and 13 µg/L (receiving 2 cm/d TFE). No additional removal was observed with additional soil treatment, resulting in the persistence of NP1EC through 240 cm of soil at concentrations ranging from 2.2 to 7.2 µg/L. Concentrations of NP, which were typically less than 6 µg/L in effluent, increased during the first 60 cm of soil treatment in all test cells to

concentrations up to 17 µg/L. Removal efficiencies in all test cells between 60 and 120 cm of soil varied from negligible removal to up to 75% removal. By 240 cm, concentrations were < 5 µg/L, and average removal efficiencies ranged from 65 to 85% as compared to concentrations in 60 cm soil solution.

In summary, at the Mines Park Test Site: 1) NP1EO was removed from soil solution within the first 60 cm of soil treatment, 2) concentrations of NP initially increased during the first 60 to 120 cm of soil before decreasing to less than 5 µg/L by 240 cm BIS, and 3) NP1EC concentrations ranged from 2 to 8 µg/L at all depths, resulting in ≥90% removal of NP1EC from STE and 9 to 60% removal from TFE. These results are similar to previous studies that have reported the reduction of NPEOs, accumulation of NP at shallow depths, and low-level persistence of NPECs during vadose zone transport. For example, during soil aquifer treatment, NPEOs were not measured at any depths (Montgomery-Brown et al. 2003). Under oxic conditions, NP and NPECs were attenuated. Under anoxic conditions, NPECs were reduced while NP was produced during the first 1.5 m of transport before decreasing during the next 1.5 m of transport. In ground water underlying a sandy onsite soil treatment unit (Swartz et al. 2006), concentrations of NP1-3EO were similar to or lower than septic tank concentrations on the same day (≤ 5 µg/L), NP concentrations were up to 6-fold greater (STE: 10 to 16 µg/L, GW: up to 84 µg/L), and NP2EC concentrations were up to 30-fold greater (STE: 1.6 to 2.3 µg/L, GW: up to 68 µg/L). In an OWTS receiving elevated levels of NPE-based laundry detergents (e.g. > 800 µg/L of NP + NP1-16EO + NP1-4EC applied to the soil treatment unit for one year), the summed concentration was < 2.5 µg/L in vadose zone soil solution 290 cm BIS (Huntsman et al. 2006).

At the Mines Park Test Site, removal of NP1EO within the first 60 cm of soil is likely due to aerobic biotransformation to NP. NP1EC removal from STE is likely due to biotransformation to NP, while untransformed product will remain in soil solution due to its acidity as compared to other degradation products. NP, in turn, is likely removed by sorption to soil (log  $K_D$  = 0.93 to 2.5 L/kg, Düring et al. 2002), though aerobic biotransformation of high concentrations of NP (e.g. 1 to 250 mg/kg) in agricultural soils has been reported (Topp and Starratt 2000). The increase in NP concentrations within the first 60 to 120 cm of vadose zone soil treatment suggests that at these depths the degradation of NPEOs and NPECs to NP is faster than the sorption and/or biotransformation of NP.

The overall removal of NPE metabolites (e.g. NP+NP1EO+NP1EC) from STE during Mines Park soil treatment averaged 78% (2 cm/d) and 70% (8 cm/d) within 60 cm of soil and 87% (2 cm/d) and 90% (8 cm/d) within 240 cm of soil receiving STE. In contrast, because the input concentrations in TFE were low, an average production of 50% (2 cm/d) and 20% (8 cm/d) of NPE metabolites within 60 cm of soil was measured. By 240 cm, an average of 21% (2 cm/d) and 32% (8 cm/d) removal was measured in soil receiving TFE.

### 6.1.2.5 Sulfamethoxazole and Other Non-Target Compounds

While there is less certainty associated with the antibiotic data because a single sample from each location was analyzed (data generously provided by Mike Meyer, USGS), the data provide important information regarding the sporadic occurrence and persistence of pharmaceuticals in the vadose zone as compared to that of consumer product chemicals. Seven out of 33 antibiotics and pharmaceuticals were identified in one or both of the wastewater effluents: sulfamethoxazole (0.02 µg/L, ponded TFE only), ofloxacin (0.45 to 0.96 µg/L), erythromycin (0.02 to 0.04 µg/L), erythromycin-H<sub>2</sub>O (0.20 to 0.32 µg/L), azithromycin (0.01 to 0.02 µg/L), trimethoprim (0.01 to 0.07 µg/L), and ibuprofen (5.1 µg/L, STE only). Three of those compounds (ofloxacin, erythromycin, and erythromycin-H<sub>2</sub>O) as well as two others (roxithromycin and tetracycline) were measured in Mines Park wastewater during the spring 2004 reconnaissance survey sampling event (from location 3). Three compounds were detected in soil solution: ofloxacin (0.01 µg/L) and erythromycin-H<sub>2</sub>O (0.03 µg/L) were each detected once in soil solution 60 cm BIS of different test cells. Sulfamethoxazole was detected more frequently than the other antibiotics, though sporadically, in soil solution. In the three test cells receiving 2 cm/d of STE, sulfamethoxazole was detected 60 cm BIS in only one of the three cells at a concentration of 7.0 µg/L. In soil solution 120 cm BIS, sulfamethoxazole was measured at 0.77 µg/L in the same test cell, and at 1.8 µg/L in one of the other cells in which the compound was not detected at 60 cm. Similarly, sulfamethoxazole was detected in only one of three test cells receiving 2 cm/d of TFE, at concentrations of 3.2 and 0.06 µg/L 60 and 120 cm BIS, respectively. The compound was present in both test cells receiving 8 cm/d of effluent: 2.2 µg/L (60 cm) and 0.04 µg/L (120 cm) in the STE test cell (no sample collected at 240 cm BIS) and 4.5 µg/L (60 cm), 4.3 µg/L (120 cm), and 0.51 µg/L (240 cm) in the TFE test cell.

In the test cells in which sulfamethoxazole was detected (Figure 13), the compound remained above the reporting level (0.005 µg/L) through 120 cm of soil and through 240 cm of soil in the one test cell analyzed at that depth. The results confirm previous reports of the sporadic, non steady-state occurrence and persistence of sulfamethoxazole in effluent through vadose zone soil to the underlying ground water (Ternes et al. 2007, Godfrey et al. 2007, Kinney et al. 2006, Hinkle et al. 2005). The persistence of sulfamethoxazole during soil aquifer treatment (Ternes et al. 2007) was attributed to low sorption affinity and biodegradability, though reported log  $K_{oc}$  values vary from -0.17 (Ternes et al. 2007) to 3.47 (Carballa et al. 2008). More research is needed to assess removal mechanisms of sulfamethoxazole during soil treatment.

## 6.2 Soil Treatment Efficiency

### 6.2.1 Percent Removal

In the previous section, it was shown that for each target compound (with the exception of EDTA) soil solution concentrations at the same depth were similar (Figure 13) in all test cells regardless of applied effluent type (STE or TFE) or design HLR (2 or 8 cm/d). This suggests that the Mines Park soil acts as a normalizing treatment unit, producing a high quality effluent regardless of the influent quality. Percent removal of DOC and trace organic contaminant concentrations during soil treatment was calculated based on the difference between the average effluent concentration applied to the infiltrative surface,  $C_{EFF}$  ( $\mu\text{g/L}$ ), where the effluent was either STE or TFE, and the average soil solution concentration,  $C_{SOIL}$  ( $\mu\text{g/L}$ ), at each depth (60, 120, or 240 cm BIS) for each design HLR (2 or 8 cm/d), according to the equation:

$$\text{Percent Removal (\%)} = \left[ 1 - \left( \frac{C_{SOIL}}{C_{EFF}} \right) \right] * 100 \quad (6-4)$$

For three compounds – caffeine, triclosan, and NP1EO – comparison of percent removals was limited due to concentrations below the reporting level in the TFE and/or soil solution (Table 18). For the other compound, NP1EC, with higher STE concentrations than TFE concentrations, a higher average percent removal was achieved during soil treatment of STE vs. TFE. NP1EC percent removal during soil treatment of STE ranged from 91 to 97% due to the reduction of high concentrations in STE ( $\sim 65 \mu\text{g/L}$ ) to concentrations generally less than  $10 \mu\text{g/L}$ . NP1EC soil solution concentrations in test cells receiving TFE were also less than  $10 \mu\text{g/L}$ , but the percent removal during soil treatment of TFE was less than 60% due to the low input concentrations ( $< 10 \mu\text{g/L}$ ) from the more highly treated TFE. A similar trend was seen for DOC removal ( $\sim 75$  to 85% removal during soil treatment of  $30 \text{ mg-C/L}$  in STE vs. 60 to 75% removal during soil treatment of  $16 \text{ mg-C/L}$  in TFE). For the compounds which had similar concentrations in STE and TFE (EDTA and NTA), percent removal with depth was similar in soil test cells regardless of effluent type. Removal of NP was low or negligible during soil treatment of both effluent types at both HLR.

Between 88 and 98% removal of sulfamethoxazole from soil solution was measured during transport between 60 cm and 120 cm BIS in three of the four test cells in which the compound was detected. In the fourth cell, the same treatment efficiency was achieved by 240 cm below the infiltrative surface.

**Table 18.** Average percent removal of dissolved organic carbon (DOC) and trace organic contaminant concentrations during soil treatment.

[Percent Removal = (1 - (Average soil solution concentration /Average effluent concentration)) \* 100; STE = septic tank effluent; TFE = textile filter effluent; HLR = design hydraulic loading rate; BIS = below the infiltrative surface; NPEs = NP1EC+NP1EO+NP; <RL = less than the reporting level. na = not applicable, effluent and soil solution concentrations <RL; italicized values in parentheses are the average percent increase in concentration; NP TFE concentration assumed = RL = 2 µg/L.]

Effluent	HLR (cm/d)	Depth BIS (cm)	Percent Removal										
			DOC	Caffeine	Triclosan	EDTA	NTA	NP1EC	NP1EO	NP	NPEs		
STE	2	60	82	>99, <RL	>97, <RL	(33)	98	91	>50 (<RL)	(130)	76		
		120	74	>99, <RL	>97, <RL	96	99	91	>50 (<RL)	2	85		
		240	82	>99, <RL	>97, <RL	98	>99, <RL	90	>50 (<RL)	46	87		
STE	8	60	79	>99, <RL	>97, <RL	(210)	99	92	>50 (<RL)	(130)	78		
		120	82	>99, <RL	>97, <RL	(18)	98	91	>50 (<RL)	(13)	84		
		240	85	>99, <RL	>97, <RL	97	99	96	>50 (<RL)	22	91		
TFE	2	60	66	>65, <RL	na	(32)	95	(3)	na	(350)	(76)		
		120	58	>65, <RL	na	92	99	50	na	(230)	(8)		
		240	63	>65, <RL	na	99	>99, <RL	41	na	(32)	21		
TFE	8	60	75	>65, <RL	na	(160)	98	43	na	(270)	(20)		
		120	72	>65, <RL	na	1	99	60	na	(380)	(26)		
		240	59	>65, <RL	na	96	>99, <RL	50	na	(39)	32		



## 6.2.2 Mass Removal

Total mass removed (Table 19) during the three years of operation was compared for test cells varying by effluent type and HLR. Mass removed,  $M_{Rem}$ , in milligrams was estimated as the difference between the total mass infiltrated at the infiltrative surface,  $M_0$ , and the total mass remaining in pore water at each depth below the infiltrative surface,  $M_X$ , where  $X = 60, 120,$  and  $240$  cm:

$$M_{Rem}(mg) = M_0 - M_X \quad (6-5)$$

$$M_0(mg) = C_{Eff}(\mu g / L) * V(L) \quad (6-6)$$

$$M_X(mg) = C_X(\mu g / L) * V(L) \quad (6-7)$$

where  $C_{Eff}$  is the average concentration in the applied effluent ( $\mu g/L$ ) and  $C_X$  is the average concentration ( $\mu g/L$ ) in the pore water at depth,  $X$  (cm), and  $V$  is the actual total infiltrated volume (L). Percent mass removal was calculated as:

$$\%M_{Rem} = \frac{M_{Rem}}{M_0} * 100 \quad (6-8)$$

Mass removal of NP through 240 cm of soil treatment was negligible for both effluent types and HLRs. For other compounds, soil test cells receiving a higher HLR (8 cm/d) removed more mass during the same depth of soil treatment than test cells receiving a typical HLR (2 cm/d) of the same effluent. For example, during three years of operation, approximately 290 mg of caffeine was removed from soil solution within 60 cm of soil treatment in the test cell receiving 8 cm/d of STE as compared to a removal of 120 mg of caffeine in test cells receiving 2 cm/d of STE. In exception, mass removal of EDTA was higher at 120 cm BIS in test cells receiving 2 cm/d vs. 8 cm/d (possibly due to pH effects, see Section 6.1.2.3).

Soil test cells receiving STE removed more mass during the same depth of soil than test cells receiving TFE at the same HLR. For example, approximately 82 mg of triclosan was removed from STE within 240 cm of soil receiving effluent at 8 cm/d as compared to 3.0 mg of triclosan removed from TFE within the same depth and applied at the same loading rate. In exception, EDTA removal, when it occurred, and NTA removal was higher in TFE test cells, which had a higher average input concentration than STE test cells.

**Table 19.** Estimated total mass removed (mg) from effluent applied to the infiltrative surface during three years of soil treatment. [HLR = design hydraulic loading rate; Effluent: STE = septic tank effluent, TFE = textile filter effluent; BIS = below infiltrative surface; EDTA = Ethylenediaminetetraacetic acid, NTA = nitritotriacetic acid, NP1EC = 4-nonyphenolmonoethoxycarboxylate, NP1EO = 4-nonylphenolmonoethoxylate, NP = 4-nonylphenol, NPEs = NP1EC + NP1EO + NP; none = no mass removal. Values for HLR = 2 cm/d at 60 and 120 cm are average of three test cells.]

HLR, Effluent	Depth BIS (cm)	Estimated Mass Removed (mg) during 3 Years of Soil Treatment							
		Caffeine	Triclosan	EDTA	NTA	NP1EC	NP1EO	NP	NPEs
2 cm/d STE	60	120	32	none	16	210	6.5	none	200
	120	120	32	86	17	220	7.1	0.40	230
	240	130	35	97	18	230	7.9	8.7	250
8 cm/d STE	60	290	81	none	42	550	18	none	520
	120	290	82	none	42	550	19	none	560
	240	290	82	220	42	580	18	10	600
2 cm/d TFE	60	4.0	1.0	none	27	2.0	none	none	none
	120	4.0	0.59	220	29	28	none	none	none
	240	3.2	0.57	190	24	18	none	none	13
8 cm/d TFE	60	10	2.8	none	76	62	5.1	none	none
	120	10	2.8	4.3	77	88	6.4	none	none
	240	10	3.0	590	77	73	6.2	none	62

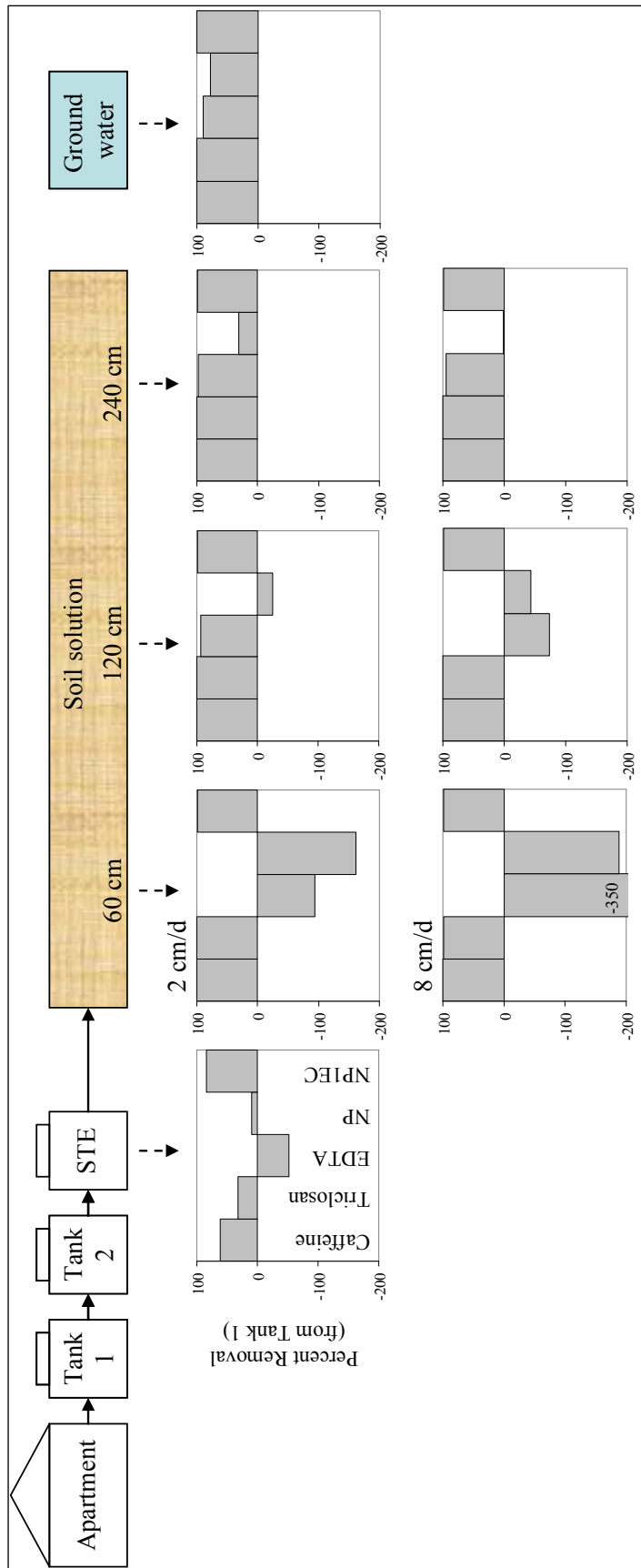
### 6.3 Occurrence in Ground Water

EDTA, NP1EC, NP, and sulfamethoxazole persisted in soil solution through 240 cm of soil treatment at the Mines Park Test Site at concentrations up to 2.4, 7.2, 4.1, and 0.51 µg/L, respectively. EDTA was measured in all ground water samples collected from the Test Site at concentrations up to 3.9 µg/L, which is similar to soil solution concentrations 240 cm BIS. This suggests that EDTA has the potential to persist at concentrations similar to those in soil solution within an OWTS soil treatment unit through additional vadose zone soil to ground water. NP1EC was present in concentrations from less than the reporting level (1 µg/L) to 3.1 µg/L. A reduction in NP1EC concentration between soil solution 240 cm BIS and ground water occurred, which could be due to biotransformation during the additional travel time in the vadose zone prior to ground water recharge. NP concentrations were below the reporting level (2 µg/L) in ground water samples, which may be due to sorption to vadose zone soil and aquifer sediments. Ground water samples were not analyzed for sulfamethoxazole. The concentrations of the other target trace organic contaminants (caffeine, triclosan, NTA, and NP1EO) were below the reporting level in ground water samples. Additional sampling of hydrologically-linked OWTS - ground water systems is needed to further assess receiving environment impacts.

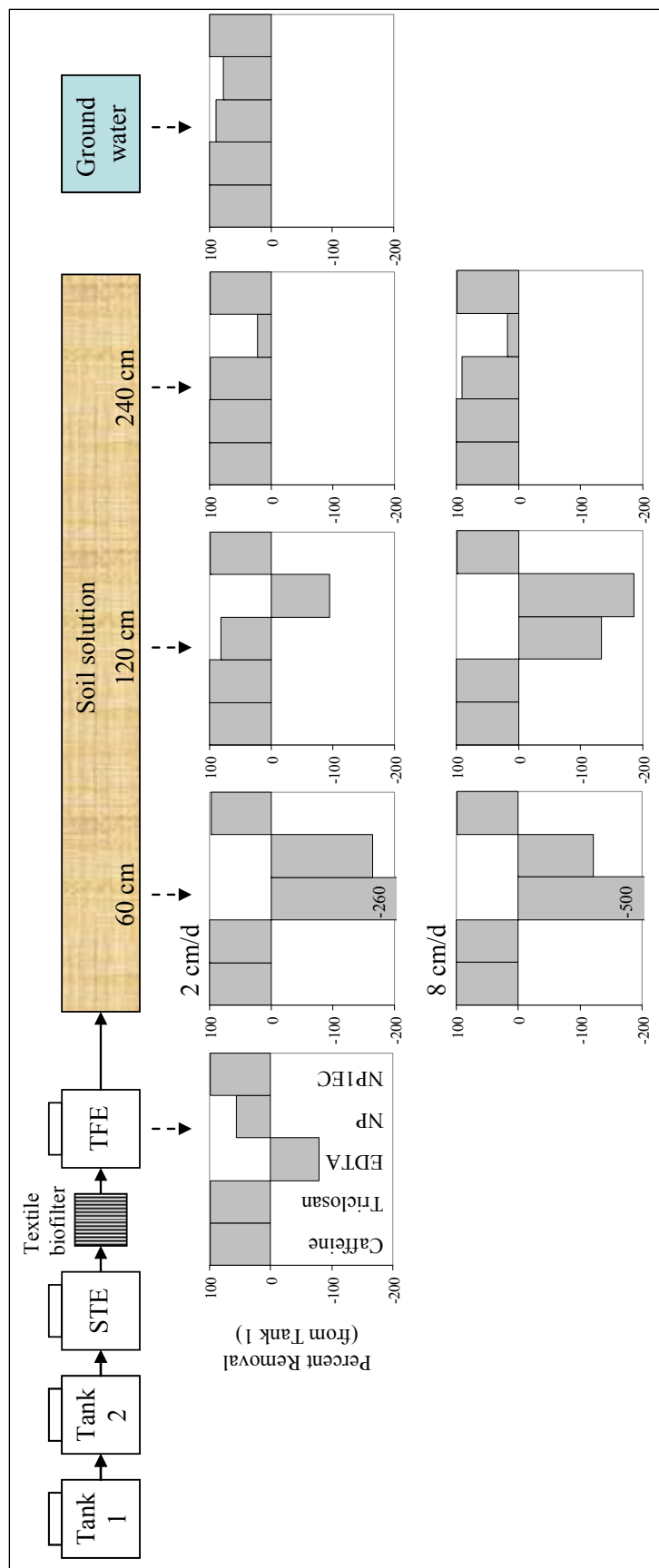
## 6.4 Whole System Treatment

At the Mines Park Test Site, treatment of residential wastewater through septic tanks and 240 cm of vadose zone soil, regardless of HLR (Figure 15, Table 20), resulted in 95% or greater removal [determined as the difference between average concentrations in Tank 1 wastewater (location 1, Figure 4) and soil solution 240 cm BIS] for caffeine, triclosan, EDTA, NTA, and NP1EC (and to <RL for NP1EO). Removal of NP was less than 35%. Low removal ( $\leq 35\%$ ) of most compounds occurred during tank-based treatment [determined as the difference between average Tank 1 and Tank 2 compartment 2 wastewater concentrations (Figure 4 locations 1 and location 3, respectively)] with the exception of NP1EC (74% removal). The majority of the treatment occurred during soil infiltration and percolation through the vadose zone. Greater than 90% removal (determined as the difference between concentrations in STE and soil solution) occurred during 240 cm of soil treatment at the Test Site for all target compounds except NP (<50% removal). For all compounds except EDTA, the high removal was achieved within 60 cm of soil treatment. To achieve >90% removal of EDTA, 120 cm (at the low HLR) and 240 cm (at the high HLR) of soil was needed.

Additional treatment of STE by a textile biofilter prior to soil application resulted in similar whole system treatment results (Figure 16, Table 20) as those observed in the conventional tank and soil treatment system. At the Mines Park Test Site, treatment through septic tanks, a textile biofilter, and 240 cm of soil, regardless of HLR, resulted in greater than or equal to 88% removal of all target trace organic contaminants with the exception of NP (< 35% removal). High removal efficiencies had already been achieved during biofilter treatment (determined as the difference between STE and TFE concentrations) for all target compounds except for EDTA and NTA (both <1% removal). Biofilter removal results from high-concentration operational systems in Colorado differed for NTA (average removal = 76%) and NP1EC (increase in  $\sum$ NPEC concentrations between STE and TFE). Sixty to 120 cm of soil was needed to reduce NTA concentrations to <RL, and, similar to the conventional system, to achieve >90% removal of EDTA, 120 cm (at the low HLR) and 240 cm (at the high HLR) of soil was needed.



**Figure 15.** Aqueous concentration percent removal of select trace organic contaminants during septic tank-based treatment at the Mines Park Test Site. [Percent removal calculated from Tank 1 (location 1, Figure 4) concentrations. Ground water removal calculated based on average concentrations in four ground water monitoring wells located 360 to 680 cm below ground surface and 8 to 100 m downgradient from the test cells. A negative percent removal indicates a concentration increase from Tank 1.]



**Figure 16.** Aqueous concentration percent removal of select trace organic contaminants during textile biofilter-based treatment at the Mines Park Test Site. [Percent removal calculated from Tank 1 (location 1, Figure 4) concentrations. Ground water removal calculated based on average concentrations in four ground water monitoring wells located 360 to 680 cm below ground surface and 8 to 100 m downgradient from the test cells. A negative percent removal indicates a concentration increase from Tank 1.]

**Table 20.** Summary of percent removal of trace organic contaminant concentrations at the Mines Park Test Site. [Percent Removal = (1 – (Average concentration at location 2 / Average concentration at location 1)) \* 100; <RL = less than the reporting level. na = not applicable, Location 1 concentration <RL; Values in parentheses indicate a percent increase in concentration; NPEs = NPIEC+NPIEO+NP.]

Treatment Type	Location 1	Location 2	Percent Removal (%) of Concentration Between Location 1 and 2										
			Caffeine	Triclosan	EDTA	NTA	NPIEC	NPIEO	NP	NPEs			
Septic tank	Tank 1	Tank 2 compartment 2	17	9	20	(25)	74	<1	(26)	72			
Textile biofilter	STE	TFE	98	>97, <RL	(59)	(9)	86	>51, <RL	>54, <RL	84			
240 cm of soil													
2 cm/d STE	STE	Soil solution 240 cm BIS	>99, <RL	>97, <RL	98	>99, <RL	90	>51, <RL	46	87			
8 cm/d STE	STE	Soil solution 240 cm BIS	>99, <RL	>97, <RL	97	99	96	>51, <RL	22	91			
2 cm/d TFE	TFE	Soil solution 240 cm BIS	>65, <RL	na	99	>99, <RL	41	na	na	21			
8 cm/d TFE	TFE	Soil solution 240 cm BIS	>65, <RL	na	96	>99, <RL	50	na	na	32			
Whole System													
2 cm/d STE	Tank 1	Soil solution 240 cm BIS	>99, <RL	>99, <RL	98	>98, <RL	98	>14, <RL	25	97			
8 cm/d STE	Tank 1	Soil solution 240 cm BIS	>99, <RL	>99, <RL	95	98	99	>14, <RL	(9)	98			
2 cm/d TFE	Tank 1	Soil solution 240 cm BIS	>99, <RL	>99, <RL	98	>98, <RL	94	>14, <RL	32	91			
8 cm/d TFE	Tank 1	Soil solution 240 cm BIS	>99, <RL	>99, <RL	88	>98, <RL	95	>14, <RL	29	92			

## **CHAPTER 7**

### **INTEGRATION OF RESULTS AND IMPLICATIONS**

Modern OWTS are designed and managed with the primary goal of protecting human health while minimizing environmental impacts. Pathogens and nutrients have traditionally been the primary constituents of concern (for example, pathogens can cause illness in exposed populations and excess nitrogen and phosphorus can cause eutrophication in receiving surface waters). An OWTS management strategy to protect water quality and public health should consider, among other things, four aspects: 1) the occurrence and levels of contaminants from various source types, 2) design of the system for treatment of these contaminants, 3) mass loading of any untreated contaminants to the receiving environment, and 4) the possible exposure pathway(s) and potential effects. Results from this research are integrated in this chapter to provide guidance for these management considerations regarding trace organic contaminants.

#### **7.1 Occurrence and Levels in Onsite Wastewaters**

Trace organic contaminants occur in OWTS wastewaters frequently (21/24 target compounds identified at least once, 10 detected in greater than 65% of samples from 30 systems) and at concentrations that range over three orders of magnitude, from levels similar to those measured in WWTP influents (ng/L to low  $\mu\text{g/L}$ ) to much higher levels (mg/L). WWTP influent composition is relatively consistent regarding trace organic contaminants due to the large number of contributing sources which attenuate fluctuations in individual sources contributing to the wastewater stream. In contrast, OWTS wastewaters originate from one source or a small number of sources and the composition depends on the source type and activities. In this study, in general, non-residential wastewaters had more trace organic contaminants at higher concentrations than residential sources. This is likely due to differences in water- and chemical-using activities at the source. Therefore, knowledge of the wastewater source, especially the water and chemical-using activities, can provide some initial information regarding the types and levels of trace organic contaminants that may be present in anaerobic wastewaters within septic tanks in an OWTS.

Wastewater is typically composed of human waste, food waste, and consumer product chemicals used for hygiene and cleaning practices that are transported in water from the source to an OWTS. Different types of trace organic contaminants originate from different activities (Table 21). Human waste primarily originates from toilets and urinals, and may be composed of fecal sterols such as

cholesterol and coprostanol and excreted parent and metabolite pharmaceuticals. Food waste originates from garbage disposals, grease collectors, kitchen sinks, and dish washers, and is composed of chemicals naturally present in food (i.e. caffeine) or synthetically added (i.e. preservatives such as EDTA, butylated hydroxyanisole, BHA, and butylated hydroxytoluene, BHT). Consumer product chemicals originate from clothes washers (i.e. laundry detergents), dish washers (i.e. dish detergents), showers (i.e. shampoo, soaps, lotions, fragrances), and general cleaning activities (i.e. all-purpose cleaners, toilet bowl deodorants, antimicrobials in toothpastes, soaps, etc.). Rinse water originates from faucets and leaks and may transport disposed household items such as unused pharmaceuticals or chemicals (i.e. bisphenol A) that may leach from the plumbing and piping infrastructure.

**Table 21.** Potential organic compounds and classes that may be present in wastewater originating from various source activities.

<b>Wastewater Composition</b>	<b>Source Activity</b>	<b>Potential Classes of Organic Contaminants</b>	<b>Example of Individual Organic Contaminants</b>
Human waste	Toilet, urinal	Sterols Pharmaceutical residues Pharmaceutical metabolites	Cholesterol, coprostanol Sulfamethoxazole 1,7-dimethylxanthine
Food waste	Garbage disposal, grease collector	Stimulants Preservatives	Caffeine BHA, BHT
Consumer product chemicals	Clothes washer, dishwasher, shower, faucets	Fragrances Soaps/Detergents Antimicrobials Deodorizers	Menthol, camphor Nonylphenoethoxylates Triclosan 1,4-Dichlorobenzene
Transport water	Faucets, leaks	Plasticizers (leaching) Pharmaceuticals (unused disposal)	Bisphenol A Sulfamethoxazole, codeine

Knowledge of the distribution of chemical- and water-using activities at the source contributing to the wastewater stream can provide information regarding the likelihood of occurrence and the levels of various trace organic contaminants in OWTS wastewater. For example, typical indoor water use for a residential source is 30% toilets, 30% dish and clothes washing, 20% bathing, 10% faucets, and 10% miscellaneous (Crites and Tchobanoglous 1998). Therefore, OWTS wastewater originating from a residential source is expected to be composed of a dilute mix of biogenic (sterols) and anthropogenic chemicals (pharmaceuticals and consumer product chemicals), as was found during the reconnaissance survey.

Sources whose wastewater primarily originates from restroom use (e.g. highway gas station convenience stores, campgrounds, parks) will likely have high levels of sterols, pharmaceuticals and pharmaceutical metabolites, and possibly hand soap chemicals and bathroom cleaning products in their



OWTS wastewaters. In this research, gas station convenience store wastewaters had the highest concentrations of 14 pharmaceuticals, as well as elevated levels of the hand soap antimicrobial triclosan and the toilet bowl deodorizer 1,4-dichlorobenzene.

Sources with intense and frequent cleaning practices (e.g. human or animal institution, food establishment, vacation residence) will likely have elevated levels of consumer product chemicals such as detergents, antimicrobials, and fragrances in their OWTS wastewaters. For example, veterinary hospital wastewater, which mainly originates from washing and disinfecting practices, had high levels of surfactant metabolites, including 4-*t*-octylphenol and 4-*t*-octylphenolethoxylates at concentrations up to 20 times greater than other sources. These are examples of insights that can be gained concerning the types of trace organic contaminants that are likely to be present in wastewater originating from different sources. Actual wastewater compositions will depend on the specific products in use within a particular residence or establishment and the actual chemical- and water-using activities, which will differ between sources and at the same source over time. For example, in this study mixed source (e.g. originating from a number of different businesses in a retail center) wastewater composition varied over time as businesses changed ownership.

Trace organic contaminants that are likely to be present in most any septic tank wastewater based on their frequent (>65%) occurrence in Colorado septic tank wastewater include the sterols coprostanol and cholesterol, the metal chelating agents EDTA and NTA, the stimulant caffeine, the surfactant metabolites NP,  $\Sigma$ NPEO,  $\Sigma$ NPEC, the disinfectant 4-methylphenol, and the antimicrobial agent triclosan. Of these, the surfactant metabolites, which are weakly estrogenic, and the antimicrobial, which may impact the development of antimicrobial-resistant bacteria, have the greatest potential risk in typical receiving environments. Other trace organic contaminants that were not analyzed for in this study may also occur in septic tank wastewater and be of environmental relevance.

## **7.2 Treatment of Trace Organic Contaminants**

Knowledge of the source helps to identify the types and levels of compounds present in wastewater. An assessment of the removal efficiencies of trace organic contaminants by conventional and advanced onsite treatment units will aid in selection and design of an OWTS.

### **7.2.1 Conventional Onsite Treatment**

The most common OWTS treats residential wastewater through one or more septic tanks in series followed by soil infiltration (e.g. 60 to 120 cm of vadose zone soil) prior to recharge of the underlying

ground water. This type of OWTS can reduce septic tank wastewater concentrations of many trace organic contaminants (e.g. caffeine, triclosan, EDTA, NTA, NP1EC, NP1EO) by greater than 95% (or to < RL), while others may be more recalcitrant (< 50% NP removal). These results are particularly applicable to OWTS utilizing sandy loam soil that is common throughout the Colorado Front Range region.

### 7.2.1.1 Septic Tank Treatment

Some removal of trace organic contaminant concentrations in wastewater may occur during septic tank treatment due to anaerobic biotransformation and sorption to solids with subsequent settling. In this research, removals during septic tank treatment were typically less than 50%. The types of compounds likely to be removed are compounds with a high organic carbon partition coefficient ( $K_{oc}$ ) or a related parameter, octanol-water partition coefficient ( $K_{ow}$ ), and low water solubility ( $C_w^{sat}$ ). Compound groups with these physicochemical properties include sterols (e.g. cholesterol and coprostanol), antimicrobials (e.g. triclosan and triclocarban), and some phenols (e.g. 4-*t*-octylphenol) as well as other hydrophobic compounds. For example,  $38 \pm 22\%$  removal of triclosan, which is a hydrophobic compound with a  $\log K_{oc} = 3.96 - 4.69$ , was observed during tank-based treatment in full-scale OWTS. Trace organic contaminants that are not removed by sorption may be discharged to the soil at concentrations similar to influent septic tank wastewater concentrations. For example, removal of EDTA ( $\log K_{ow} = -3.86$ ,  $C_w^{sat} = 1000$  mg/L) was negligible during tank-based treatment (removal =  $12 \pm 12\%$ ) in operating systems.

Based on relevant removal mechanisms, important design features of a septic tank unit to help achieve for the greatest removal of trace organic contaminants are: 1) a long hydraulic residence time (e.g. multiple days) to allow for sorption and settling of solids, 2) a long solids retention time (e.g. months to years) to enhance anaerobic biotransformation, and 3) the containment of solids within the septic tank to minimize solids discharge (and therefore, discharge of hydrophobic trace organic contaminants sorbed to the solids) to the next treatment unit. Many design requirements for full-scale systems already lead to some optimization these design features. For example, Colorado systems are designed according to State code to achieve a minimum of a 30-hour hydraulic retention time. Septic tank solids typically accumulate for 6 months to more than three years between tank pumping events. Many states require multi-compartment septic tanks or multiple septic tanks in series to maximize solids separation and retention and thereby minimize solids discharge to the soil treatment unit.

However, water usage will vary from the design usage, and the actual tank hydraulic retention time may be shorter or longer than the design hydraulic retention time (e.g., shorter during periods of relatively more intense source activity (i.e. during tourist season at a restaurant), or for extended periods

of time (i.e. if there is a change in ownership with different water use practices). The change in water usage could be estimated by the management entity during a change of property ownership, and if the new water usage is expected to be significantly higher such that it would consistently decrease the hydraulic retention time, the system may need to be modified (e.g. with the addition of septic tanks). While an extended solids retention time is good for anaerobic digestion, tank pumping should occur frequently enough so as not to adversely affect system performance (e.g. by an overflowing tank). The frequency of pumping is determined by the system owner and depends on the source- it may be as often as every few months in a commercial system or more than three years for a residential system. Older systems are more likely to utilize a single compartment septic tank. An owner could have a filter or screen retrofit on the effluent pipe of all operational single compartment tanks as a relatively inexpensive and easy way to manage solids discharge.

#### **7.2.1.2 Soil Treatment**

The majority of removal of many trace organic contaminants in a conventional OWTS will occur during soil infiltration and percolation through the vadose zone. Likely removal mechanisms include volatilization, sorption, and aerobic biotransformation. In this research, greater than 90% removals of STE concentrations of many trace organic contaminants were achieved within 240 cm of sandy loam soil treatment. Compounds with a high Henry's Law constant ( $K_H$ ) such as VOCs (e.g. benzenes, toluenes, xylenes) may be removed by volatilization through solution-air and soil-air interfaces at the infiltrative surface and in the vadose zone. Hydrophobic compounds, such as those which can be partially removed during septic tank treatment, can partition from solution to organic matter in the infiltrative surface biofilm and in the soil. Acclimated microbial communities in the biofilm and in the soil below may biotransform amenable compounds. These include compounds that have been previously shown to aerobically biodegrade in soil microcosms and activated sludge systems, such as caffeine and NP1EO. For example, at Mines Park caffeine removal was >99% during transport through 60 cm of aerobic sandy loam soil as compared to <20% during anaerobic septic tank treatment.

Compounds that are not removed from effluents by sorption, volatilization, or biotransformation may be transported in soil solution as it migrates through the vadose zone. At Mines Park, EDTA, which appears to be biodegradable only in alkaline environments, persisted through at least 60 to 120 cm of acidic soil at concentrations similar to STE concentrations. Concentrations of transformation products may increase during shallow soil treatment as parent compounds degrade. For example, concentrations of NP, a degradation product of NP1EC, NP1EO, and other NPEs, increased by 200 to 500% during the first 60 cm of soil.

Non-residential wastewaters often had much higher concentrations of trace organic contaminants than residential wastewaters, and the treatment effectiveness achieved during infiltration and percolation through soil receiving these non-residential effluents has not been investigated. Results from the Mines Park soil test cell receiving a higher mass loading of trace organic contaminants (by applying a higher HLR of residential STE) may provide some information regarding the soil treatment of non-residential wastewater. Mass removal in this test cell was generally higher than that of the test cells receiving a typical HLR, suggesting that soil treatment units may be capable of treating higher-strength effluents and removing trace organic contaminants as effectively as for lower-strength effluents. The additional carbon and nutrient loading in a higher-strength effluent may enhance the soil microbial community and lead to fortuitous degradation of trace organics.

The soil treatment unit should be designed, therefore, to optimize volatilization, sorption, and biotransformation. A key component is the natural development of a biofilm of organic-rich particulate matter and microorganisms at the infiltrative surface and extending a few centimeters or deeper into the native soil. Hydrophobic trace organic contaminants in the applied effluent should partition into the organic rich biofilm and may be biotransformed by the microbial community there. As particulates accumulate and the biofilm develops, the infiltration rate normally decreases to a fraction of the hydraulic conductivity of the native soil. This maintains aerobic conditions in the vadose zone below the location of soil infiltration and vadose zone travel times can enhance removal processes such as sorption to organic soil surfaces, aerobic biotransformation, and soil solution/gas exchange. Disinfection of treated effluent prior to soil application, which may be a treatment consideration to minimize risk regarding pathogenic organisms, is not recommended for treatment of trace organic contaminants due to the importance of a biologically-active soil treatment zone.

The HLR should be high enough to enhance development of the biofilm but low enough to maintain an average daily infiltration rate similar to the daily application rate. In this research, vadose zone soil solution concentrations were similar in soil treatment units with infiltration rates 2 to 3 times higher than in soil treatment units with infiltration rates similar to a typical design HLR. Therefore, the results suggest that the design HLR could be increased (for example, from 2 cm/d to 4 cm/d) without adversely affecting the treatment capacity of the soil regarding trace organic contaminants.

Other design considerations include the effluent delivery method, the surface area layout, the soil properties, and the vadose zone depth. The use of a dosing delivery method rather than traditional gravity flow likely enhances the development of a more uniform biofilm over the entire infiltrative surface, which can help maximize the surface area for infiltration and soil treatment. Narrow and shallow infiltration trenches may enhance gas exchange between the soil solution and the atmosphere as compared to an infiltration bed or pit. While the biofilm development and soil pore clogging controls the infiltration rate

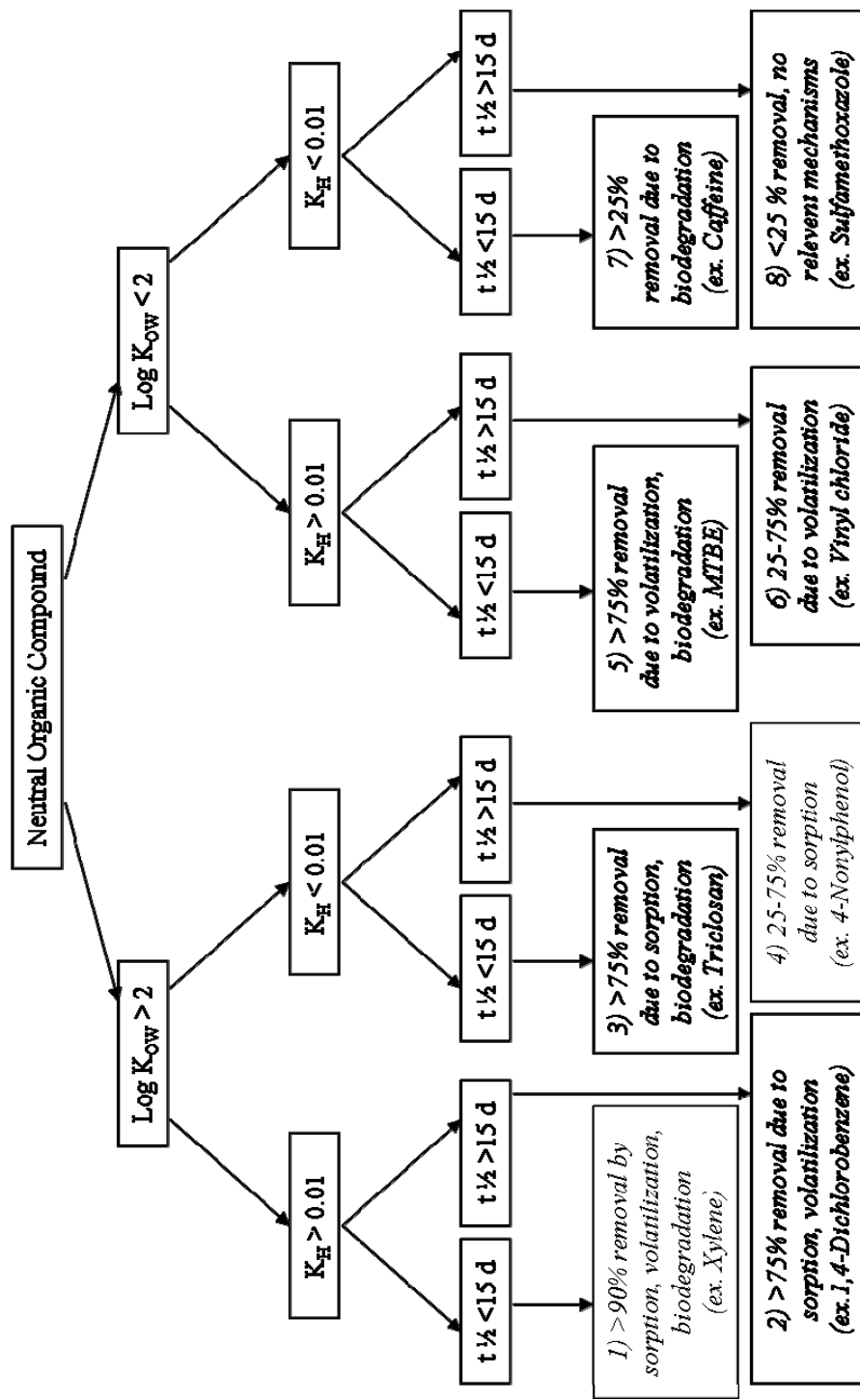
capacity and is the location where much treatment occurs, the vadose zone soil properties are still important to system design and performance. In particular, preferred soils are those with appreciable organic matter contents and sufficient permeability and structure for air and water flow. Many trace organic contaminants were removed from soil solution within 60 cm of vadose zone transport through sandy loam soil, but others persisted through 240 cm of soil. The minimum necessary depth of the vadose zone to achieve adequate treatment of trace organics is difficult to generalize and depends on factors such as the types and levels of compounds present, the extent of additional treatment that can result during ground water recharge and transport, the proximity to surface water or a supply well, and no-effect levels in exposed populations.

### **7.2.1.3 Qualitative Prediction of Compound Behavior**

Target compounds were selected for the Mines Park research with one or more of the following characteristics: they are likely to be present in onsite wastewater (based on results from the reconnaissance survey), they have known or potential adverse effects or may be an appropriate indicator compound, and they are amenable to the sample collection and analysis methodologies employed during the Mines Park Test Site characterization studies. The ability to qualitatively predict the fate of these and other trace organic contaminants during onsite treatment may be a useful tool for engineers, practitioners, and regulators, especially given the time-consuming analysis of trace organic contaminants. Important characteristics that determine a compound's fate during onsite treatment include its ionic character at environmental pH values ( $pK_a$ ), hydrophobicity ( $K_{ow}$ ), vapor pressure and water solubility ( $K_H$ ), and biodegradability (rate constant,  $k$ , or half life,  $t_{1/2}$ ). Compounds that are ionic at environmental pH values may sorb to soil surfaces through electrostatic interactions (to either positive or negative surfaces). A hydrophobic compound (e.g.  $\log K_{ow} > 2$ ) may be removed during onsite treatment by sorption to septic tank solids, biofilm organic matter, and soil organic matter. A compound with a high vapor pressure and low water solubility (e.g.  $K_H > 0.01 \text{ atm-L/mol}$ ) may be removed during onsite treatment from the aqueous phase to the gaseous phase by volatilization during infiltration and percolation through the soil vadose zone. A biodegradable compound may be removed during onsite treatment by aerobic biotransformation during infiltration and percolation through the vadose zone by acclimated biofilms and soil microbial communities. The biodegradability of a compound during soil treatment may be estimated based on published values, e.g. an apparent aerobic 1st-order biodegradation half life,  $t_{1/2}$ , in activated sludge or soil systems, and compared to an estimated vadose zone travel time, e.g.  $\sim 15 \text{ d}$  travel through 60 cm of vadose zone soil receiving 2 cm/d HLR with a porosity  $\sim 0.5$ .

A preliminary prediction diagram (Figure 17) was adapted from methodology used by Bellona (2007) as a first attempt to develop a framework to qualitatively predict the fate of organic compounds during onsite treatment, with the following boundary conditions: 1) the diagram considers conventional onsite treatment only (e.g. through septic tank(s) and soil, not including additional engineered unit operations), and 2) only compounds that are neutral at environmental pH values are considered. In applying the logic presented in Figure 17, the predicted removal was generally similar to the observed removal of target compounds monitored at Mines Park (Table 22). For example, at  $\text{pH} < 7.9$ , triclosan is primarily a neutral hydrophobic compound ( $\log K_{\text{OW}} = 4.76$ ) with low volatility ( $K_{\text{H}} = 5.0 \times 10^{-6} \text{ atm-L/mol}$ ) that is readily biotransformed in aerobic soil and activated sludge (Ying et al. 2007, Heidler and Halden 2007, Bester 2003, Singer et al. 2002). Triclosan falls into Category 3 in the diagram, with  $>75\%$  expected removal during onsite treatment due to sorption and biotransformation. Actual removal during treatment through septic tanks and 60 cm of soil at the Mines Park Test Site was greater than 99%. In contrast, sulfamethoxazole is a non-hydrophobic ( $\log K_{\text{OW}} = 0.89$ ), non-volatile ( $K_{\text{H}} = 5.8 \times 10^{-13} \text{ atm-L/mol}$ ) compound that is not biodegradable in neutral or acidic environments. Sulfamethoxazole falls into Category 8 in the diagram, with low removal ( $<25\%$ ) attributed to the three relevant mechanisms. Sulfamethoxazole persisted through 240 cm of soil treatment at the Mines Park Test Site.

The diagram shown in Figure 17 is a preliminary attempt at a prediction tool based on the current knowledge of trace organic contaminant fate during onsite treatment. Actual removal efficiencies may fit more of a spectrum than a category system. For example, hydrophobic sorption may only become relevant to onsite removal for compounds with a  $\log K_{\text{OW}}$  greater than 3. The sorption distribution coefficient,  $K_{\text{D}}$ , or organic carbon partition coefficient,  $K_{\text{OC}}$ , may be better predictors of sorption during onsite treatment; however, values for  $K_{\text{OW}}$  are more widely available, and often  $K_{\text{D}}$  and/or  $K_{\text{OC}}$  are empirically derived from  $K_{\text{OW}}$ . The diagram considers aerobic biodegradation only, under the assumption that anaerobic biodegradation occurs much more slowly, if at all, compared to aerobic biodegradation. Also, the biodegradability is based on literature values that may or may not be relevant to onsite systems (e.g. 1<sup>st</sup>-order vs. zero-order kinetics, activated sludge vs. a soil system). The extent of removal by each of these mechanisms – sorption, volatilization, and biodegradation – depends not only on the physicochemical properties of the compound but also on environmental conditions, many of which were discussed in Sections 7.2.1.1 and 7.2.1.2. For example, the actual vadose zone travel time will vary based on infiltration rate, porosity, water content, depth to the water table, etc. Additional research assessing the relative importance of these and other chemical and treatment properties is needed to refine this prediction diagram prior to its routine and reliable use as a management tool.



**Figure 17.** Preliminary diagram for qualitatively predicting the removal of trace organic contaminants during conventional onsite wastewater treatment using septic tank and soil treatment units. [Adapted from Bellona 2007. Only valid for neutral compounds at environmental pHs.  $K_H$  (atm-L/mol),  $t_{1/2}$  is for aerobic environmental biodegradation. This is a preliminary diagram and should not be used as a management tool until further modification have been made. See Section 7.2.1.3 for further explanation of boundary conditions.]

**Table 22.** Properties of example compounds and predicted and observed removal using Figure 17. [Adapted from Bellona 2007. NM = not measured in current study; conc. = concentration; literature subsurface occurrence reported when available.]

Group (Fig. 17)	Compound	Log $K_{ow}$	$K_H$ (atm-L/mol)	$K_H > 0.01?$	aerobic $t_{1/2}$ (d)	$< 15$ d?	Predicted OWTS removal	Observed OWTS removal (tank and 60 cm soil)	Notes (references)
1	Xylene	3.2	6.63	Y	<2	Y	>90%	NM	Rare GW contaminant
2	1,4-Dichlorobenzene	3.44	2.41	Y	~ 10 - 15	N	>75%	81% 98%	45 cm soil, all isomers (Roberston et al. 1994) Tank/biofilter (Current)
3	Triclosan NP1EO	4.76 4.17	5.00E-06 <0.01	Y	< 10	Y	>75%	>99% >75, >87% (<RL)	(Current study) (Current study)
4	NP Carbamazepine	4.48 2.45	3.40E-02 1.08E-04	Y	> 30 63	N	25-75%	None, 190% increase in conc. in GW below OWTS	(Current study) (Godfrey et al. 2007)
5	MBTE	0.94	0.587	Y	Variable	Y	>75%	NM	Commonly reported GW contaminant
6	Vinyl Chloride	1.62	27.8	Y	28	N	25-75%	NM	Commonly reported GW contaminant
7	Caffeine	-0.07	3.60E-08	N	<2	Y	>25%	>99%	(Current study)
8	Sulfamethoxazole	0.89	6.42E-10	N	>15	N	<25%	detected through 240 cm	(Current study)



## 7.2.2 Additional Engineered Treatment

Addition of an advanced engineered unit operation to the treatment train may be considered when conventional treatment is not expected to sufficiently protect environmental and human health. For example, textile biofilters are used in mountainous regions in Colorado when additional nitrogen removal is needed prior to discharge to a fractured bedrock soil system. Additional engineered treatment through a textile biofilter can enhance removal of many trace organic contaminants as compared to septic tank treatment alone likely due to volatilization, sorption and filtration of sorbed particulates, and aerobic biotransformation. In the reconnaissance survey, operating systems with additional aerobic treatment had lower median concentrations compared to anaerobic tank treatment ( $p < 0.05$ , Mann-Whitney U test) for 10 of the 12 compounds with median concentrations greater than the reporting level, regardless of source. In systems enhancing volatilization, such as aerobic units and spray recirculation systems, additional removal is expected of volatile compounds with a high Henry's law constant ( $K_H$ ). For example, the greater removal of 1,4-dichlorobenzene ( $K_H = 2.40 \text{ atm-L/mol}$ ) during biofilter treatment (98%) as compared to tank treatment ( $40 \pm 26\%$ ) is likely due to enhanced volatilization through increased air-water exchange and turbulence.

In systems enhancing sorption and filtration of particulates, such as sand, peat, and textile filters, additional removal is expected of compounds with a high  $\log K_{OC}$  and  $\log K_{OW}$ . In systems enhancing aerobic biotransformation, such as bioreactors and biofilters, additional removal is expected of compounds that can be degraded by an acclimated microbial population in similar environments such as WWTP activated sludge units (e.g. caffeine, NP1EO). The greater removal of triclosan during biofilter treatment ( $92 \pm 1\%$ ) as compared to tank treatment ( $38 \pm 22\%$ ) in operational systems is likely due to aerobic biotransformation and filtration of particulates containing sorbed triclosan.

Compounds that are not removed from effluents by sorption, volatilization, or biotransformation may persist during additional engineered treatment such as biofilter treatment. EDTA persisted through biofilter treatment in operational systems and at Mines Park. Concentrations of transformation products may increase during biofilter treatment as parent compounds degrade. For example,  $\Sigma\text{NPEC}$ , an acidic surfactant degradation product, persisted as the predominant NPE metabolite in aerobic effluents from high use sources.

While TFE has a higher quality regarding many trace organic contaminants as compared to STE, no differences in soil solution concentrations 60 cm BIS were observed in soils receiving STE vs. TFE at similar HLRs. Therefore, there is no apparent added benefit to including a textile biofilter in an OWTS design regarding the removal of trace organic contaminants from typical residential wastewater if the effluent is applied to a well-designed and operated soil treatment unit utilizing an appropriate soil with an

adequate depth of vadose zone (e.g. sandy loam soil profile with  $\geq 120$  cm to groundwater). In situations when treatment within the vadose zone may be limited (e.g. shallow ground water table, unacceptably fast or slow infiltration rate, nearby well or surface water, etc.), use of a textile biofilter can provide a higher quality effluent for some trace organic contaminants that is similar to soil solution 60 cm below an infiltrative surface receiving STE (Table 23). For example, at the Mines Park Test Site, >97% removal of caffeine and >98% removal triclosan occurred during textile biofilter treatment of STE as compared to >99% removal of both compounds during 60 cm of soil treatment of STE. However, differences between a textile biofilter and soil regarding treatment efficiencies of other compounds, such as NP, confirm that a textile biofilter can not be considered a replacement for a soil treatment unit.

**Table 23.** Comparison of percent removal of trace organic contaminants from septic tank effluent (STE) through textile biofilter treatment or 60 cm of soil. [<RL = less than the reporting level. <sup>a</sup> Average NTA removal in high-concentration operational systems.]

Compound	Percent Removal during Treatment of STE	
	Textile biofilter	60 cm of soil
Caffeine	97	<RL (>99)
Triclosan	98	<RL (>99)
EDTA	Negligible	Negligible (50% concentration increase)
NTA	76 <sup>a</sup>	95
NP1EC	92	86
NP1EO	<RL (>63)	<RL (>63)
NP	50	Negligible (>200% concentration increase)

### 7.2.3 Recalcitrant Compounds

Compounds that are not removed by volatilization, sorption, or biotransformation are expected to persist through OWTS. For example, the primary removal mechanism of EDTA is photolysis, which is not relevant in the vast majority of OWTS, and EDTA persisted at concentrations similar to input concentrations through engineered treatment and soil treatment (under acidic or neutral conditions).

“Removal” from the aqueous phase can be different from “treatment” of an organic compound. “Removal” may be a phase transfer (i.e. volatilization into the gaseous phase), a chemical transfer (i.e. adsorption to soil), or a biological transfer (i.e. to a degradation product), while “treatment” can refer to complete mineralization of a compound (i.e. conversion to carbon dioxide and water). In some cases, a biological transfer may result in the accumulation of a more toxic degradation product. For example, while moderate removal (25-75%) by sorption of NP is predicted (Category 4, Figure 17, Table 22), actual concentrations of NP increased 200 to 500% during shallow soil treatment at the Mines Park Test Site. This is likely due to the biotransformation of NP1EC and other NPEs to NP at a greater rate than the biotransformation and/or sorption of NP to organic matter. The results suggest that effective treatment of

NPEs during onsite treatment may require an alternative treatment design. One possible design might utilize an anaerobic septic tank followed by an aerobic bioreactor (to convert all NPE to NP1EC) which discharges into a second anaerobic septic tank with an extended hydraulic residence time and an abundance of solids (to convert all NP1EC to NP with subsequent sorption to the organic matter) prior to discharge to the soil (where final sorption of NP occurs near the biofilm). Prior to implementation of OWTS design changes for individual chemicals, however, a management strategy should also consider loading to and additional treatment during ground water recharge and the exposure pathways and effect levels.

### **7.3 Mass Loading to Receiving Environments**

While OWTS can be effective in reducing septic tank wastewater concentrations of trace organic contaminants by greater than 95%, some contaminants can persist in measureable concentrations during transport through 120 and 240 cm of sandy loam soil (Table 24). Therefore, receiving environments such as ground waters located 240 cm or less below the infiltrative surface may be impacted by some trace organic contaminants originating from a typical OWTS. In Colorado and many other U.S. states, the minimum required distance to ground water is 120 cm below the infiltrative surface of an onsite soil treatment unit. EDTA, NP, and NP1EC were regularly measured in soil solution 120 cm below the infiltrative surface of a typically operated (HLR = 2 cm/d) residential OWTS at concentrations around 1, 4, and 4 µg/L, respectively, indicating their potential to reach shallow ground water. Soil treatment units loaded at a typical HLR (2 cm/d) can maintain a long-term acceptance rate high enough to hydraulically process all effluent applied, as was seen in the Mines Park test cells after three years of operation. Mass loading rates to the underlying ground water were estimated assuming that all of the volume applied to the soil infiltrative surface reaches the underlying ground water.

In a household producing 1000 L of wastewater per day (typical of a four-person home) that is treated by an OWTS with an actual HLR of 2 cm/d, daily mass loadings to an underlying ground water 120 cm below the infiltrative surface may reach 1 mg of EDTA, 4 mg of NP1EC, and 4 mg of NP. Potential watershed-scale loading can be estimated assuming this household is located in an OWTS-reliant residential community. For example, in a community with 1000 residences located on 2023 m<sup>2</sup> (0.5 acre) lots that are each served by an OWTS, total daily mass loading to the underlying ground water from the 2.02 km<sup>2</sup> (500-acre) community could reach 1 g of EDTA, 4 g of NP1EC, and 4 g of NP. Other compounds may also persist and reach ground water such as sulfamethoxazole (detected at concentrations up to 4 µg/L in Mines Park soil solution 120 cm BIS) and carbamazepine (Carrara et al. 2008, Godfrey et al. 2007).

**Table 24.** Range of concentrations ( $\mu\text{g/L}$ ) of trace organic contaminants measured in residential OWTS soil solution.  
 [Results from the Mines Park Test Site. HLR = design hydraulic loading rate. BIS = below the infiltrative surface.]

HLR, Effluent	Depth BIS (cm)	Caffeine	Triclosan	EDTA	NTA	NP1EC	NP1EO	NP
2 cm/d STE	60	<0.2	<0.2 - 0.23	29 - 40	<0.02 - 0.24	3.0 - 8.0	<1.0	5.7 - 14
	120	<0.2	<0.2	0.27 - 1.5	<0.02 - 0.14	3.6 - 6.7	<1.0	2.2 - 8.9
	240	<0.2	<0.2	<0.1 - 0.59	<0.02	4.9 - 7.2	<1.0	2.1 - 2.6
8 cm/d STE	60	<0.2	<0.2	47 - 89	<0.02 - 0.04	4.3 - 4.5	<1.0	5.0 - 14
	120	<0.2	<0.2	11 - 41	<0.02 - 0.12	4.9 - 5.2	<1.0	4.3 - 5.4
	240	<0.2	<0.2	0.72	0.02	2.2	<1.0	2.7 - 4.1
2 cm/d TFE	60	<0.2	<0.2	22 - 43	<0.02 - 1.4	4.6 - 13	<1.0 - 1.8	2.1 - 17
	120	<0.2	<0.2	0.79 - 5.3	<0.02 - 0.12	1.2 - 7.7	<1.0	2.1 - 11
	240	<0.2	<0.2	0.10 - 0.29	<0.02	4.4 - 5.5	<1.0	2.1 - 2.3
8 cm/d TFE	60	<0.2	<0.2	66	0.06 - 0.12	4.2 - 5.3	<1.0	6.3 - 8.6
	120	<0.2	<0.2	34 - 37	<0.02 - 0.06	2.2 - 3.9	<1.0	7.6 - 12
	240	<0.2	<0.2	0.47 - 2.4	<0.02	3.8 - 4.5	<1.0	2.3 - 3.3

Actual mass loading to receiving environments may be less than the calculated loading based on a number of real conditions that may differ from the assumptions above. The average number of people per U.S. home is between two and three rather than four, so the average volume of effluent produced per household may be lower. Some volume losses may occur during soil infiltration (Paul et al. 2007), reducing the recharge volume. Treatment within a different soil, such as a high organic carbon soil, may be greater due to additional sorption and biotransformation. An increased vadose zone residence time may allow for removal processes (i.e. volatilization, sorption, biotransformation) to occur to a greater extent. The ground water table is often much deeper than the required 120 cm BIS. OWTS use in low-density regions as compared to the example 1000-residence community is common, resulting in lower watershed-scale loadings.

Conversely, potential impacts to the underlying ground water may be greater than those calculated above. High water table levels in coastal areas may be near the ground surface. All of the target compounds (except caffeine) were detected at least once in Mines Park soil solution 60 cm BIS, and concentrations of EDTA reached 89 µg/L (in a soil test cell receiving 8 cm/d of TFE). In a system with different soil conditions (e.g. higher hydraulic conductivity, lower organic carbon content) and 60 cm or less of unsaturated soil, faster travel times to the underlying ground water may result in higher mass loadings.

## **7.4 Exposure Pathways and Effects**

Regardless of loading rates to the environment, adverse effects on organisms can only occur through exposure to a contaminant. Two exposure pathways- encompassing the aquatic environment and the particulate-bound fraction- are presented, and potential effects are discussed.

### **7.4.1 Aquatic Environment**

OWTS effluents recharge the local receiving environment which is often the underlying ground water. The ground water, in turn, may supply water to the local population and/or feed nearby surface waters. Exposure of humans to pathogenic organisms present in drinking water obtained from a ground water supply well is often a primary concern regarding the design and performance of OWTS. The effects of trace organic contaminants, such as endocrine disrupting compounds, on humans are complex to understand and currently unknown, therefore the risk to humans is also unknown.

Surface water/ground water interactions may be especially important in regions where concentrated OWTS are located near streams. Shallow ground water can discharge to streams within 5 years of recharge (Szabo et al. 1996, Modica et al. 1998), a time frame that may not be adequate for degradation of some recalcitrant compounds. Exposure to NP can disrupt the normal function of the endocrine system of aquatic organisms, as measured with indicators such as an increase in plasma vitellogenin levels, though there is variability in the literature regarding the lowest no-effect concentration. Current literature suggests that concentrations around 10 µg/L have adverse effects (Knoebl et al. 2004, Hemmer et al. 2001, Jobling et al. 1996), though one study reported effects from exposure to concentrations of NP as low as 2 µg/L (Zha et al. 2007). NP1EO and NP1EC have similar estrogenic potencies as NP (Routledge and Sumpter 1996). The EPA has established toxicity-based water quality criteria for NP (USEPA 2005), with the 4-day average concentration in freshwater systems not to exceed 6.6 µg/L. No water quality criteria have been established for NP in ground water and no U.S. endocrine disruption-based water quality criteria have been established for trace organic contaminants, though there is an awareness of the need (USEPA 2008).

To assess potential effects, three exposure scenarios are considered by varying the Dilution Attenuation Factor, DAF (USEPA 1996), which is the ratio of the trace organic contaminant concentration in soil solution to its concentration at the point of exposure from recharged ground water and/or surface water. In the first scenario (worst-case), the shallow ground water (i.e. 120 cm BIS) recharged by OWTS effluent directly supplies a nearby well or surface water with short travel times and/or minimal additional treatment within the aquifer. For example, compounds have the potential to persist during anaerobic ground water transport (Ying et al. 2008, Ahel et al. 1996) at concentrations similar to or higher than those in the septic tank effluent (Swartz et al. 2006). Under these conditions, a DAF of 1 is assumed, and concentrations measured in OWTS soil solution (e.g. up to 14 µg/L NP and up to 8 µg/L NP1EC) could persist in ground water or surface water. At these concentrations, some effects on exposed aquatic organisms could occur.

In a second scenario (best-case), drinking water wells and surface waters are supplied by an aquifer that is not in the OWTS effluent recharge zone. Under these conditions with no direct hydrologic connection, the DAF is not relevant, and no impacts from OWTS in ground waters supplying wells or surface waters is expected, resulting in no adverse effects on exposed organisms.

In a third scenario (real-world), supply wells and/or surface waters are located some distance down gradient of the OWTS (e.g. 100 ft. and 50 ft., respectively, as per Colorado regulations). Once the OWTS-derived compounds reach ground water, their concentrations can be further reduced by dilution and mixing during recharge and through sorption and aerobic biotransformation (Ying et al. 2008, Ahel et al. 1996), resulting in a DAF greater than 1. Under these conditions, concentrations that are lower than

soil solution concentrations are expected in ground water and surface water. For example, assuming a DAF of 10 results in NP concentrations of 1.4 µg/L or less in ground water or surface water at the point of exposure. NP concentrations were <2 µg/L in Mines Park ground water located 360 to 680 cm BIS and 0 to 100 m away from the soil test cells. At these levels, no adverse effects on exposed populations are expected to occur.

To complicate the issue, however, studies have indicated an additive effect from multiple endocrine disruptors, including several of the compounds studied here, even when individual compound concentrations were below an observed effect level (Brian et al. 2007, Brian et al. 2005). Conversely, low concentrations of NP (5 µg/L) had a positive effect on reproductive behavior, as evidenced by an increase in nest-holding ability of exposed fathead minnows, while exposure to higher levels of alkylphenolic mixtures had negative effects (Bistodeau et al. 2006). The assessment of potential adverse effects on human and aquatic organisms from trace organic contaminants in OWTS will continue to evolve as the assessment of acute and chronic effects from individual compounds and mixtures of compounds on ecosystems and humans evolves.

#### **7.4.2 Particulate-Bound Fraction**

A secondary concern regarding trace organic contaminant occurrence in onsite systems is associated with the accumulation of parent compounds or their metabolites on septic tank solids and soil surfaces. Septic tank solids from five reconnaissance survey sites contained concentrations of 34 trace organic contaminants, including NP, NP1EO, and triclosan at concentrations up to 1,800,000 µg/kg, 44,000 µg/kg, and 19,000 µg/kg, respectively. Septic tank solids are periodically pumped and treated for discharge to a landfill or for use as biosolids. Biosolids that can be land-applied have the potential to impact nearby surface waters through overland transport.

Trace organic contaminant removal from soil solution may be through hydrophobic partitioning onto soil organic matter surfaces, resulting in the accumulation of hydrophobic compounds in the subsurface. In biosolid-amended agricultural soil (Kinney et al. 2008), trace organic contaminants including NP and triclosan that were present in the soil also bioaccumulated in terrestrial organisms (earthworms). Of 77 target compounds, triclosan had the highest bioaccumulation factor (BAF = 27). The movement and bioaccumulation of trace organic contaminants from soil surfaces and land-applied biosolids to earthworms up the food chain to birds, mammals, reptiles, and fish may present an additional exposure pathway, the effects of which are currently unknown.

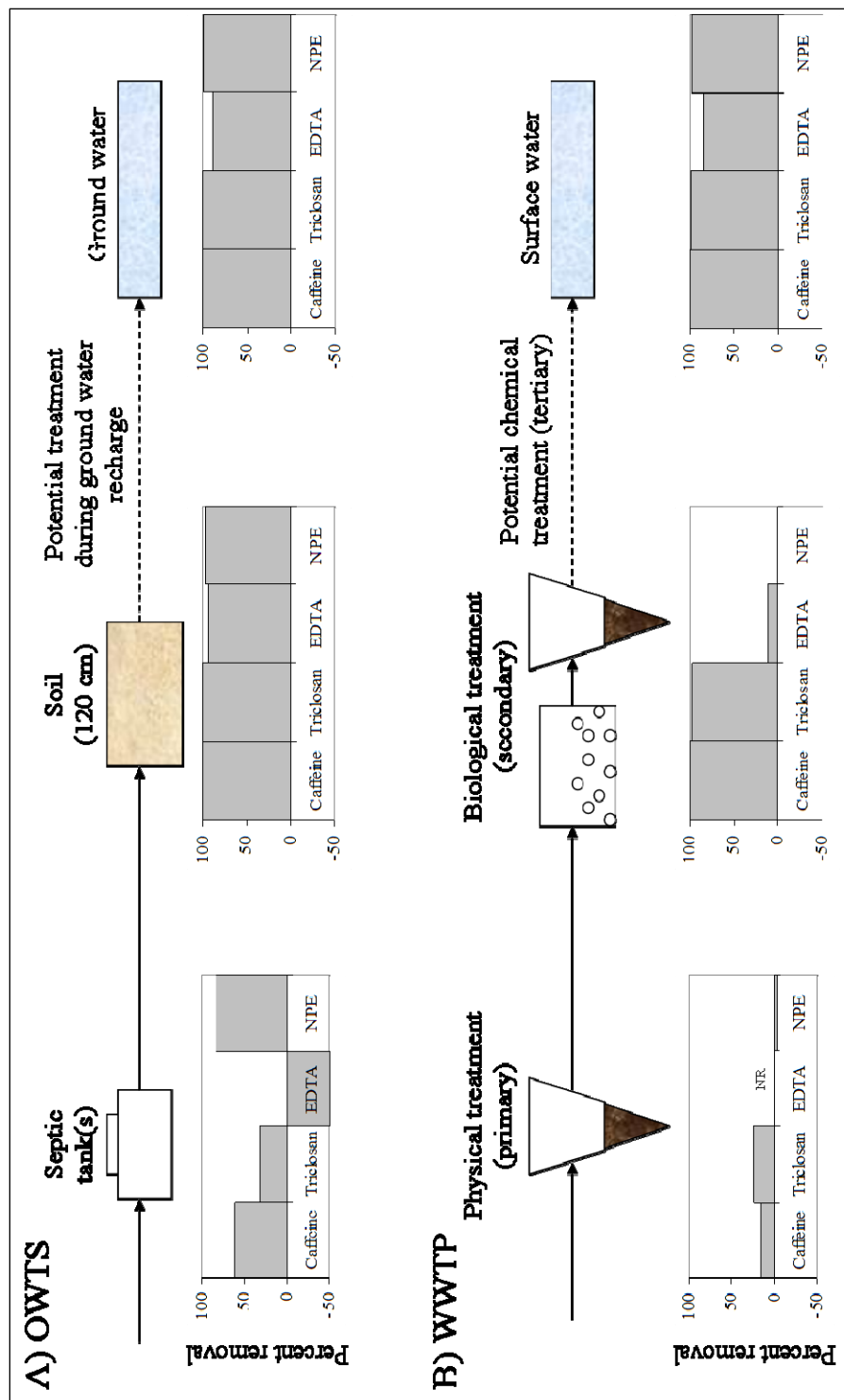
## 7.5 Comparison to WWTP

Removals of select trace organic contaminants during treatment in an OWTS were compared to WWTP removal efficiencies reported in the literature. Included studies measured aqueous concentrations in the influent, after primary treatment, and after secondary treatment in the WWTP and in downstream surface water (caffeine: Thomas and Foster 2005; EDTA: Kari and Giger 1996, Barber et al. 2000; NPE: Ahel et al. 1987, Ahel et al. 1994, Barber et al. 2000). Percent removals from the influent concentrations were calculated and compared to the percent removals in an OWTS including those achieved during septic tank treatment, soil treatment, and ground water recharge.

In general, removal during onsite treatment is similar to removal during municipal treatment (Figure 18). Septic tank treatment, though anaerobic, is similar to aerobic primary treatment in a centralized plant which utilizes physical separation and settling for removal (note that the high removal of NP1EC during septic tank treatment may be an anomaly of the Mines Park Test Site). Treatment during the soil vadose zone is similar to secondary biological treatment in a centralized plant which enables volatilization, sorption, and aerobic biotransformation. In some cases, greater removal may occur during soil treatment than during secondary treatment (e.g. biodegradation of EDTA in deep alkaline soils or greater NPE removal due to transformation of the aerobic degradation product NP1EC to NP and subsequent sorption during soil treatment). Additional treatment generally occurs in both systems before and during recharge of the local receiving environment. A WWTP may employ tertiary chemical treatment prior to effluent discharge and additional removal may occur in the deep vadose zone below an OWTS prior to reaching the ground water table. Dilution will occur during recharge of the receiving environment (either ground water or surface water) and additional treatment may occur during transport, such as sorption to stream or aquifer sediments. Compared to influent concentrations from both a WWTP and an OWTS, receiving environment concentrations were less than 5% of influent wastewater concentrations for caffeine, triclosan, and NPE, and for EDTA, concentrations were typically <15% of influent concentrations.

While there is uncertainty associated with these calculations based on differing influent wastewater compositions and analytical methodologies, this exercise portrays the ability of an OWTS to remove trace organic contaminants from the influent wastewater as well or better than a municipal WWTP. Exposure of aquatic organisms to trace organic contaminants in WWTP effluents may occur immediately since the effluent is most commonly discharged directly into the surface water where organisms live. In contrast, most OWTS discharge to ground water, which may ultimately recharge surface waters, thus providing a barrier between the effluent and the primary exposed population.





**Figure 18.** Comparison of A) onsite wastewater treatment system (OWTS) and B) centralized wastewater treatment plant (WWTP) removal efficiencies for select trace organic contaminants. [NPE = sum of NP + NP1EO + NP1EC. Data: OWTS (this research), WWTP caffeine and triclosan (Thomas and Foster 2005), EDTA (Kari and Giger 1996, Barber et al. 2000), NPE (Ahel et al. 1987, Ahel et al. 1994, Barber et al. 2000)].

## 7.6 Risk Reduction through Effective Management

In summary, results from this research suggest that a conventional OWTS including a septic tank(s) and soil treatment unit can provide good treatment (>90%) of many trace organic contaminants. Therefore, many currently operating systems may be removing trace organic contaminants even though they were not specifically designed for that purpose. The results suggest that additional engineered treatment units such as a textile biofilter are not necessary when appropriate soil and site conditions are available, though engineered treatment units may be useful when limiting conditions exist (e.g., shallow ground water). Removal of more recalcitrant compounds, such as NP, may require additional treatment units within an OWTS to reduce concentrations by 90% or more. However, under many conditions, additional treatment will occur during ground water recharge and transport, further reducing potential effects on potentially exposed populations. A more quantitative assessment of risk from trace organic contaminants in OWTS will evolve as more is learned regarding the acute and chronic effects and effect levels of trace organic contaminants in exposed populations.

Risk reduction is a multi-tiered strategy to be considered not only by the wastewater treatment system engineer and manager, but also by the chemical manufacturer during consumer product production and by the homeowner/business owner during product selection and during water use activities. Products may be manufactured using less persistent and/or toxic chemicals, such as the use of alcohol ethoxylates rather than alkylphenol ethoxylates in surfactants. Consumers can select household chemicals with less toxic ingredients, and can also minimize chemical use at the source of wastewater generation. If regulations are implemented, they may also reduce risk to receiving environments. For example, a restriction on NPE discharges from an industrial source led to an upgrade of treatment technologies which resulted in decreases in NPE concentrations in the WWTP effluent and in the estrogenic effects on fish in the receiving environment within 1 year of implementation (Sheahan et al. 2002).

The occurrence of trace organic contaminants in OWTS is a function of the wastewater source characteristics as well as the level of treatment performance achieved. While non-residential sources represent a small proportion of onsite systems, they can have specialized chemical and water uses that are reflected in the wastewater composition. Treatment efficiencies are controlled by the physicochemical properties of the compound and the removal mechanisms employed within an engineered or soil treatment unit. As an increasing proportion of the U.S. and global population rely on onsite treatment for long-term wastewater management, often in areas dependent on local ground water resources, understanding the occurrence and fate of trace organic contaminants in OWTS will aid in developing appropriate strategies and measures to minimize public health and environmental impacts.

## **CHAPTER 8**

### **CONCLUSIONS AND RECOMMENDATIONS**

Onsite wastewater treatment systems currently serve approximately one quarter of the U.S. population and a growing proportion of new development in the U.S. and worldwide. These systems treat wastewater near the source through engineered and natural treatment units prior to recharge of the local receiving environment. Often the receiving environment is the underlying ground water which may recharge surface water and/or supply water to the local population. Therefore, effective removal of contaminants during onsite treatment can be critical to ecosystem and human health. While much is known regarding the occurrence and fate of bulk wastewater parameters (e.g., BOD<sub>5</sub>, TSS, N) during onsite treatment, less is known regarding the occurrence and fate of trace organic contaminants, such as pharmaceuticals and consumer product chemicals. These chemicals may disrupt the endocrine system of exposed populations, may stimulate the development of antibiotic resistance in the environment, or may otherwise adversely impact the environment.

The research described in this report was conducted with the goal of improving the current understanding of the occurrence and fate of trace organic contaminants in OWTS. The research involved a reconnaissance field survey of 30 currently operating OWTS in Colorado varying by source and treatment type and 18 receiving environments. Controlled field-scale experimentation was conducted at the Mines Park Test Site to assess fate and variability of trace organic contaminants and surrogates during treatment within engineered unit operations and the soil. Results were integrated into an OWTS design and management strategy specific to trace organic contaminants. The specific objectives of the current research on trace organic contaminants were to: 1) quantify occurrence in OWTS varying by source, 2) assess removal efficiencies during treatment within engineered unit operations, 3) assess removal efficiencies during soil treatment, and 4) provide guidance for design and management of OWTS to minimize potential risk.

#### **8.1 Conclusions**

##### **8.1.1 Objective 1: Occurrence**

- Trace organic contaminants including surfactant metabolites, metal-chelating agents, antimicrobials, stimulants, and deodorizers were present in septic tank wastewaters from OWTS serving a variety of residential and non-residential sources.

- Individual compounds were detected in 0 to 100% of wastewater samples in concentrations ranging from <0.5 µg/L to >1000 µg/L.
- The levels and frequency of occurrence depended on the source, likely due to differences in chemical- and water-using activities. In general, non-residential wastewaters had more trace organic contaminants at higher concentrations than residential wastewaters.
- Individual compounds were detected less frequently ( $\leq 25\%$ ) and at lower concentrations (max = 19 µg/L) in potential receiving environments. (Note: selected sites were in OWTS-reliant regions but hydrologic connections to specific anthropogenic sources were not attempted or made as part of this research.)

### **8.1.2 Objective 2: Engineered Treatment**

- Removal efficiencies of trace organic contaminants during onsite treatment in engineered unit operations (i.e. septic tank, biofilter, or constructed wetland) ranged from <1% to >99%.
- In general, removal efficiencies during septic tank treatment were low (<35%), attributed to hydrophobic sorption to solids with subsequent settling. Therefore, in a conventional onsite system, trace organic contaminants in septic tank effluent could be loaded to the soil at concentrations similar to influent septic tank wastewater concentrations.
- Additional aerobic biofilter-based treatment beyond the traditional anaerobic tank-based treatment enhanced removal for many trace organic contaminants, likely due to volatilization and aerobic biotransformation.
- Compounds that are not hydrophobic, volatile, or biodegradable persisted through onsite engineered unit operations.
- Concentrations of transformation products often increased as parent compounds degraded.

### **8.1.3 Objective 3: Soil Treatment**

- Greater than or equal to 90% removals (or to <RL) of trace organic contaminants from septic tank effluent were achieved:
  - during effluent infiltration and percolation through 60 cm of sandy loam soil, with the exception of EDTA and NP (which both had negligible removals), and
  - during 240 cm of sandy loam soil with the exception of NP (<50% removal).

- Soil solution concentrations at the same depth in the soil profile receiving STE or TFE were similar; therefore soil solution concentrations of trace organic contaminants 60 cm BIS and deeper were not affected by effluent type (e.g. STE vs. TFE).
- Soil solution concentrations at the same depth from test cells receiving a design hydraulic loading rate of 2 vs. 8 cm/d were similar; therefore soil solution concentrations of trace organic contaminants 60 cm BIS and deeper were not affected by design hydraulic loading rate (e.g. 2 vs. 8 cm/d) with the exception of EDTA. A higher HLR resulted in higher soil solution EDTA concentrations at the same depth as compared to a system with a lower HLR.
- With a few exceptions, total mass removals of trace organic contaminants during three years of soil treatment were greater in test cells receiving STE than in those receiving TFE and also greater in test cells receiving a high HLR than in those receiving a typical HLR of the same effluent.

#### **8.1.4 Objective 4: Design and Management Considerations**

- Knowledge of the distribution of water- and chemical-using activities contributing to the wastewater can provide initial information regarding the types and levels of trace organic contaminants that will be present in OWTS wastewater.
- A conventional OWTS (e.g. utilizing septic tank and sandy loam soil treatment) can provide good treatment (>90%) of many trace organic contaminants, even though it was not specifically designed to do so. Therefore, the addition of an engineered treatment unit, such as a textile biofilter, is not pro forma necessary for high removal of trace organic contaminants.
- Removal of trace organic contaminants during onsite treatment may be optimized by a number of design features, such as: 1) increasing the hydraulic and sludge retention time within a septic tank(s), 2) minimizing solids discharge from the tank, 3) applying effluent to the soil at an appropriate HLR (~2 to 4 cm/d) to maintain its infiltrative capacity, and 4) selection of an appropriate soil profile (e.g. sandy loam) with adequate vadose zone depth (e.g., >60 cm) and an appreciable organic carbon content and moderate permeability with sufficient structure for air and water movement.
- While high removal can be achieved during onsite treatment, low levels of some trace organic contaminants can reach ground water that is less than 240 cm below the soil infiltrative surface.
- Under typical conditions, trace organic contaminant concentrations in OWTS effluent will be further reduced during ground water recharge and transport prior to potential exposure through a supply well or surface water, thereby reducing the risk to ecosystem and human health. Risk assessment regarding trace organic contaminants on OWTS will evolve as effects and effect levels of individual compounds and mixtures of compounds are better understood.

## 8.2 Recommendations for Future Research

- Additional source characterization is needed in systems serving non-residential sources that were not included in the current study, such as human medical facilities like dental offices, doctor offices, and elderly care facilities that may have unique water- and chemical-using activities as compared to residential sources.
- Large variations in trace organic contaminant concentrations were found not only between different systems but also within a single system during different sampling events. This is likely due to changing water- and chemical-using activities at the source at different times of the year, as well as differences in system characteristics that may affect treatment. Frequent sampling of a single source over an extended period of time (e.g. one year or more) while monitoring chemical- and water-use at the source would provide additional insight into the expected variability of trace organic contaminants within a single site and the relevant factors affecting this variability.
- Other trace organic contaminants with known or potential adverse effects should be quantified in OWTS wastewaters. For example, some natural and synthetic hormones, such as  $17\beta$ - estradiol, estriol, and  $17\alpha$ -ethynylestradiol, though typically present in wastewaters at concentrations orders of magnitude lower than the range measured in this study, have endocrine disrupting potencies orders of magnitude higher than surfactant metabolites. Quantification of these low-concentration compounds requires additional method development (clean-up step after extraction, derivatization, and often more advanced instrumentation, e.g. GC/MS/MS).
- A textile biofilter can reduce the concentrations of many trace organic contaminants as compared to septic tank effluent concentrations. A number of other engineered unit operations are available, such as single- and multi-pass sand filters, bioreactors, and constructed wetlands, which are designed for bulk parameter removal but may have the added benefit of trace organic contaminant removal. Additional research could compare removal efficiencies of trace organic contaminants in various types of engineered treatment units.
- Controlled laboratory-scale experiments are needed to identify the relevant contributions of specific removal mechanisms during treatment within an engineered unit operation. For example, batch sorption experiments of trace organic contaminants to septic tank solids could identify the relevance of sorption vs. anaerobic biotransformation during tank-based treatment. Controlled laboratory-scale experiments could also determine the primary factors effecting treatment within engineered unit operations. For example, biodegradation rates may vary depending on many conditions, such as effluent concentration, seasonal temperature changes, and redox conditions.

- Controlled laboratory-scale experiments will aid in identifying the relevant contributions of specific removal mechanisms within soil treatment. For example, batch sorption experiments of trace organic contaminants to soil from increasing depths below the infiltrative surface could identify the changes in relevance of sorption vs. biotransformation during soil infiltration treatment.
- The long hydraulic residence time within the sandy loam soil at the Mines Park Test Site resulted in effective treatment of many trace organic contaminants. However, persistence of these trace organic contaminants through other soil systems has been reported. Column experiments comparing removal of organic contaminants from the same effluent through different types of soil (e.g. varying by hydraulic conductivity, organic carbon content, clay content, etc.) is needed to quantify effects on trace organic contaminant removal due to soil properties.
- A comparison of alternative soil treatment units to conventional soil infiltration could identify more appropriate methods for the removal of trace organic contaminants. For example, drip-dispersal networks are installed within the shallow rhizosphere where there may be enhanced microbial activity and higher organic carbon contents as compared to deeper soils.
- Sampling of OWTS effluent and receiving environments with a hydrologic connection is needed to better assess transport and treatment of trace organic contaminants to and within ground water prior to surface water recharge.
- Modeling the fate of trace organic contaminants during onsite treatment and recharge of the receiving environment (with tools such as Hydrus -1D) could aid in extending the Mines Park-specific results to additional locations and conditions.

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