Emerging Contaminants: Occurrence of ECs in Two Virginia Counties Private Well Water Supplies and Their Removal from Secondary Wastewater Effluent

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Abstract (Academic)

Emerging contaminants (ECs) are chemicals such as pharmaceuticals and personal care products that have been detected in various environmental matrices, including drinking water supplies at trace concentrations (ng/L-µg/L or ng/kg-µg/kg). Current wastewater treatment plant technology is largely ineffective at removing ECs. The objectives of this investigation were to: 1) determine the occurrence of ECs in private well water supplies in Montgomery and Roanoke County, VA 2) quantify the concentrations of three ECs in selected private water supplies; 3) examine the relationship between water quality constituents (nitrate, bacteria, pH and total dissolved solids) to EC occurrence in private water supplies; and 4) determine the ability of the MicroEvap^{TM}, a novel wastewater treatment technology, to remove ECs from secondary wastewater effluent. In partnership with the Virginia Household Water Quality Program, 57 private water supplies were sampled and tested for the occurrence of 142 ECs and 43 other water quality constituents. Up to 73 ECs were detected in the sampled private water supplies. Higher numbers of ECs detected in the tested private water supplies were related with nitrate >1 mg/L, total dissolved solids >250 mg/L, and the presence of total coliform bacteria. Results indicate the MicroEvap^{TM} technology had >99% removal effectiveness for all 26 tested ECs from three secondary wastewater effluent. With the increasing detection of ECs in water bodies, it is essential to understand the occurrence of ECs and environmental predictors of EC presence in different water matrices and continue to develop water treatment technology capable of treating wastewater for EC removal.

Abstract (General Audience)

Emerging contaminants (ECs) are compounds intended to improve human and animal well-being, and include pharmaceuticals, personal care products, and human/veterinary antibiotics. ECs have been frequently detected in water resources worldwide including drinking water. The release of ECs from wastewater treatment plant (WWTP) effluent is their primary route into the environment. The inability of most current wastewater treatment technologies to fully remove ECs necessitates further development of technology that can effectively remove ECs. Emerging contaminants such as pharmaceuticals enter WWTPs because the human body does not fully metabolize the compound and the remainder exits in waste. Private well water is largely unregulated and often untreated and has been relatively less evaluated for EC presence in the literature. The objectives of this study were 1) determine the occurrence of ECs in private well water supplies in Montgomery and Roanoke County, VA 2) quantify the concentrations of three ECs in selected private water supplies; 3) examine the relationship between well age and depth and water quality constituents (nitrate, bacteria, pH and total dissolved solids) to EC occurrence in private water supplies; and 4) determine the ability of the MicroEvap^{TM}, a novel wastewater treatment technology, to remove ECs from secondary wastewater effluent. Emerging contaminants were detected in southwest Virginia private well water. Knowing the ECs present in private well water is necessary to allow for eventual human risk assessment of ECs for people consuming the water. The MicroEvap^{TM} was highly effective at EC removal from wastewater with removal rates >99%. The removal of all ECs from wastewater is essential to ensure purified WWTP effluent. The continued detection of ECs and the unknown human health risks from these contaminants in drinking water means ECs are a significant pollution concern that requires continued assessment.

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List of Abbreviations

DWTP	Drinking Water Treatment Plant
EC	Emerging Contaminant
EDC	Endocrine Disrupting Compound
EPA	Environmental Protection Agency
HPLC	High Performance Liquid Chromatography
IRB	Institutional Review Board
MCL	Maximum Contaminant Level
MD	Mass Distribution
MDW	Municipal Drinking Water
MS	Mass Spectrometry
NO_3-N	Nitrate-Nitrogen
PPCP	Pharmaceutical and Personal Care Product
QA/QC	Quality Assurance and Control
RE	Removal Efficiency
SDWA	Safe Drinking Water Act
SPE	Solid Phase Extraction
TDS	Total Dissolved Solids
UPLC	Ultra Performance Liquid Chromatography
UV	Ultra-Violet
VAHWQP	Virginia Household Water Quality Program
WWTP	Wastewater Treatment Plant

Chapter 1 Literature Review

1. Literature Review

1.1 Sources of Emerging Contaminants to the Environment

Emerging contaminants (ECs) are defined as "chemicals that have been detected in various environmental matrices at trace concentrations (i.e. ng/L- µg/L or ng/kg- µg/kg) and for which the risk to human health is not yet known" (US Environmental Protection Agency, 2008). Emerging contaminants are comprised of human and veterinary antibiotics and pharmaceuticals and personal care products (PPCPs), as well as their transformation products (Kolpin et al., 2002; Ternes, 1998). Fire retardants, hormones, plastic nanoparticles, and surfactants can also be considered ECs (Stuart et al., 2011) but are outside the scope of this review. Emerging contaminants are used in various anthropogenic activities including: human and animal medical care, food production, and industrial processes. Research has shown that ECs are not fully attenuated by environmental processes or treatment processes used in wastewater and drinking water treatment plants, so thus, are frequently detected in the environment (Ternes, 1998). Herein lies the concern for biomagnification and unintended impacts on humans and wildlife (Halling-Sorenson et al., 1998).

Human and livestock use are the primary source of ECs into the environment. When pharmaceuticals or antibiotics are taken, they are not fully metabolized by the human or animal body. A mixture of the original compound and/or metabolite(s) (metabolic processing may change the chemical structure of an EC) exit the body in the waste (feces or urine). Human waste is then transferred into a city sewer or a septic system (Kummerer, 2008), and the animal waste may be stored in manure lagoons or pits, or spread on fields for fertilizer. Personal care products such as hand soap, mouth wash, shampoo, and toothpaste are released through the drain after use, entering a city sewer or a septic system (Kummerer, 2008). Livestock antibiotics are also not fully metabolized by animals, so the original compound and/or metabolite(s) are present in their waste. The pharmaceuticals and antibiotics given to household pets (dogs, cats, etc.) can also enter water resources through their waste (Lin and Tsai, 2009). The surfaces of biosolids can adsorb a variety of ECs during wastewater treatment plant (WWTP) treatment (Topp et al., 2008). Biosolids are commonly used as fertilizers for agricultural production, resulting in possible introduction of ECs associated with biosolids into the environment.

1.2 Pathways from Sources of Emerging Contaminants to the Environment

Wastewater effluent is the primary pathway of ECs from human sources to the environment due to the inadequacy of wastewater treatment systems to fully degrade ECs (Benotti et al., 2009b). Stormwater systems and urban runoff also load ECs into surface water (Boyd et al., 2004). Emerging contaminants can also enter surface water bodies through the effluent of hospitals, industrial plants, and pharmaceutical production facilities (Lin and Tsai, 2009). Emerging contaminants can enter groundwater from landfill leachate, septic system leakage, and resource extraction processes such as mining (Seiler et al., 1999). In some large cities, urban stormwater is pumped or slowly infiltrated into groundwater, which can introduce ECs into groundwater (Figure 1.1).

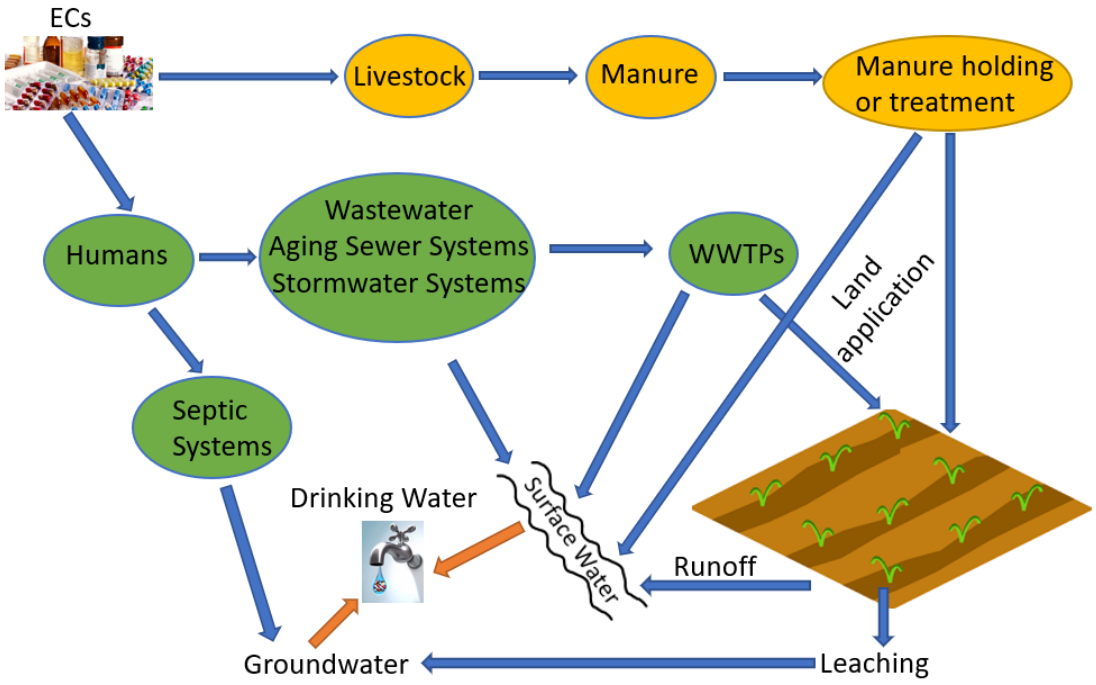


Figure 1.1: Schematic diagram of ECs sources and pathways to the environment.

Agricultural operations are another major pathway of ECs into the environment. The storage of livestock waste (livestock waste lagoons) can breach during large precipitation events, thus releasing ECs into surface water (Mallin et al., 1999). Improper construction of a livestock waste lagoon can lead to seepage of ECs into groundwater (Batt et al., 2006; Mallin et al., 1999). The application of animal manure and biosolids on crop fields as fertilizer can lead to ECs released during runoff events (Figure 1.1; Clarke and Cummins, 2015). If the ECs are not fully degraded, they can leach into the soil or groundwater (Kummerer, 2008).

1.3 Occurrence of Emerging Contaminants in the Aquatic Environment

The first EC, a synthetic estrogen hormone, was detected in the environment in the 1970s and the occurrence was attributed to its ability to withstand biodegradation (Tabak and Bunch, 1970). Research in the occurrence of ECs in the environment, specifically antibiotics and pharmaceuticals, began in the mid-1990s due to the improved understanding of the negative impact of ECs on the environment, and potentially human and ecological health. As of 2018, several hundred investigations worldwide have tested for ECs in various water matrices and over 200 ECs have been detected (Table 1.1; (Kummerer, 2008)) .

Table 1.1: Occurrence, source(s), and pathway(s) of ECs in various water matrices worldwide.

Water Matrix	Locations	Concentration Range of Most Detected Emerging Contaminants (ng/L)	Suspected Sources/Pathways of ECs	Citation
Groundwater	US UK	Acetaminophen (60-1,890) Caffeine (100-290) Carbamazepine (30-214) Sulfamethoxazole (80-170)	Urban runoff, Wastewater effluent	(Fram and Belitz, 2011; Knee et al., 2010; Stuart et al., 2011)
Landfill Leachate	Spain US Denmark	Caffeine (80-140) Cotinine (50-130) DEET (80-13,000) Sulfonamides (20-10,000)	Landfill	(Albaiges et al., 1986; Barnes et al., 2004; Eckel et al., 1993; Holm et al., 1995)
Stormwater	Louisiana Canada	Caffeine (3-53,000) Carbamazepine (1-161) Ibuprofen (3-2,674) Triclosan (1-29)	Urban runoff	(Boyd et al., 2004; Sauve et al., 2012)
Surface Water	US UK Switzerland	Caffeine (7-4,500) Carbamazepine (1-400) Lidocaine (1-400) Metformin (2-2,500)	Urban runoff	(Bartelt-Hunt et al., 2009; Bradley et al., 2016; Hedgespeth et al., 2012; Roberts and Thomas, 2006; Tixier et al., 2003)
Treated and Untreated Drinking Water	Canada Spain US	Acetaminophen (9-40) Caffeine (50-200) Carbamazepine (4-150) Cotinine (15-30)	City sewer systems, Urban runoff	(Benotti et al., 2009b; Radjenovic et al., 2008; Servos et al., 2007;

				Stackelberg et al., 2004)
Treated Wastewater	Germany UK US	Atenolol (100-400) Carbamazepine (250-6,300) Ibuprofen (150-1,600) Metoprolol (730-2,200)	WWTPs effluent	(Hedgespeth et al., 2012; Kostich et al., 2014; Roberts and Thomas, 2006; Ternes, 1998)
Untreated Wastewater	Spain Germany	Bezafibrate (100-1,000) Carbamazepine (50-800) Cotinine (1,050-1,850) Furosemide (100-1,400)	Urban systems	(Hedgespeth et al., 2012; Jelic et al., 2011; Ternes, 1998)

Emerging contaminants are highly variable in their chemical structures, functionality, polarity, and half-life (Kummerer, 2008). Because of this, the occurrence of ECs in water bodies varies greatly from compound to compound. The frequency of usage by humans is a valuable predictor of the occurrence of ECs. However, environmental persistence (resistance to biotic and abiotic degradation and sorption to sediment/soil) is considered the most useful predictor of ECs in water matrices (Benotti et al., 2009b). For example, bench-scale experiments determined the environmental half-life of carbamazepine (an anticonvulsant) is 82 days, 75 days longer than that of atorvastatin (a cholesterol reducing agent), which is the 2016 third most prescribed compound in the US (IQVIA Institute, 2017; Lam et al., 2004). This means even if atorvastatin has a higher input into a water body due to its considerably greater human use, it may break down before it reaches drinking water, whereas carbamazepine, although less-frequently used, may be more often detected in water due to its persistence (Kummerer, 2008). The occurrence of an EC can also depend on other environmental conditions, such as seasonally variable chemical or biological conditions. For example, ivermectin (an antiparasitic) has six times longer half-life in winter conditions compared to summer conditions, and ivermectin degrades more quickly in sandy soils compared to sandy loam soils (Halley et al., 1993).

Emerging contaminants have been primarily studied in surface water bodies and WWTP effluent. The most commonly detected ECs in surface water are acetaminophen (pain reliever),

carbamazepine (anticonvulsant), caffeine (psychoactive drug), cotinine (nicotine metabolite), and metformin (antidiabetic) (Heberer, 2002). The focus on surface water and wastewater stems from the highest concentrations of ECs being detected in wastewater and the greatest mass quantity of ECs detected in surface water (Halling-Sorenson et al., 1998). Emerging contaminants are also detected at trace concentrations in groundwater, though occurrence of ECs in this matrix is less well understood than in surface water (Fram and Belitz, 2011). The most commonly detected ECs in groundwater worldwide have been caffeine, carbamazepine, diclofenac (anti-inflammatory), ibuprofen (pain reliever), and sulfamethoxazole (antibiotic) (Lapworth et al., 2012). The occurrence of ECs in domestic groundwater (better known as private water supply wells) has been less investigated compared to groundwater resources used for municipal water supplies.

1.4 Water Quality and Occurrence of Emerging Contaminants in Private Water Supplies– Existing Information and Knowledge Gap

Approximately 45 million people in the US rely on private water supplies as their primary drinking water source (Benham et al., 2016; Maupin et al., 2010). Private water supplies are most common in rural areas, but are becoming more prevalent in suburban developments. Private water supplies can be more susceptible to water quality issues because they are not required to meet the water quality standards of the US Safe Drinking Water Act (SDWA) (Environmental Protection Agency, 1974). Omitted from the SDWA, private water supplies have no requirement for routine water quality testing or treatment after initial construction in most states (Environmental Protection Agency, 1974). While private water supplies may have some state-level regulations regarding initial construction and location, they have minimal or no water quality testing requirements in most states, including Virginia. Routine maintenance and testing of a private well is the responsibility of the owner. Although private wells may be more susceptible to water quality issues, there are documented cases where they have no water quality issues (Focazio et al., 2006). Overall, private water supplies have a higher susceptibility to water quality problems compared to EPA-regulated municipal water because of the lack of routine testing and mandated treatment to address contamination.

Private water supplies are susceptible to water quality issues from a variety of anthropogenic land uses (Seiler et al., 1999). Agricultural practices can degrade water quality in nearby private water supplies from the over application of fertilizers (nitrogen and phosphorous), pesticides and

manure due to leaching or runoff (Charrois, 2010). For example, in Iowa the water quality of the analyzed shallow (<15 m) private wells near agricultural operations, 35% of wells exceeded 10 mg/L of nitrate (an indicator that other water quality issues may exist) (Charrois, 2010; Kross et al., 1993). Excessive nitrate levels in water consumed by infants can lead to a fatality in extreme cases. In a nation-wide study of over 2,000 private wells, a variety of pesticides (e.g., alachlor, atrazine) were detected in 60% of the wells (DeSimone, 2008). Pesticides can have health impacts including cancer and birth defects (Charrois, 2010). Total coliform bacteria were found in 40-50% of wells in two national water quality investigations of over 2,000 private wells. Total coliform bacteria are not a major health concern but can be an indicator of pathogenic bacteria presence (e.g. *E. coli*, *Shigella*, *Salmonella*). Pathogenic bacteria can cause severe infectious diseases (e.g., tuberculosis, pneumonia) (Charrois, 2010). Programs are available in some states to assist private water supply users with water quality testing and understanding system care and maintenance (Benham et al., 2016).

As of 2018, six investigations that screened for ECs reported detecting them at trace concentrations (ng/L-µg/L) (Table 1.2). One that study screened for selected ECs tested 17 private wells in 10 states and Puerto Rico (Focazio et al., 2008). The other five investigations analyzed for ECs in specific areas, including rural Idaho, coastal Massachusetts, urban Minnesota, urban Nebraska, and urban Nevada (Batt et al., 2006).

Table 1.2: Occurrence and source(s) of ECs in the US private well water.

Emerging Contaminants (ECs) Detected/Screened	Location	No. of Private Wells	Concentration Range of Most Detected ECs (ng/L)	Suspected Sources/Pathways of ECs	Citation
2/2	Weiser, ID	6	Sulfadimethoxine (46-68) Sulfamethazine (76-220)	Livestock waste	(Batt et al., 2006)
38/127	Urban MN	118	Azithromycin (5-23) Diphenhydramine (16-58) Sulfamethoxazole (5-171)	Landfill, Septic	(Erickson et al., 2012)
25/100	48 US states & Puerto Rico	17	Caffeine (N/A) Carbamazepine (N/A)	Human waste, Livestock waste	(Focazio et al., 2008)
27/121	Cape Cod, MA	20	Acesulfame (42-5300) Carbamazepine (1-62) Sulfamethoxazole (1-60)	Septic	(Schaider et al., 2011)
4/4	Reno, NV	6	Caffeine (1-230) Carbamazepine (N/A)	Septic	(Seiler et al., 1999)
14/60	Omaha, NE	26	Acetaminophen (9-15) Caffeine (14-120) Caffeine Metabolite (19-22)	Septic	(Verstraeten et al., 2005)

The most commonly detected ECs in US private well water have been caffeine, carbamazepine, and sulfamethoxazole (antibotic), based on studies conducted thus far (Table 1.2). There is evidence that septic systems are a source of ECs in private well water from the positive correlation of ECs with boron, dissolved organic carbon (DOC), fecal bacteria, and nitrate (indicators of septic contamination) that were also present in the water (Verstraeten et al., 2005). Concentrated animal feeding operations in Idaho were a possible source of cattle antibiotics detected in these systems (Batt et al., 2006). Cotinine (metabolite of nicotine) and DEET (insect repellant) were detectected in landfill leachate plumes contaminating groundwater supply wells in Norman, OK (Barnes et al., 2004). Further exploration of the occurrence of ECs in private well water is necessary to better understand presence of these compounds and associated human exposure.

1.5 Impacts of Emerging Contaminants on Environmental and Human Health

As of April 2018, the US EPA regulates a select number of ECs in drinking water. Of the 142 ECs analyzed in this investigation, only one, atrazine (a corn pesticide) is currently regulated by the EPA primary water quality standards. Erythromycin (an antibiotic) is under consideration for water quality regulation and is currently on the contaminant candidate list 3. The EPA regulation contaminant candidate process considers a few new contaminants for regulation every five years, making it challenging to account for potentially hundreds or even thousands of ECs that currently exist. The lack of a treatment technique that can fully remove ECs and the difficulty of analyzing for them makes it challenging for the EPA to regulate them. ECs are also a lesser concern to the EPA because the concentrations detected in US municipal drinking water are typically significantly lower than a daily dosage of a compound (Kim and Aga, 2007). For example, it would take over 76,000 years to receive a daily dosage (1000 mg) of carbamazepine from drinking 2 L of US municipal drinking water a day based on its current detected concentrations (Benotti et al., 2009b). ECs are not historically considered contaminants of concern to the extent that they are regulated in municipal water supplies, but garner increased attention due to documented ecological impacts and potential impacts on human health.

EC occurrence in the environment poses risks to wildlife, primarily from low dosage bioactivity being misdirected on non-target organisms (Kummerer, 2008). ECs typically do not have health-based guidelines by the EPA, but some state environmental agencies do have guidelines. Even though most antibiotics and PPCPs are used for therapeutic uses, their presence

in water still poses an unknown risk. Some ECs are endocrine disrupting compounds (EDCs) that are designed to alter hormones, and they can indirectly disrupt the hormone operations of an organism (Markman et al., 2011). The risks and effects of metabolites and transformation products of ECs has not been well documented in the literature. If multiple ECs are present in water, possible unintended interactions could occur posing a potential higher risk. The environmental persistence, concentration, and the toxicity of an EC determines the potential risk to non-target organisms.

Several studies have documented the impact of ECs on wildlife, primarily focusing on aquatic organisms. Serious wildlife impacts are due mainly to spills rather than environmental background levels (Arnold et al., 2014). ECs have impacted the predator-prey relationship and reproductive functions in aquatic organisms. For example, waters spiked with fluoxetine (antidepressant) reduces the instinctive aggression used by Siamese fighting fish to ward off predation of their eggs (Arnold et al., 2014; Dzieweczynski and Hebert, 2012). A spill of synthetic estrogenic compounds in British Rivers led to feminization of male fish and a similar spill in Connecticut led to feminization of male frogs (Smits et al., 2014; Sumpter, 1995). During lab experiments, fluoxetine was shown to accumulate in the tissues of mussels due to a high bioconcentration factor (ability of a chemical to accumulate in organisms) of fluoxetine (Hazelton et al., 2014). The larger concern with fluoxetine accumulation in mussels is the potential of ECs for biomagnification up the food chain, affecting higher-level biota. Trace concentrations of ciprofloxacin (antibiotic) altered the growth of an aquatic photosynthetic organism (freshwater algae) in a lab setting (Wilson, 2003). Marine organisms have been impacted as well, specifically, the development of a juvenile cuttlefish was altered by fluoxetine in a lab setting (Di Poi et al., 2013)

Most research has concentrated on aquatic organisms but impacts on terrestrial animals have also been reported (Arnold et al., 2014). The proper development of juvenile starlings was altered by EDCs in England. The starlings were exposed to high concentrations of EDCs from their food source (worms) derived from ground adjacent to a sewage treatment plant (Markman et al., 2011). Three *Gyps* vulture populations on the Indian subcontinent were brought to the brink of extinction because of the vultures eating domesticated animal carcasses concentrated with diclofenac (veterinary anti-inflammatory) (Green et al., 2004). The collapse of the *Gyps* vultures caused disruption in their ecosystem due to the absence of the scavenging animal. The

subsequent banning of diclofenac for veterinary usage resulted in the recovery of the *Gyps* vulture population (Prakash et al., 2012). The occurrence of ECs in aquatic systems as well as use in land activities continue to make ECs a concern for terrestrial animals.

There has been no documented evidence of the occurrence of ECs in water bodies affecting human health on a short-term scale (Kummerer, 2008). Human risk assessment empirical models have shown that ECs at current drinking water concentrations likely have a negligible effect on human health (Cunningham et al., 2009). For example, an investigation in coastal Massachusetts analyzed for a connection between a local increase in breast cancer and occurrence of ECs with no conclusive evidence found (Schaider et al., 2011). The mass of antibiotics entering water bodies has been a factor in the increase of antibiotic resistant bacteria and bacterial genes in the environment (Kim and Aga, 2007). A rise in the antibiotic-resistant genes has the potential to cause persistent bacterial infections from these genes being transferred to pathogenic bacteria (Kim and Aga, 2007). Overall, there is a concern that risk of ECs to human health could be amplified by biomagnification in the environment and, in the case of antibiotics, could lead to the rise of resistant bacteria and genes (Kummerer, 2008).

1.6 Water Treatment Technology for Removal of Emerging Contaminants from Wastewater

There is interest in the development of water treatment technology that can effectively remove ECs. The removal efficiencies for treatment techniques vary based on the water chemistry, the maintenance of the treatment system, environmental constraints, and the physiochemical properties of each EC. The chemical characteristics of water that affect removal effectiveness of a treatment systems include the *p*H (can alter the charge of an EC, affecting its transport), water temperature, and organic matter content. For example, the presence of organic matter in water (can be high in wastewater) reduces the removal effectiveness of carbon activated filters by competing for binding sites to the filter (Snyder et al., 2007). The ability of ozonation to remove ECs varied greatly based on the type of water (bank filtrate or lake water), the dosage of ozonation (0.1-2 mg/L), and the ECs present (Huber et al., 2003). The contact time between a treatment system and an EC can have a major influence on the removal efficiency (Huber et al., 2003). An EC with a higher sorption affinity to a filter can prevent other ECs from sorbing (Kummerer, 2008). The physiochemical properties of an EC (polarity, biodegradability, and cation exchange potential) affects how effectively a treatment system removes an EC.

As mentioned previously, most WWTPs and DWTPs are not designed to remove ECs (Benotti et al., 2009b). The fate of an EC during wastewater processing is impacted by the operation and design of a WWTPs treatment systems. Conventional physiochemical and disinfection WWTP treatment mechanisms (e.g., coagulation, flocculation, sedimentation, and chlorination) are generally not effective in removing ECs from wastewater (Gibs et al., 2007; Vieno et al., 2006). Activated sludge, a conventional microbiological treatment, has shown up to 40% EC removal efficiencies through biodegradation and charge exclusion of ECs (Radjenovic et al., 2009). The overall integrity of the microbial community in a WWTP can influence the number of ECs removed. The fate of an EC during wastewater processing is impacted by the operation and design of a WWTPs treatment systems.

Advanced WWTP treatments utilizing carbon activated filters, ultraviolet (UV) light disinfection, and ozonation have shown variable effect on removal of ECs. Carbon activated filters, advanced adsorption treatment, are effective in removing ECs due to their high sorption capacities. Their widespread usage is limited due to high costs (Snyder et al., 2007). UV light systems, an advanced disinfection treatment, uses concentrated UV energy that can degrade some ECs (Kim et al., 2009). In bench-scale experiments, UV light treatment was not highly effective (47% removal) at EC removal but its removal effectiveness increased by 50% when paired with a powerful oxidative agent, hydrogen peroxide (H_2O_2). The presence of a pre-filter to remove particulates before UV disinfection and the UV dosage influences the effectiveness of a UV system (Kim et al., 2009). Ozonation, an advanced oxidation treatment, reduced occurrence of ECs by 61% through oxidation. When paired with another strong oxidizer, hydrogen peroxide, the removal efficiency increased by 30% (Huber et al., 2003). Nanofiltration and reverse osmosis (pressure-driven membrane purification processes) design is capable of micro-contaminant removal, so are of interest for EC removal. In a drinking water treatment plant (DWTP) study, UV light pre-treated samples were processed through nanofiltration (82% removal effectiveness) and reverse osmosis membranes (90% removal effectiveness). Nanofiltration and reverse osmosis membranes remove ECs from water through charge and size exclusion properties (Radjenovic et al., 2008).

Unconventional water treatment technology could be an effective solution to account for the chemical heterogeneity of ECs. Natural clay minerals (e.g., goethite, montmorillonite, zeolite) are a viable option because they exclude positively charged compounds (common charge

of ECs in normal water pH (6-8) with its charge exclusion properties. Natural clay minerals removed >88% of ECs in bench-scale experiments (Grassi et al., 2012). Natural clay minerals could be effective practical EC treatment technique because of their relatively low cost, abundance, and high sorption capacity (Grassi et al., 2012). Agricultural waste (plant materials and sawdust) and industrial waste material (fly ash and sludge) could be reutilized as carbon activated filters. These type of carbon activated filters have yet to be tested for EC removal efficiency (Grassi et al., 2012). Membrane bioreactors (the pairing of nano-filtration technology with activated sludge principles) have greater bacterial retention times than activated sludge and improved filtration (Radjenovic et al., 2009). Membrane bioreactors have shown a 15% greater EC removal efficiency compared to activated sludge. The membrane bioreactor is a more realistic biological degradation option due to its comparatively lower costs (Radjenovic et al., 2009). Nano-scale zero valent iron particles are a promising approach to EC removal due to its ability to remove metronidazole (antibiotic) during bench-scale experiments (Fang et al., 2011). Titanium dioxide (emerging photocatalytic treatment) is another promising approach and titanium dioxide paired with hydrogen peroxide was able to remove 70% of 32 target ECs in bench-scale experiments (Benotti et al., 2009a).

2. Objectives

This literature review identifies the need to document the occurrence of ECs in private well water. The ability to quickly a screen large number of ECs (142) is a novel aspect of this investigation that sets it apart from previous investigations, which will provide a detailed look into a variety of ECs present in select Virginia private well water and for comparison, several nearby municipal water samples. The objectives of this investigation were: 1) determine the occurrence of ECs in private well water supplies in Montgomery and Roanoke County, VA 2) quantify the concentrations of three ECs in selected private water supplies; 3) examine the relationship between well age and depth and water quality constituents (nitrate, bacteria, pH and total dissolved solids) to EC occurrence in private water supplies. The literature review also identifies the need for exploration into potential EC water treatment technologies. Through partnering with Micronic, we tested a novel wastewater purification technology, the MicroEvap^{TM} (Aerial 2.0 system, Micronic Technologies, Wise, VA). Based on the MicroEvap^{TM} treatment technique, it has the potential to remove all ECs. These investigations will help bridge the knowledge gap of what compounds occur in private well water and if ECs

can be effectively removed by a wastewater treatment technology. The objectives of the MicroEvap^{TM} investigation was to determine 1) the occurrence of 36 ECs in southwest Virginia WWTP secondary wastewater effluent; 2) determine the ability of the MicroEvap^{TM}, a novel wastewater treatment technology, to remove ECs from secondary wastewater effluent.

3. References

Albaiges J., Casado F., Ventura F. (1986) Organic Indicators of Groundwater Pollution by a Sanitary Landfill Water Resources 20:7.

Arnold K.E., Brown A.R., Ankley G.T., Sumpter J.P. (2014) Medicating the environment: assessing risks of pharmaceuticals to wildlife and ecosystems. Philosophical Transactions of the Royal Society B: Biological Sciences 369.

Barnes K.K., Christenson S.C., Kolpin D., Focazio M.J., Furlong E.T., Zaugg S.D., Meyer M., Barber L.B. (2004) Pharmaceuticals and Other Organic Waste Water Contaminants Within a Leachate Plume Downgradient of a Municipal Landfill Groundwater Monitoring and Remediation 24:8.

Bartelt-Hunt S.L., Snow D.D., Damon T., Shockley J., Hoagland K. (2009) The occurrence of illicit and therapeutic pharmaceuticals in wastewater effluent and surface waters in Nebraska. Environ Pollut 157:786-91.

Batt A.L., Snow D.D., Aga D.S. (2006) Occurrence of sulfonamide antimicrobials in private water wells in Washington County, Idaho, USA. Chemosphere 64:1963-1971.

Benham B., Ling E., Ziegler P., Krometis L.A. (2016) What's in Your Water? Development and Evaluation of the Virginia Household Water Quality Program and Virginia Master Well Owner Network. Journal of Human Sciences and Extension 4:15.

Benotti M.J., Stanford B.D., Wert E.C., Snyder S.A. (2009a) Evaluation of a photocatalytic reactor membrane pilot system for the removal of pharmaceuticals and endocrine disrupting compounds from water. Water Res 43:1513-22.

Benotti M.J., Trenholm R.A., Vanderford B.J., Holady J.C., Stanford B.D., Snyder S.A. (2009b) Pharmaceuticals and Endocrine Disrupting Compounds in U.S. Drinking Water. Environmental Science & Technology 43:597-603.

Boyd G.R., Palmeri J.M., Zhang S., Grimm D.A. (2004) Pharmaceuticals and personal care products (PPCPs) and endocrine disrupting chemicals (EDCs) in stormwater canals and Bayou St. John in New Orleans, Louisiana, USA. Sci Total Environ 333:137-48.

Bradley P.M., Journey C.A., Button D.T., Carlisle D.M., Clark J.M., Mahler B.J., Nakagaki N., Qi S.L., Waite I.R., VanMetre P.C. (2016) Metformin and Other Pharmaceuticals Widespread in Wadeable Streams of the Southeastern United States. Environmental Science & Technology Letters 3:243-249.

Charrois J.W.A. (2010) Private drinking water supplies: challenges for public health. CMAJ : Canadian Medical Association Journal 182:1061-1064.

Cunningham V.L., Binks S.P., Olson M.J. (2009) Human health risk assessment from the presence of human pharmaceuticals in the aquatic environment. Regul Toxicol Pharmacol 53:39-45.

DeSimone L.A. (2008) Quality of Water from Domestic Wells in Principal Aquifers of the United States,1991–2004, US Department of the Interior

US Geological Survey, Reston, VA. pp. 127.

Di Poi C., Darmaillacq A.S., Dickel L., Boulouard M., Bellanger C. (2013) Effects of perinatal exposure to waterborne fluoxetine on memory processing in the cuttlefish Sepia officinalis. Aquat Toxicol 132-133:84-91.

Eckel W.P., Ross B., Isensee R.K. (1993) Pentobarbital Found in Ground Water. Ground Water 31:4.

Environmental Protection Agency. (1974) Safe Water Drinking Act, in: U. Congress (Ed.), Washington DC.

Erickson M., Langer S., Roth J., Kroening S. (2012) Contaminants of Emerging Concern in Ambient Groundwater in Urbanized Areas of Minnesota, 2009-12, in: USGS (Ed.). pp. 38.

Fang Z., Chen J., Qiu X., Qiu X., Cheng W., Zhu L. (2011) Effective removal of antibiotic metronidazole from water by nanoscale zero-valent iron particles. Desalination 268:60-67.

Focazio M.J., Kolpin D.W., Barnes K.K., Furlong E.T., Meyer M.T., Zaugg S.D., Barber L.B., Thurman M.E. (2008) A national reconnaissance for pharmaceuticals and other organic wastewater contaminants in the United States--II) untreated drinking water sources. Sci Total Environ 402:201-16.

Focazio M.J., Tipton D., Shapiro S., Geiger L. (2006) The Chemical Quality of Self-Supplied Domestic Well Water in the United States. Ground Water Monitoring and Remediation 26:13.

Fram M.S., Belitz K. (2011) Occurrence and concentrations of pharmaceutical compounds in groundwater used for public drinking-water supply in California. Sci Total Environ 409:3409-17.

Gibs J., Stackelberg P.E., Furlong E.T., Meyer M., Zaugg S.D., Lippincott R.L. (2007) Persistence of pharmaceuticals and other organic compounds in chlorinated drinking water as a function of time. Sci Total Environ 373:240-9.

Grassi M., Kaykioglu G., Belgiorno V., Lofrano G. (2012) Removal of Emerging Contaminants from Water and Wastewater by Adsorption Process:15-37.

Halley B.A., VandenHueval W., Wislocki P.G. (1993) Environmental effects of the usage of avermectins in livestock. Veterinary Parasitology 48:16.

Halling-Sorenson B., Nielsen S., Lanzky P.F., Ingerslev F., Lutzhoft H.C., Jorgensen S.E. (1998) Occurrence, Fate and Effects of Pharmaceutical Substances in the Environment- A Review. Chemosphere 36.

Heberer T. (2002) Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: a review of recent research data. Toxicology Letters 131:13.

Hedgespeth M.L., Sapozhnikova Y., Pennington P., Clum A., Fairey A., Wirth E. (2012) Pharmaceuticals and personal care products (PPCPs) in treated wastewater discharges into Charleston Harbor, South Carolina. Sci Total Environ 437:1-9.

Holm J., Rugge K., Bjerg P., Christenson T. (1995) Occurence and Distribution of Pharmaceutical Organic Compounds in the Groundwater Downgradient of Landfill Environmental Science & Technology 29:6.

Huber M.M., Canonica S., Park G.-Y., Gunten U.V. (2003) Oxidation of Pharmaceuticals during Ozonation and Advanced Oxidation Processes. Environmental Science & Technology 37:9.

IQVIA Institute. (2017) Medicines Use and Spending in the U.S.: A Review of 2016 and Outlook to 2021, IQVIA Institute, Parsippany, NJ.

Jelic A., Gros M., Ginebreda A., Cespedes-Sanchez R., Ventura F., Petrovic M., Barcelo D. (2011) Occurrence, partition and removal of pharmaceuticals in sewage water and sludge during wastewater treatment. Water Res 45:1165-76.

Kim I., Yamashita N., Tanaka H. (2009) Performance of UV and UV/H2O2 processes for the removal of pharmaceuticals detected in secondary effluent of a sewage treatment plant in Japan. J Hazard Mater 166:1134-40.

Kim S., Aga D.S. (2007) Potential ecological and human health impacts of antibiotics and antibiotic-resistant bacteria from wastewater treatment plants. J Toxicol Environ Health B Crit Rev 10:559-73.

Knee K.L., Gossett R., Boehm A.B., Paytan A. (2010) Caffeine and agricultural pesticide concentrations in surface water and groundwater on the north shore of Kauai (Hawaii, USA). Mar Pollut Bull 60:1376-82.

Kolpin D.W., Furlong E.T., Meyer M., Thurman E.M., Zaugg S.D., Barber L.B., Buxton H.T. (2002) Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams,1999-2000: A National Reconnaissance. Environmental Science & Technology 36:10.

Kostich M.S., Batt A.L., Lazorchak J.M. (2014) Concentrations of prioritized pharmaceuticals in effluents from 50 large wastewater treatment plants in the US and implications for risk estimation. Environmental Pollution 184:354-359.

Kross B., Hallberg G., Bruner R., Cherryholmes K., Johnson K. (1993) The Nitrate Contamination of Private Well Water in Iowa. American Journal of Public Health 83:3.

Kummerer K. (2008) Pharmaceuticals in the Environment--A Brief Summary Springer

Lam M., Young C., Brian R., Johnson D., Hanson M., Wilson C., Richards S., Solomon K., Mabury S. (2004) Aquatic Peristence of Eight Pharmaceuticals in Microosm Study Environmental Toxicology and Chemistry 23:10.

Lapworth D.J., Baran N., Stuart M.E., Ward R.S. (2012) Emerging organic contaminants in groundwater: A review of sources, fate and occurrence. Environ Pollut 163:287-303.

Lin A.Y., Tsai Y.T. (2009) Occurrence of pharmaceuticals in Taiwan's surface waters: impact of waste streams from hospitals and pharmaceutical production facilities. Sci Total Environ 407:3793-802.

Mallin M.A., Posey M.H., Shank G.C., McIver M.R., Ensign S.H., Alphin T.D. (1999) Hurricane Effects on Water Quality and Benthos in the Cape Fear Watershed: Natural and Antrhopogenic Effects Ecological Society of America 9:13.

Markman S., Mueller C.T., Pascoe D., Dawson A., Backus S. (2011) Pollutants affect development in nestling starlings Sturnus vulgaris. Journal of Applied Ecology 48:7.

Maupin M.A., Kenny J.F., Huston S.S., Lovelace J.K., Barber N.L., Linsey K.S. (2010) Estimated Use of Water in the United States in 2010, in: U. G. Survey and U. D. o. Interior (Eds.). pp. 56.

Prakash V., Bishwakarma M.C., Chaudhary A., Cuthbert R., Dave R., Kulkarni M., Kumar S., Paudel K., Ranade S., Shringarpure R., Green R.E. (2012) The population decline of Gyps vultures in India and Nepal has slowed since veterinary use of diclofenac was banned. PLoS One 7:e49118.

Radjenovic J., Petrovic M., Barcelo D. (2009) Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment. Water Res 43:831-41.

Radjenovic J., Petrovic M., Ventura F., Barcelo D. (2008) Rejection of pharmaceuticals in nanofiltration and reverse osmosis membrane drinking water treatment. Water Res 42:3601-10.

Roberts P.H., Thomas K.V. (2006) The occurrence of selected pharmaceuticals in wastewater effluent and surface waters of the lower Tyne catchment. Sci Total Environ 356:143-53.

Sauve S., Aboulfadl K., Dorner S., Payment P., Deschamps G., Prevost M. (2012) Fecal coliforms, caffeine and carbamazepine in stormwater collection systems in a large urban area. Chemosphere 86:118-23.

Schaider L., Ackerman J., Rudel R., Dunagan S., Brody J. (2011) Emerging Contaminants in Cape Cod Private Drinking Well Water Silent Spring Institute:13.

Seiler R.L., Zaugg S.D., Thomas J.M., Howcroft D.L. (1999) Caffeine and Pharmaceuticals as Indicators of Waste Water Contamination in Wells Groundwater 37:5.

Servos M., Smith M., McInnis R., Burnison K., Lee B., Seto P., Backus S. (2007) The Presence of Selected Pharmaceuticals and the Antimicrobial Triclosan in Drinking Water in Ontario, Canada Water Quality Resources Journal of Canada 42:8.

Smits A.P., Skelly D.K., Bolden S.R. (2014) Amphibian intersex in suburban landscapes. Ecosphere 5.

Snyder S.A., Adham S., Redding A.M., Cannon F.S., DeCarolis J., Oppenheimer J., Wert E.C., Yoon Y. (2007) Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals. Desalination 202:156-181.

Stackelberg P.E., Furlong E.T., Meyer M.T., Zaugg S.D., Henderson A.K., Reissman D.B. (2004) Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water-treatment plant. Sci Total Environ 329:99-113.

Stuart M.E., Manamsa K., Talbot J.C., Crane E.J. (2011) Emerging Contaminants in Groundwater. British Geological Survey:112.

Sumpter J.P. (1995) Feminized responses in fish to environmental estrogens. Toxicology Letters 82:737-742.

Tabak H.H., Bunch R. (1970) Steroid hormones as water pollutants. I. Metabolism of natural and synthetic ovulation-inhibiting hormones by microorganisms of activated sludge and primary settled sewage. Dev. Ind. Microbiol 11:367-376.

Ternes T. (1998) Occurrence of Drugs in German Sewage Treatment Plants and Rivers. Pergammon 32:16.

Tixier C., Singer H.P., Oellers S., T. M.S. (2003) Occurrence and Fate of Carbamazepine, Clofibric Acid, Diclofenac, Ibuprofen, Ketoprofen, and Naproxen in Surface Waters. Environmental Science & Technology 37:8.

Topp E., Monteiro S.C., Beck A., Coelho B.B., Boxall A.B., Duenk P.W., Kleywegt S., Lapen D.R., Payne M., Sabourin L., Li H., Metcalfe C.D. (2008) Runoff of pharmaceuticals and personal care products following application of biosolids to an agricultural field. Sci Total Environ 396:52-9.

US Environmental Protection Agency. (2008) Contaminants of Emerging Concern including Pharmaceuticals and Personal Care Products, in: U. EPA (Ed.), Washington DC.

Verstraeten I.M., Fetterman G.S., Meyer M.T., Bullen T., Sebree S.K. (2005) Use of Tracers and Isotopes to Evaluate Vulnerability of Water in Domestic Wells to Septic Waste. Groundwater Monitoring and Remediation 25:11.

Vieno N., Tuhkanen T., Kronberg L. (2006) Removal of Pharmaceuticals in Drinking Water Treatment: Effect of Chemical Coagulation. Environmental Technology 27:183-192.

Wilson B.A. (2003) Effects of Three Pharmaceutical and Personal Care Products on Natural Freshwater Algal Assemblages. Environmental Science & Technology 37:7.

Chapter 2 Occurrence of Emerging Contaminants in Montgomery and Roanoke County, Virginia Private Well Water

Abstract:

In the US, emerging contaminants (ECs) have been primarily studied in EPA regulated municipal drinking water and WWTP effluent. Limited research has focused on the occurrence of ECs in private well water. Fifty-seven private wells were sampled in Montgomery and Roanoke County, VA, along with six municipal drinking water samples from the same areas (for comparison) and were screened for 142 ECs. The objectives of this study were to 1) determine the occurrence of ECs in private well water supplies in Montgomery and Roanoke County, VA 2) quantify the concentrations of three ECs in selected private water supplies; 3) examine the relationship between well age and depth and water quality constituents (nitrate, bacteria, pH and total dissolved solids) to EC occurrence in private water supplies. Of the 142 ECs screened, 73 ECs were detected in sampled private well water and 16 ECs were detected in the sampled municipal drinking water. Private well water with nitrate >1 mg/L, total dissolved solids <250 mg/L, or total coliform bacteria presence had a higher number of ECs detected. The number of ECs found, on average, in private wells compared to municipal drinking water was not significantly different, but EC concentrations are comparable to municipal drinking water. Household treatment systems appeared to have a varying impact on removal of ECs, but we were not able to verify enough information about the type of device, whether there were multiple devices installed and whether treatment devices were installed and maintained properly, to conclude the effect of these devices on EC presence.

1. Introduction

Emerging contaminants have been detected at trace concentrations (i.e. ng/L-µg/L or ng/kg-µg/kg) in surface water and groundwater, and even treated municipal drinking water (Batt et al., 2006; Benotti et al., 2009b; Bradley et al., 2016; Schaider et al., 2011; Seiler et al., 1999; Servos et al., 2007). “Emerging contaminants” is a blanket term for human and veterinary antibiotics and pharmaceuticals and personal care products (PPCPs), as well as their transformation products. Emerging contaminants are produced and used for various anthropogenic purposes, and, consequently, are ubiquitous in the environment (Kummerer, 2008). Emerging contaminants (ECs) are primarily released into water sources from wastewater

treatment plant (WWTP) effluent, due to the inability of most WWTPs to fully remove the compounds and in the effluent of hospital, pharmaceutical production facilities, and large-scale industrial operations (Lin and Tsai, 2009). Agricultural operations (livestock antibiotics and application of manure or biosolids as fertilizer) are another major source of ECs into water (Burkholder et al., 2007). ECs are bioactive at low doses, thus their presence at low concentrations may pose a potential risk to human health and wildlife.

US research has focused on the occurrence thus far has been primarily focused on EPA regulated municipal drinking water (waters required to meet the standards of the 1974 Safe Drinking Water Act (SDWA)) and wastewater effluent (Benotti et al., 2009b). Limited information is available on the occurrence of ECs for the 45 million people who rely on private water supplies (waters exempt from routine and treatment testing by the SDWA) (Maupin et al., 2010). Private well water may be more susceptible to water quality issues because routine treatment and testing is the responsibility of the owner. Private wells are common in rural and suburban areas where connection to municipal infrastructure is difficult or not possible. Thus, private wells are often located on the same property with septic systems. Septic systems can be a water quality concern if not properly maintained or constructed. Maintenance is the responsibility of the owner, and often routine pumpouts are not required or enforced (Environmental Protection Agency, 2002).

As of 2018, only six studies focused on EC presence in US private well water (Batt et al., 2006; Erickson et al., 2012; Focazio et al., 2008; Schaider et al., 2011; Seiler et al., 1999; Verstraeten et al., 2005). Overall, these studies documented that ECs are often present at trace concentrations in private well water. Fourteen ECs were detected in shallow urban private well water in Nebraska and 27 ECs were documented in coastal Massachusetts wells. Both studies were conducted with wells located in sand and gravel aquifers (Schaider et al., 2016; Verstraeten et al., 2005). In urban Minnesota private well water, characterized by bedrock and glacial aquifers, 38 ECs were detected (Erickson et al., 2012). Caffeine and carbamazepine metabolites were detected in Nevada private well water (Seiler et al., 1999). Several cattle antibiotics were detected in Idaho private well water (Batt et al., 2006). Most studies examined a relatively small number of wells and ECs. No studies published so far have focused on the southeastern US, or on Virginia, in particular.

Potential predictors and sources of ECs in private well water have been suggested. Correlation between the occurrence of ECs and nitrate, boron, and dissolved organic compound (often tracers of septic contamination) in coastal Massachusetts was evidence that septic leakage was a possible source of ECs (Schaider et al., 2016). Similar results were reported in Nevada private well water but the source was unclear (Seiler et al., 1999). The detection of beef cattle antibiotics (sulfonamide drugs) in Idaho private water well water documented that concentrated cattle feeding operations were a possible source of ECs (Batt et al., 2006). Antimicrobial agents, found downgradient of landfill operations, were detected in private groundwater systems, was evidence that landfill leachate could be a source (Holm et al., 1995). Additional information is needed about the occurrence of ECs in southeastern US private well water.

Approximately 20% of residents in Virginia (1.7 million) rely on private well water (Benham et al., 2016; Maupin et al., 2010). In 1992, a Virginia law was enacted to ensure that installation of a private well does not negatively affect groundwater or public health, and regulates well placement and construction, administered by the Virginia Department of Health (Virginia Department of Health, 1992). A Cooperative Extension program offered through Virginia Tech, the Virginia Household Water Quality Program (VAHWQP) helps homeowners learn about their water quality and how to maintain their private water supply system. VAHWQP provides water quality clinics in roughly 60 Virginia counties annually, where private well users can purchase a water quality testing kit and learn about well maintenance, groundwater protection, and addressing problems (Benham et al., 2016). Following each clinic, VAHWQP holds a results interpretation meeting where participants learn about their sample results and potential water treatment options, if needed. Since 1989, VAHWQP analyzed over 26,000 samples in Virginia serving nearly 60,000 Virginians.

This research effort relied on a partnership with the VAHWQP to identify 57 private wells in Montgomery County and Roanoke County, VA for EC analysis. The objectives of this investigation were to 1) determine the occurrence of ECs in private well water supplies in Montgomery and Roanoke County, VA 2) quantify the concentrations of three ECs in selected private water supplies; 3) examine the relationship between well age and depth and water quality constituents (nitrate, bacteria, pH and total dissolved solids) to EC occurrence in private water supplies.

2. Methods and Materials

2.1 Field Sites and Sample Collection

The geology of Montgomery and Roanoke County affects the chemistry and quality, as well as the movement of groundwater (Woodward, 1932). The rock types in these counties are a mix of crystalline, metamorphic rocks (primarily gneisses and schists), limestone, and shales. The geological structure of these rocks is highly complex (folds and thrust faults), typical of mountainous areas in the Appalachian Highlands (Woodward, 1932). Some sections of this area are rich in limestone and, as a result, have large underground karst channels due to the high solubility of limestone (Woodward, 1932). Due to the sections of karst, there are areas with high aquifer connectivity and significant surface and groundwater interaction. Overall, the geology in these counties is highly complex and non-uniform. The geology is significant to this research because it could influence the number of detected ECs in each private well.

An Institutional Review Board (IRB) protocol through Virginia Tech was created and approved to document how participants were recruited, samples were collected, and data was handled to protect the confidentiality of participants. Counties were selected using past VAHWQP water quality data. Montgomery and Roanoke County were chosen because the counties had >200 total participants in past drinking water clinics, environmental and well characteristics were applicable to the investigation's variables of interest, and the counties were within a one hour driving time of Virginia Tech. Past VAHWQP drinking water clinic participants from these two counties were recruited to participate voluntarily. Water samples were collected from 34 private wells in Montgomery County and 23 private wells in Roanoke County (**Error! Reference source not found.**). Six homes serviced by municipal drinking water systems were also sampled, three in Montgomery County homes, two in Roanoke County homes, and one in a Botetourt County home (**Error! Reference source not found.**). The water supply system that served the home sampled in Botetourt use groundwater wells, while Montgomery and Roanoke County system use surface waters. The sampling of EPA regulated municipal

drinking water allowed for comparison between occurrence of ECs in systems that are regulated by the EPA and those that are not.

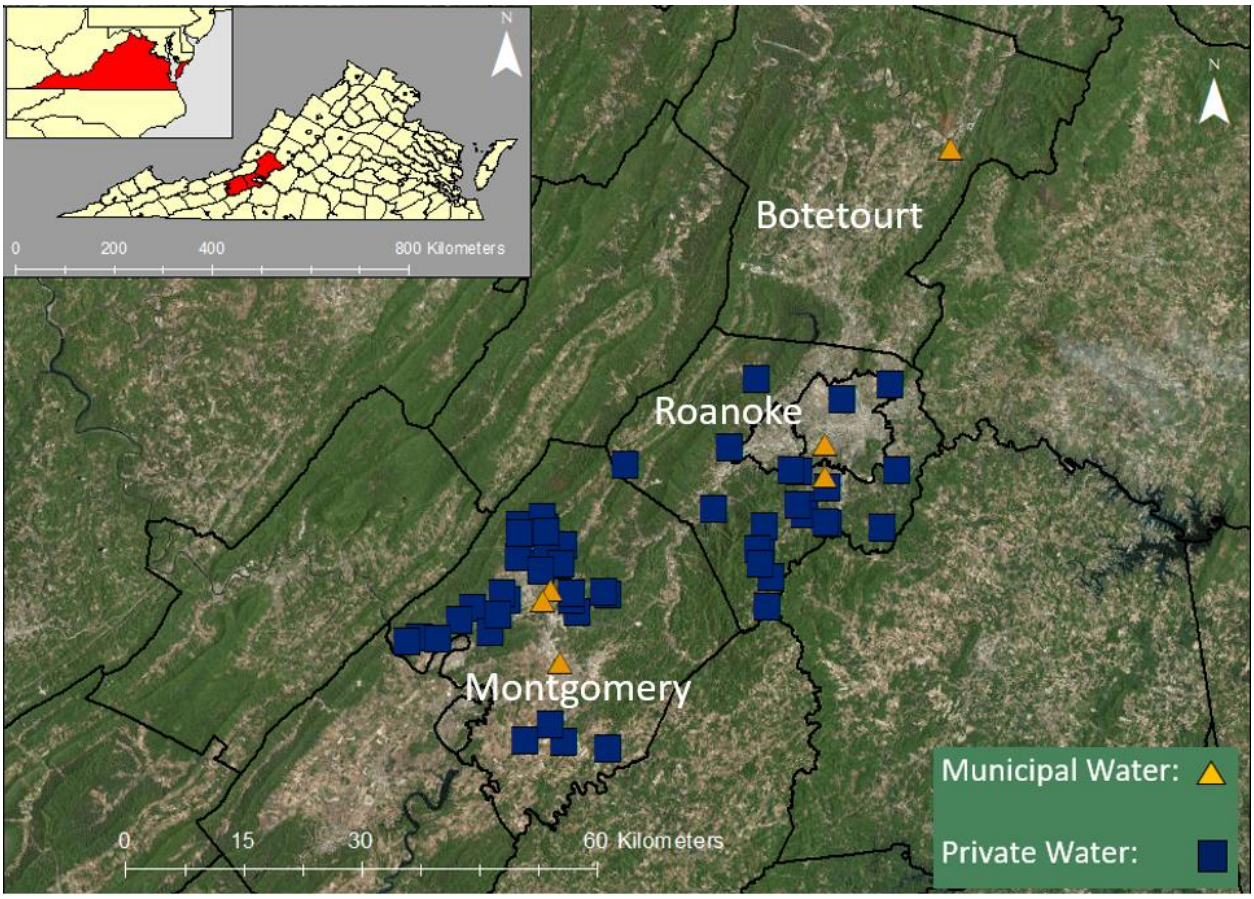


Figure 2.1: The 57 private well locations sampled in Montgomery and Roanoke County, VA and 6 municipal drinking water locations sampled in Montgomery, Roanoke, and Botetourt County, VA.

Past VAHWQP participants were contacted by email by the VAHWQP coordinator to find out if they were interested in participating in this study (Appendix F**. Chapter 2 Recruitment Letter**). The private well water users who volunteered for the study were contacted to set up a convenient time for a site visit at their home to collect the samples and complete the participant survey. During the visit, participants were asked to sign a consent from (Appendix G**. Chapter 2 Private Well Consent Form**) and were surveyed about their well characteristics (well age and depth), septic system history, treatment system(s) (if applicable), and household use medications

and other products that may become ECs once disposed of **(**Appendix H**. Chapter 2 Private Well Water Survey**; Table 2.1).

Table 2.1: Private well water survey variables.

Private Well Survey Parameters		
Household Medication Usage	Livestock Presence	Pesticide Usage
Pet Medication	Proximity to Cropland	Septic Age
Septic Distance to Well	Septic Pumping Frequency	Pharmaceutical Disposal Method
Treatment System	Well Age	Well Depth

A shorter survey was administered to the municipal drinking water users to determine who supplies their water, how many people use the water, treatment devices, and the water taste (Appendix I. Chapter 2 Municipal Drinking Water Consent Form:

Survey of **Pharmaceuticals and Personal Care Products (PPCPs) and Pesticides in**

Virginia Well and Municipal Tap Water Supplies

The objective of the Virginia Household Water Quality Program (VAHWQP) is to improve the water quality and health of Virginians reliant on private water supplies, such as wells, springs, and cisterns. Researchers from the Department of Crop and Environmental Soil Sciences and Biological Systems Engineering at Virginia Tech have undertaken an additional volunteer study with participants from VAHWQP to better understand the occurrence of PPCPs and pesticides in private well water supplies. For comparison, researchers will also collect and analyze municipal source (regulated) tap water from the same counties where well water samples are being collected.

Participation in this study is voluntary. Should you choose to participate, your responses and data generated from your samples will kept confidential, and will not be linked with your contact information at any time. Summary results of this study may be published. Please read over the attached consent form and feel free to contact us with any questions or concerns.

Graduate Student:
Will Vesely veselywc@vt.edu 404-862-5629

Investigators:
Dr. Brian Benham benham@vt.edu 540-231-5705
Ms. Erin Ling ejling@vt.edu 540-231-9058
Dr. Kang Xia kxia@vt.edu 540-231-9323

Methods/Procedures
The method of data collection for this study will include completion of a short survey, onsite collection of tap water samples from your residence at a scheduled, convenient time, and sample analysis at Virginia Tech. The survey will include questions about the demographics of those living in your home and the taste of the water. During the scheduled visit, samples will be collected from your water supply at your residence and the graduate student will transport the samples to Virginia Tech. Analysis of the water samples for PPCPs and pesticides will be done in
the Environmental Organic Chemical Analysis Laboratory at Virginia Tech by a trained graduate student and supervised by a faculty member. Analytical data about PPCPs and pesticides for the sample from your household will be provided to you upon your request.

Confidentiality
All the confidentiality measures for the VAHWQP will be applied to this study. There will be no identifying information used in any written reports or publications resulting from this study. Your participation in this evaluation will be strictly confidential. All findings used in any written reports or publications that result from this project will be reported in aggregate form with no identifying information. The Virginia Tech Institutional Review Board and federal regulatory

agencies may look at records related to this study for quality improvement and regulatory functions.

Risks and Inconveniences
There are no anticipated physical risks to participants. Visits for sample collection will only be scheduled at a convenient time for you, and participation is completely voluntary.

Benefits
Potential benefits of participating in this study include: the opportunity to assist researchers to better understand the occurrence of PPCPs and pesticides in Virginia municipal water.

Questions
If you have any questions about this study at any time, you may contact Will Vesely at Virginia Tech (email: veselywc@vt.edu; phone: 404-862-5629) or any of the faculty investigators listed above.

Should you have any questions or concerns about the study's conduct or your rights as a research participant, or need to report a research-related injury or event, you may contact the Virginia Tech Institutional Review Board at irb@vt.edu or (540) 231-3732.

Subject's Consent
You will be given a copy of this consent form to keep for your records. Once again, we thank you for taking time out of your busy schedule to assist with this study.
I have read the Consent Form and conditions of this project. I have had all my questions answered. I hereby acknowledge the above and give my voluntary consent:

Printed Name of the Participant _____

Signature of the Participant _____

Date_____

Printed Name of the Investigator _____

Signature of the Investigator _____

Appendix J. Chapter 2 Municipal Drinking Water Survey

Approximately 1.5 L of water was collected from each household tap in acid-rinsed mason jars. The water was collected directly from the kitchen faucet, after allowing it to run for one minute before sampling (Schaider et al., 2016). If the private well had a water treatment system, the water was sampled before the water treatment system from a bypass valve on the treatment system or at an outdoor spigot that preceded the treatment system and from the tap (treated water) and both samples were analyzed for ECs. For the municipal drinking water systems with a water treatment device (PUR, Brita filter, etc.), samples were collected from the system both before and after the filtration device. The collected water samples for the EC and water quality analysis were stored in a cooler at ≈4°C for transport back to the labs. The samples for EC analysis were stored in a -20°C freezer until analysis.

2.2 Analysis of Water Quality Constituents

Private well participants were provided a complimentary VAHWQP water testing kit as compensation for participation in the study ($55 value). The water quality testing kits were dropped off at the VAHWQP Biological Systems (BSE) Water Quality lab the same day as collection by the homeowner and were analyzed separately from the samples for ECs analysis. The water quality testing kits were analyzed within 24 hours of collection to ensure accurate bacterial testing.

The VAHWQP water quality testing samples were analyzed for 43 water quality constituents (Table 2.2). The water quality analysis was conducted by the Virginia Tech BSE Water Quality Lab and the Virginia Tech Environmental and Water Resources Engineering Water Quality Lab following the same procedures and standard methods used for VAHWQP drinking water clinics. Results from the VAHWQP analysis were returned separately to participants following standard operating procedures. Select homes chose to use their complimentary water quality analysis at a future date so their most recent water quality data was used in the data analysis instead.

Table 2.2: VAHWQP water quality constituents tested.

VAHWQP Water Quality Constituents		
Aluminum	Arsenic	Cadmium

Calcium	Chromium	Cobalt
Copper	*E. coli*	Fluoride
Hardness	Iron	Lead
Manganese	Magnesium	Molybdenum
Nickel	Nitrate-Nitrogen	pH
Phosphorus	Potassium	Silicon
Silver	Sodium	Sulfate
Tin	Total Coliform Bacteria	Total Dissolved Solids
Vanadium	Zinc	

Bacterial analysis (*E. coli* and total coliform) was conducted using IDEXX (Westbrook, ME) Colilert MPN 2000 method (American Public Health Association et al., 2012). Nitrate and fluoride concentration were quantified on an Ion Chromatogram with a detection limit of 0.1 mg/L using standard method SM 4220-B (American Public Health Association et al., 2012). pH and conductivity (proxy for total dissolved solids (TDS)) were measured using standard methods 4500-H^+-B and 2510-B, respectively (American Public Health Association et al., 2012). For QA/QC for the above methods, blanks and spikes of known concentrations were used every 10-15 minutes to ensure accurate results. Trace metals (aluminum, arsenic, cobalt, cadmium, calcium, chromium, copper, iron, lead, magnesium, manganese, molybdenum, nickel, potassium, silicon, silver, sodium, tin, vanadium, and zinc) were analyzed at the Virginia Tech Environmental and Water Resources Engineering Water Quality Lab on an inductively coupled plasma-mass spectrometry (ICP-MS) (X-Series, Thermo-Scientific, Waltham, MA) per standard method 3125-B (American Public Health Association et al., 2012). Samples and calibration standards were prepared in a matrix of 2% nitric acid by volume. The trace metal and elemental analysis on both the first draw and flushed (after water ran for one minute) after collecting the first draw sample for each household. Hardness was calculated from the calcium and magnesium concentrations.

2.3 Analysis of Emerging Contaminants in Water

2.3.1 Water Sample Extraction and Cleanup Using Solid Phase Extraction

Approximately 200 mL from each water sample with triplicates were used for processing through solid phase extraction (SPE). Blank ultra-pure water (Millipore, Billerica, MA) was used

during sample processing to discover any background or experimental contamination. Two high purity (>90%) antibiotic standards: tylosin and sulfamethazine, purchased from Sigma-Aldrich, (St. Louis, MO), were spiked into ultra-pure water at 50 µg/L for quality assurance and control (QA/QC). The spikes were used to determine SPE processing recovery rates (what portion of an EC is retained during SPE processing). All samples were filtered through a 0.7-micron 55 mm glass fiber filter (Whatman, Maidstone, UK). Samples were then concentrated and purified through hydrophilic-lipophilic balance cartridges (Waters, Milford, MA) on a SPE manifold. Before samples were concentrated through the cartridges, the cartridges were conditioned with 3 mL HPLC-grade methanol and 3 mL ultra-pure water. The water samples were processed through the cartridges at 5 mL/min. The cartridges were then dehydrated for 10 mins to remove any remaining water. The concentrated cartridges were eluted with 3 mL HPLC-grade methanol. The eluted samples were dried on a vacuum evaporation system (Labconco Kansas City, MO) and then reconstituted with 1:1 LC-grade acetonitrile:ultra-pure water. The reconstituted concentrates were filtered through an 0.2-micron polytetrafluoroethylene (Thermo Scientific, Waltham, MA) syringe filter into 2 mL amber vials (Agilent, Santa Clara, CA). The reconstituted concentrates were stored in a -80°C freezer until analysis.

2.3.2 UPLC/MS/MS Operation Conditions for Screening of Emerging Contaminants

The SPE processed samples were screened for 142 ECs with three select ECs (caffeine, triclosan, and tylosin) quantified for concentration on an ultra-performance liquid chromatography tandem mass spectrometry (UPLC/MS/MS) (6490, Agilent, Santa Clara, CA). The instrument operating conditions are listed in Table 2.3. The MassHunter™ software (Agilent, Santa Clara, CA) controlled the operation of the UPLC/MS/MS data collection and processing.

Table 2.3: Measurement conditions of the UPLC/MS/MS.

Agilent 6490 UPLC		
Column: Agilent Zorbax Extend C-18 (5 µm)		
Column Temp: 40°C		
Flow Rate: 0.3 mL/min		
Injection Volume: 20 µL		
Mobile Phase:		
	A: Water w/ 0.1% Formic Acid	B: 95% Acetonitrile/5% Water

Gradient:		
Time (min)	A (%)	B (%)
0	95	5
15	10	90
17.5	10	90
18	95	5
MS/MS: Agilent 6490 Triple Quad		
Ionization: Electrospray Ionization Positive and Negative		
Capillary Voltage: 3500 V		
Capillary Temp: 250°C -Source Temp: 200°C		

The 142 EC screening method was developed from an Agilent Technology database, that is specifically designed for the Agilent 6490 UPLC/MS/MS and provides EC analysis information including parent ion, daughter ions, and the collision energy (Yang, Murphy, et al., 2014). The 142 ECs were selected to represent the most detected ECs in the environment (Yang, Murphy, et al., 2014). The developed screening method was tested on southwest Virginia wastewater samples to determine its applicability and repeatability for this project.

The average recovery rate for all the SPE processing runs for sulfamethazine and tylosin was 83% and 65%, respectively. DEET, the main ingredient in many insect repellants, was detected in all the instrumental and SPE processing blanks. DEET has been present in the field and sample processing blanks in another investigation (Erickson et al., 2012). However, there were no other ECs were detected in the SPE processing blanks and instrumental blanks.

Three high purity (>90%) EC analytical standards, caffeine (psychoactive drug), triclosan (antibacterial agent), and tylosin (antibiotic) were purchased from Sigma-Aldrich for concentration quantification. These three ECs were chosen for quantification because they were the most frequently detected in the initial 10 well water samples analyzed. Triclosan and caffeine were frequently detected in the remaining samples but tylosin was less frequently detected. Stock solutions of 1000 ppm were prepared for each standard and stored in -80ºC until use. The concentration for the three ECs were calculated from a calibration curve developed from standard solutions derived from the stock solution. The standard concentrations differed for each quantified compound.

2.3.3 UPLC/MS/MS Data Analysis

The chromatograms produced from the UPLC/MS/MS analysis were analyzed on two software packages: Masshunter™ Qualitative and Quantitative version 6.0 (Agilent, Santa Clara, CA). Qualitative Analysis was used to determine the occurrence of an EC in each water sample.

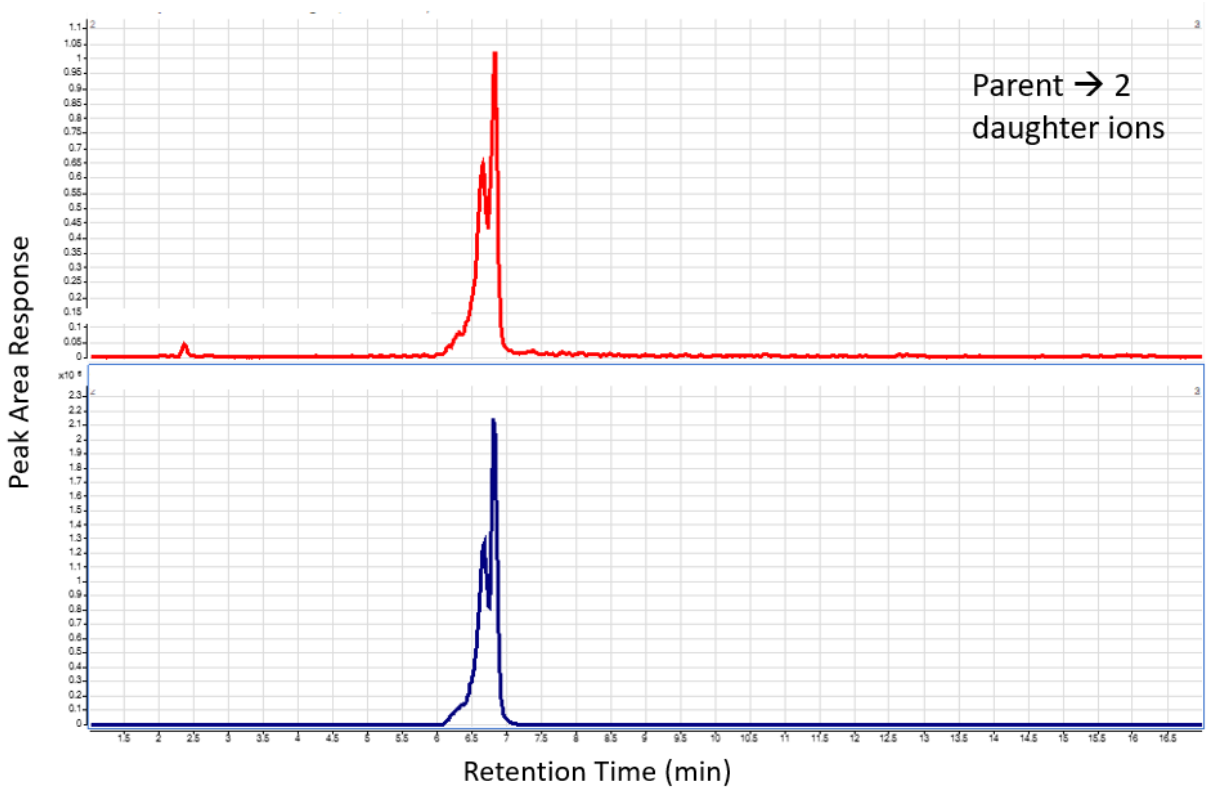


Figure 2.2: An example chromatogram showing a positive identification for tramadol (a narcotic pain reliever).

The positive identification of an EC in a water sample was determined by the identification of the same peak shape at the same retention time for both daughter ions of a compound (Figure 2.2). The retention time of an EC was determined from previous testing of local wastewater and available analytical standards. The Quantitative Analysis software was used to quantify the peak area of the present ECs and quantify concentration for caffeine, triclosan, and tylosin. Compounds were qualified for occurrence by the presence of a distinctive peak at a specific retention time with a signal to noise ratio >3 and a signal to noise ratio >10 was required for quantification of an EC.

2.4 Survey Data and Statistical Analysis

The impact of human, livestock, and household pet medication usage by a household was evaluated by comparing the number of medication general categories used (as reported by the homeowner) and the number of ECs detected in a well. The impact of pesticide usage was compared by comparing the number of pesticides reportedly used and number of ECs detected in a well to understand potential agricultural impact. The proximity of cropland comparison was not used because of the lack of information regarding a cropland distance from well. For homes with treatment systems, the number of ECs present before treatment and after treatment were compared to make observations of the ability of treatment to remove ECs.

Correlation was determined for well age, well depth and the number of detected ECs detected in a given well. The other independent variables (septic system distance to well and water quality constituents) were assessed using analysis of variances (ANOVAs). Unequal variances were assumed and a significance level of 0.05 was used. The relationship was considered significant for a p-value <0.05.

3. Results and Discussion

3.1 Occurrence of Emerging Contaminants in Private Wells

Of the 142 ECs screened, 73 ECs (51%) were detected in at least one private well sample (Table 2.4). Although, 73 ECs were detected only 24 ECs (34%) were detected at least more than 10% of the private wells samples. 10% of the private wells. This was the first time many ECs (e.g., aripiprazole, levorphanol, montelukast, n-butylparaben, ritalinic acid, tylosin, etc.) were detected in US private well water based on reported studies. An average of eight (±4) were detected per well in this study.

Table 2.4: The 73 ECs detected in at least one of the 57 private wells sampled.

Emerging Contaminant	Treatment Usage	# of Wells	Emerging Contaminant	Treatment Usage	# of Wells
6-Acetylmorphine	metabolite of heroin	2	Meprobamate	Anxiolytic	2
9carboxy-THC	metabolite of marijuana	2	Metformin	Antidiabetic	37
Acebutolol	beta blocker	2	Methylparaben	cosmetic preservative	67
Acetaminophen	pain reliever	7	Metoprolol	beta blocker	2

Aripiprazole Metabolites: Dehydroariprazole	antipsychotic	2 2	Montelukast	anti-inflammatory	2
Atenolol	beta blocker	2	n-Butylparaben	Antimicrobial	4
Atrazine	Pesticide	39	Norfluoxetine	metabolite of fluoxetine	4
Buprenorphine	pain reliever	28	Norverapamil	metabolite of verapamil	2
Bupropion Metabolites: Hydroxybupropion	antidepressant	2 12	Oxcarbazepine	Anticonvulsant	68
Caffeine	psychoactive drug	51	Oxidized Nifedipine	metabolite of nifedipine	2
Carbamazepine Metabolites: 10,11-hydroxycarbamazepine Carbamazepine 10,11 epoxide	Anticonvulsant	12 4 4	Oxycodone	pain reliever	12
Carisoprodol	muscle relaxant	18	Paroxetine	antidepressant	23
Celecoxib	anti-inflammatory	4	Phenobarbital	anticonvulsant	2
Clenbuterol	decongestant	2	Phentermine	psychostimulant	12
Clopidogrel carboxylic acid	metabolite of clopidogrel	5	Pioglitazone	antidiabetic	5
Cotinine	metabolite of nicotine	14	Pregabalin	anticonvulsant	12
Desmethylcitalopram	metabolite of citalopram	4	Primidone	anticonvulsant	4
Dextromethorphan	sedative	4	Pseudoephedrine	Decongestant	9
Diphenhydramine	allergies	28	Ritalinic acid	metabolite of Ritalin	4
Donepezil	Alzheimer's	2	Sertraline Metabolites: Norsertraline	antidepressant	2 7
EDDP	metabolite of methadone	2	Sildenafil	antidepressant	4
Escitalopram	antidepressant	4	Sulfamethazine	Antibiotic	18
Famotidine	antacid	9	Sulfamethoxazole	Antibiotic	11
Fenbufen	anti-inflammatory	2	Thiabendazole	Fungicide	14
Furosemide	diuretic	2	Tramadol	pain reliever	12

Gabapentin	pain reliever	56	Trazadone	antidepressant	4
Hydrochlorothiazide	beta blocker	12	Triamterene	Diuretic	2
Hydrocodone	pain reliever	2	Triclocarban	antibacterial agent	4
Hydromorphone	pain reliever	7	Triclosan	antibacterial agent	61
Ibuprofen	pain reliever	2	Trimethoprim	Antibiotic	14
Ketoprofen	anti-inflammatory	5	Tylosin	Antibiotic	26
Lamotrigine	anticonvulsant	7	Venlafaxine Metabolites: Desmethylvenlafaxine	antidepressant	2 16
Levorphanol	pain reliever	4	Zolpidem	Sedative	2
Lidocaine	numbing agent	11			

The five most detected ECs in the 57 sampled private wells were oxcarbazepine (68% of wells), methylparaben (67% of wells), triclosan (61% of wells), gabapentin (56% of wells), and caffeine (51% of wells) (Table 2.4). Oxcarbazepine (an anticonvulsant) has not been frequently detected in surface and groundwater but carbamazepine, a structural derivative of oxcarbazepine, has been frequently detected (Benotti et al., 2009b). Methylparaben has been frequently detected in groundwater in the US and UK at concentrations ranging from 5-5000 ng/L (Lapworth et al., 2012). Triclosan is commonly included as a target EC in groundwater monitoring and has been frequently detected at concentrations ranging from 10-2100 ng/L (Postigo and Barcelo, 2015). In South Wales groundwater, gabapentin was the most detected EC out of 56 ECs screened for in groundwater (Kasprzyk-Hordern et al., 2008). Caffeine has been frequently detected in groundwater in European ranging from 13 ng/L-4500 ng/L but is found less frequently in the US (Postigo and Barcelo, 2015).

The 73 detected ECs were divided into 17 general use categories based on the treatment usage and/or compound type most common. The five most frequently detected general use categories were as follows: antibacterial agents (including antibiotics), anticonvulsants, narcotic pain relievers, and pain relievers (Figure 2.3). The primary usage of the detected ECs was human medical use.

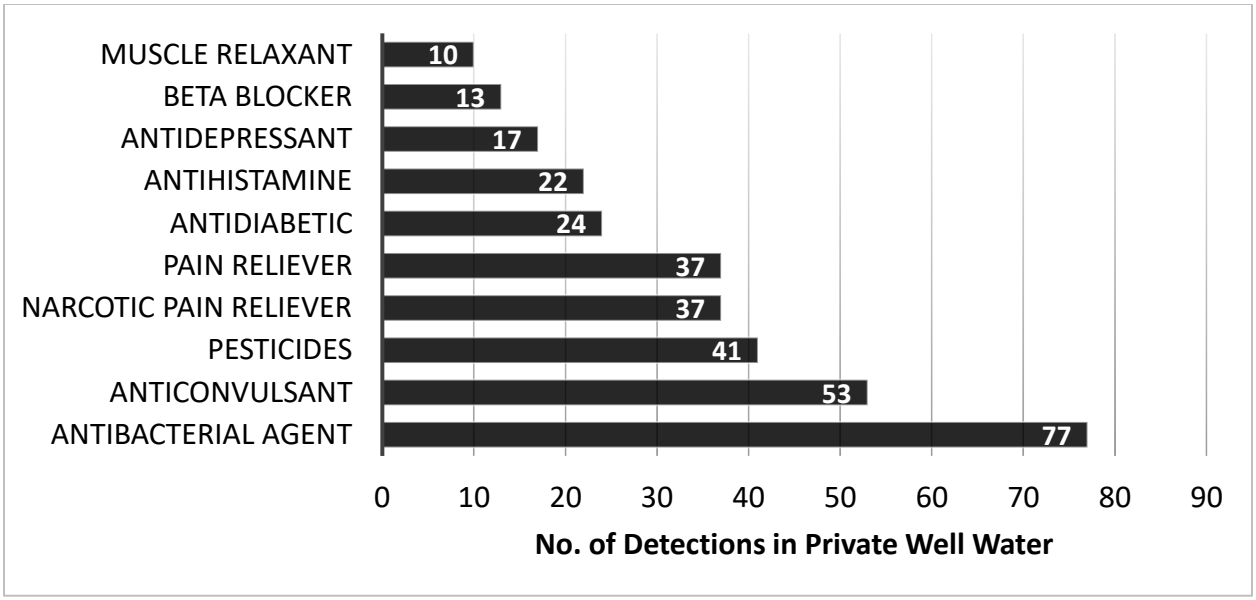


Figure 2.3: Number of detected ECs in private well water based on their general use.

Detected ECs were a combination of highly used (e.g., gabapentin was the 10th most prescribed compound in US in 2016) and lesser used medicines (zolpidem) (IQVIA Institute, 2017). As previously stated, it is a challenge to predict whether EC occurrence is related to its environmental persistence or frequency of use (Benotti et al., 2009b). The reported use of ECs by participating homeowners surveyed (livestock medication, human medication, and pet medication) appeared to have no relationship with number and category of ECs detected in their private well water. The survey did not ask for specific medicine usage which made it difficult to determine if use by category of EC is a valuable predictor of EC presence in a well.

The number of ECs detected is not significantly different in private well water compared to municipal drinking water (Figure 2.4). Additional municipal drinking water samples are needed to better understand this relationship.

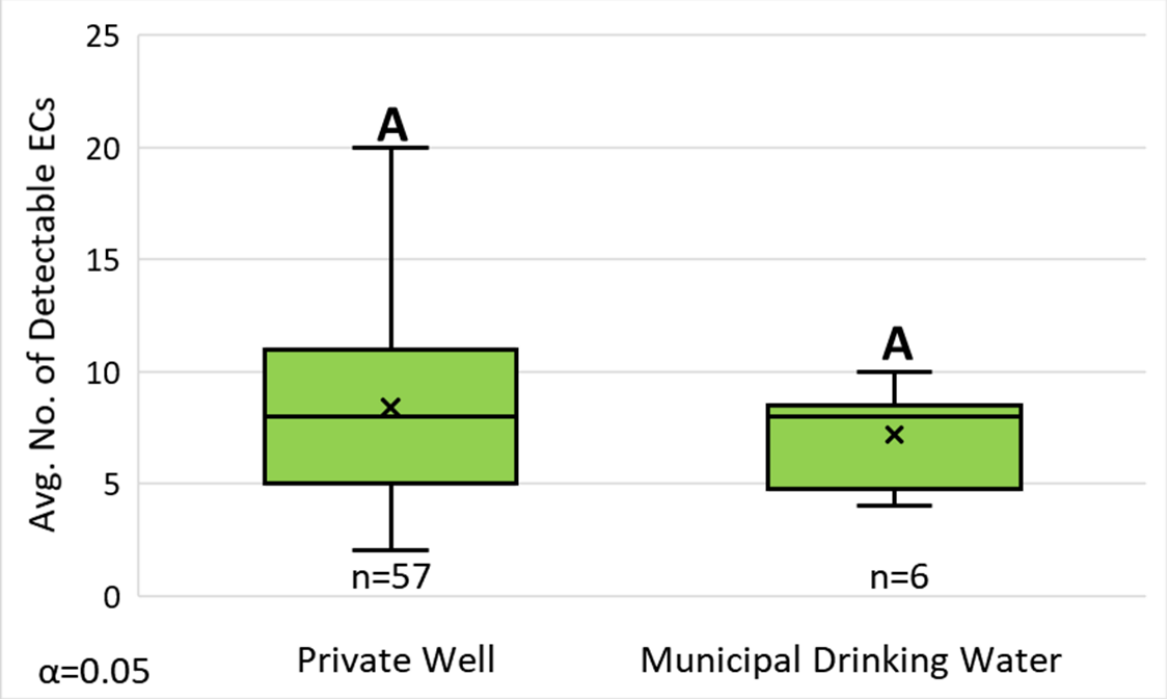


Figure 2.4: The number of detected ECs in the 57 private well water samples compared to the 6 municipal drinking water samples. Letters above column indicate statistical differences at $p<0.05$.

Of the 142 ECs screened in the six municipal drinking samples, 16 ECs (11%) and one pesticide were detected in at least one sample. Atrazine, caffeine, and metformin were detected in every municipal drinking water sample (Figure 2.5).

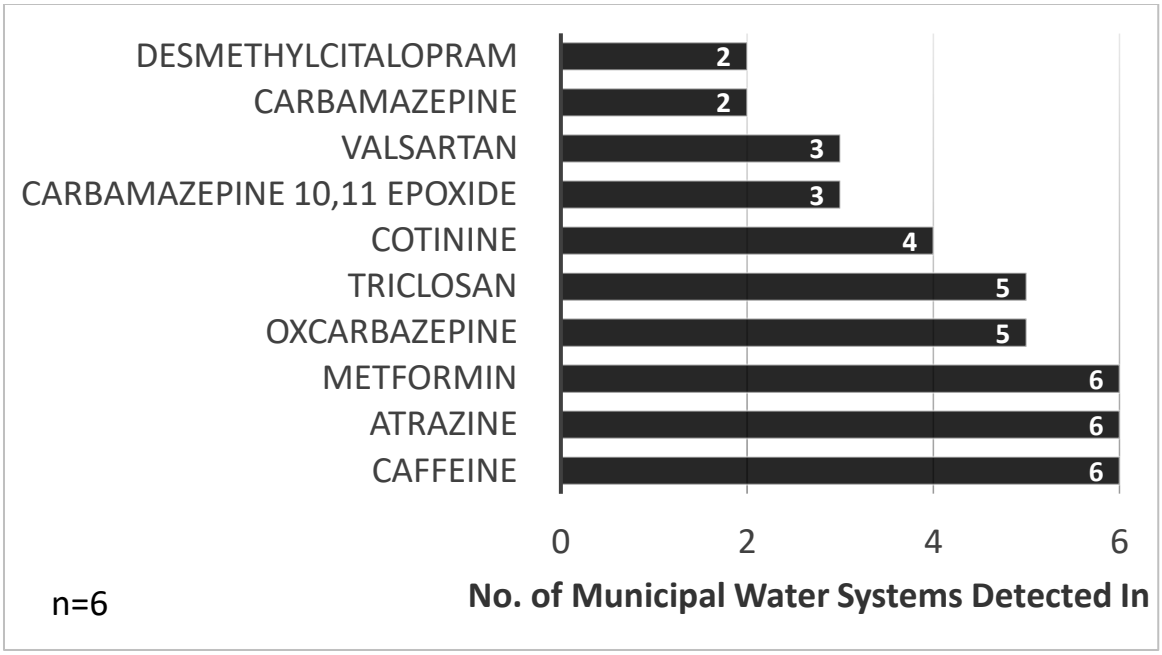


Figure 2.5: Ten most detected ECs in the tested municipal drinking water from Botetourt, Montgomery, and Roanoke County, VA.

Atrazine has been frequently detected in municipal drinking water and is EPA regulated as a primary contaminant (primary drinking water standard of 3 ppb). Caffeine (psychoactive drug) is used in some form by 90% of American adults every day, and is persistent enough to be frequently detected in the municipal drinking water nationwide (Bruton et al., 2010). Metformin (antidiabetic) was the seventh most prescribed medicine in 2016 (87 million prescriptions) and its ability to withstand water treatment allows it to be highly prevalent in drinking water (IQVIA Institute, 2017; Scheurer et al., 2012). There were significantly fewer total number of detected ECs in the municipal drinking water compared to the private well water. Valsartan (antihypertensive drug) was the only compound detected in the municipal drinking water that was not detected in private well water.

3.2 Concentrations of Selected Emerging Contaminants in Private Wells

Concentrations of caffeine, tylosin, and triclosan, which were among the top ten most frequently detected ECs in the well samples were analyzed for nine private wells (Figure 2.6). Concentrations of these three compounds were quantified for the nine well samples with highest peak areas in these well water samples compared to other well water samples in the study. To

simplify, this study quantified the concentrations of these three compounds in wells with the highest peak areas of ECs and does not provide an estimated average for the 57 sampled wells.

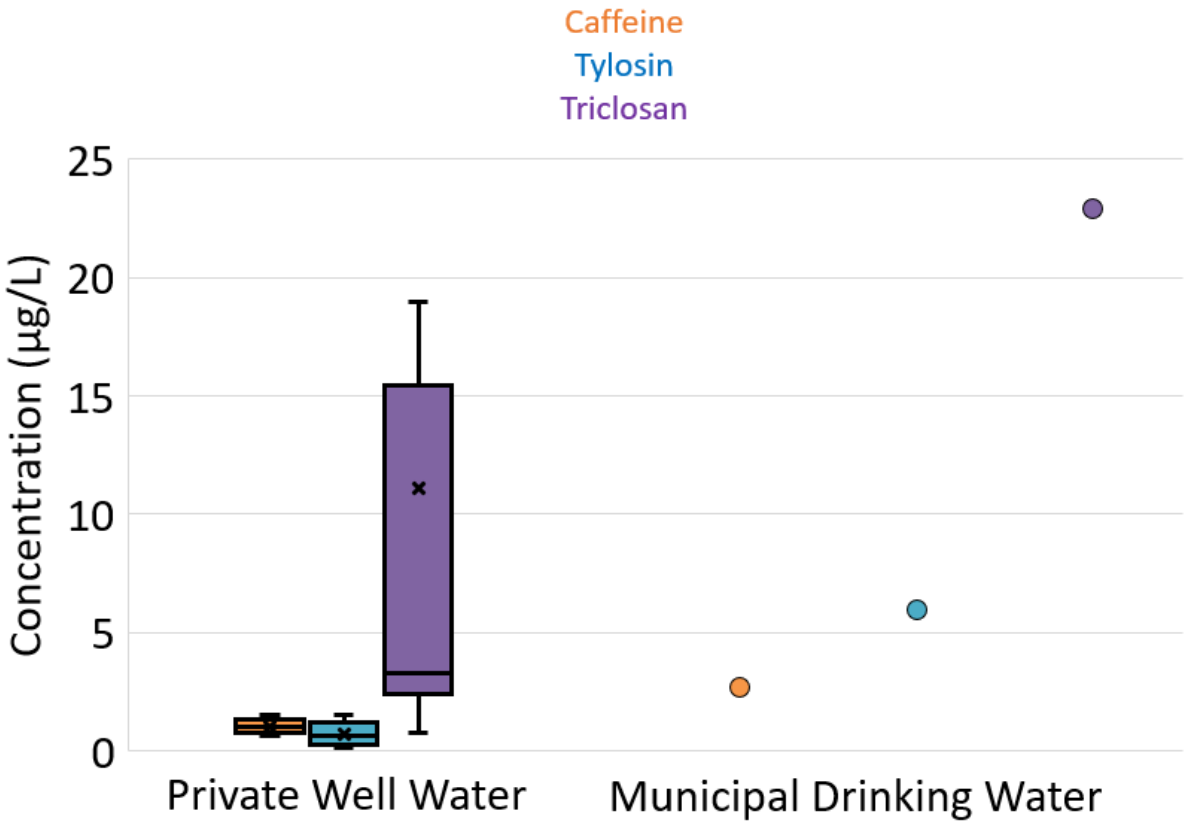


Figure 2.6: The concentration (µg/L) of caffeine, tylosin, and triclosan in nine private well water samples and one private well water.

The concentration ranges for the nine analyzed private wells ranged were: caffeine (0.69-1.53 µg/L); tylosin (0.13-1.54 µg/L); and triclosan (0.78-53.55 µg/L). The concentration for the three ECs for the one municipal drinking water quantified were: caffeine (3 mg/L), tylosin (6 mg/L), and triclosan (23 mg/L).

Caffeine has been detected in three other US private well water investigations: once in Minnesota at an average concentration of 0.100 µg/L (Erickson et al., 2012), nine times in Nebraska as high as 0.129 µg/L (Seiler et al., 1999), and in multiple wells in Nevada at up to 0.230 µg/L (Erickson et al., 2012; Seiler et al., 1999; Verstraeten et al., 2005). The average caffeine concentration of 1.03 (±0.3 µg/L) quantified in this investigation was greater compared to the previously reported values. The caffeine concentrations found in this investigation were

comparable to what has been reported in groundwater with up to 4.5 μg/L detected in the United Kingdom (Stuart et al., 2011). Caffeine has been frequently detected in US municipal drinking water with concentrations from 100 to 1000 ng/L (Stackelberg et al., 2004). Triclosan has been analyzed once in US private drinking water but it was unclear whether it was detected in private well water (Focazio et al., 2008). Triclosan has been detected in various US municipal drinking water at concentrations ranging from 1 to 100 ng/L. Tylosin was analyzed for in the US-wide private drinking water investigation but was not detected (Focazio et al., 2008). Tylosin has not been detected previously in municipal drinking water.

3.3 Impact of Well Age and Depth, and Septic System History on Occurrence of Emerging Contaminants

The well characteristics that were reported by homeowners on the survey are found in Table 2.5. The homeowner-reported data in the survey was not verified, so errors are possible in their assessments.

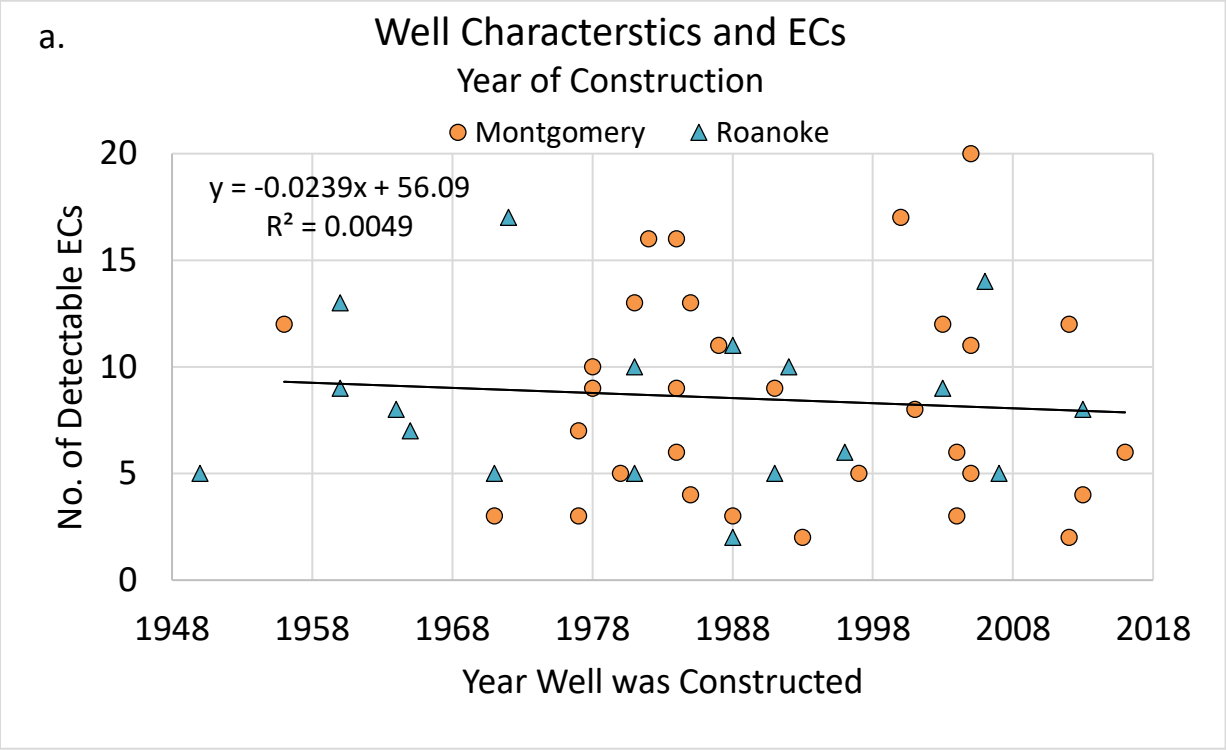
Table 2.5: Well characteristics of the sampled private wells.

	Montgomery County (Avg.±Std. Dev.)	**Roanoke County (Avg.±Std. Dev.)**
Well Depth (m)	125±72	70±45
Well Age (yr)	1992±14	1983±19
Drilled Wells (n=57 wells)	82%	88%

The private wells in this investigation had greater depth than private wells (Massachusetts: 18 m, Nebraska: 10 m, and Nevada: 40 m) that have been sampled and reported in the literature (Schaider et al., 2016; Verstraeten et al., 2005).

Overall, there was no correlation between reported well age and the number of detected ECs (Figure 2.7a). It was expected that wells constructed after 1992 would have fewer detected ECs because of the implementation of the Virginia private well construction regulations enacted in 1992 (Virginia Department of Health, 1992). The 1992 regulations required wells to be at least 50 ft from a septic system (considered a source of ECs into private well water) to reduce septic

leakage into wells (Schaider et al., 2016), and included other requirements for well construction and location.



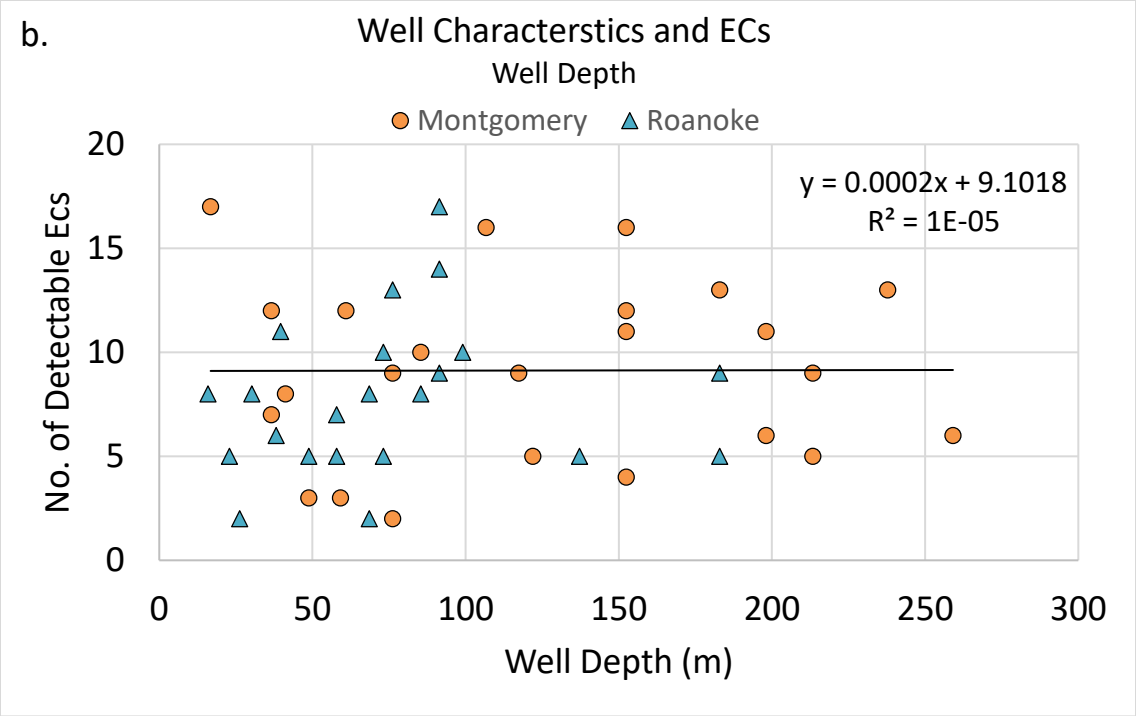


Figure 2.7: a) The correlation between the well age and the number of ECs detected in Montgomery and Roanoke County, VA; b) The correlation between well depth (m) and the number of ECs detected in Montgomery and Roanoke County, VA.

There was no correlation between well depth and number of detected ECs (Figure 2.7b). Well depth was negatively correlated with number of ECs detected in coastal Massachusetts private wells, especially, for wells less than 18 m (Schaider et al., 2011). In California public supply wells (average depth=134 m), well depth was not correlated with the occurrence of ECs (Fram and Belitz, 2011). The depth relationship observed in Virginia private well water was similar to what has been observed in California public wells (Figure 2.7b).

Of the households sampled, the vast majority were connected to septic systems rather than city sewer (55 of 57), which is expected homes for on private wells. Estimated distance of the septic system from each private well was evaluated with regard to number of ECs detected (Figure 2.8). The exact distance of the wells from the septic systems were unknown, thus, estimated ranges (<30 m and >30 m) were used. The distances ranges were chosen based on the required distance a septic system from a well must be, instituted by the 1992 Virginia well construction regulation. There was no relationship between the distance of a septic system from the private well and the number of ECs detected in this study (Figure 2.8).

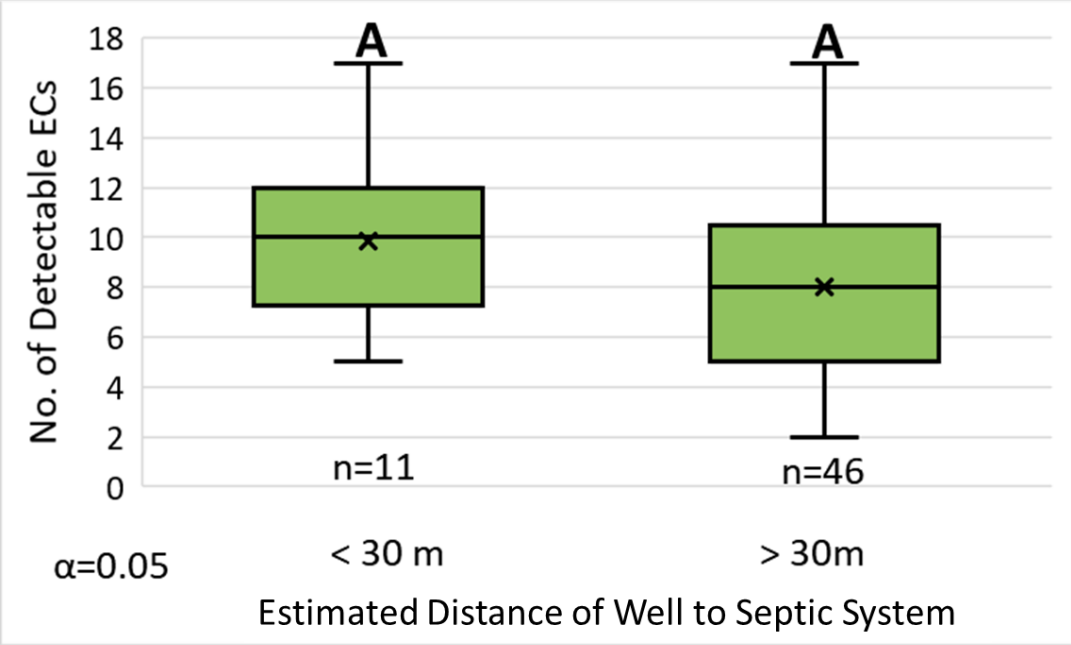


Figure 2.8: Occurrence of detected ECs in select Virginia private well water within 30 m of a septic system or greater than 30 m from a septic system. Letters above column indicate statistical differences at $p<0.05$.

The distance of a private well from a septic system was found to impact the occurrence of ECs in Nebraskan, coastal Massachusetts, and Nevada systems (Schaider et al., 2016; Seiler et al., 1999; Verstraeten et al., 2005). Detailed information regarding the septic system (septic system pumping history, major repairs, exact distance from well, etc.) was not known by most homeowners making it difficult to make conclusions regarding the impact. The detailed information was difficult to obtain because many current homeowners moved in after the septic system had been installed.

3.4 Relationship Between Water Quality Constituents and the Occurrence of Emerging Contaminants in Private Well Water

3.4.1 Water Quality Constituents Results

The VAHWQP water quality data provided general water characteristics of the private well water samples analyzed (Table 2.6).

Table 2.6: Water quality constituents of the 57 tested private wells for EC analysis. NO_3-N stands for nitrate-nitrogen. TDS stands for total dissolved solids.

	Mean	**Median**	**Maximum**	**Minimum**
NO_3-N (mg/L)	1.6	0.4	12.2	0.0
pH	7.4	7.4	9.1	6.1
TDS (mg/L)	302.3	297.8	639.2	29.5

Only one well was above the EPA regulated primary maximum contaminant level (MCL) (10 mg/L) for nitrate-nitrogen. The average nitrate concentration (1.6 mg/L) was lower than the national reconnaissance of 3,465 US private wells, 3.6 mg/L, and less than 20 coastal Massachusetts private wells, 2.9 mg/L (Focazio et al., 2006; Schaider et al., 2016). The average water pH, 7.4, was is in the EPA acceptable range for drinking water (6.5-8.5). The pH was relatively neutral, likely due to the prevalent carbonate geology in the sampled areas (Woodward, 1932). Of the 56 households with water quality data available, 23 wells (41%) had total coliform bacteria present and three wells (5%) had *E. coli* present. The bacterial presence percentages are almost equal to the average percentages reported for the >2,000 samples, VAHWQP analyzed in 2017. Three homes (5%) were above the EPA secondary drinking water standard MCL (500 mg/L) for TDS.

3.4.2 Emerging Contaminants Relationship with Water Quality Constituents

The occurrence of ECs with selected water quality constituents (nitrate, total coliform bacteria, and TDS) was examined. With respect to nitrate-nitrogen (NO_3-N), more ECs were found in wells that had NO_3-N concentrations > 1 mg/L than those with concentrations <1 mg/L ($p<0.05$) (Figure 2.9). This result is consistent with previous research in the coastal plain of Massachusetts (Schaider et al., 2016). The presence of nitrates in a well can be an indicator of septic contamination, a source of ECs. However, a detailed isotopic analysis of the nitrate would be needed to determine its source since nitrate related to ECs occurrence could also be related to agricultural practices.

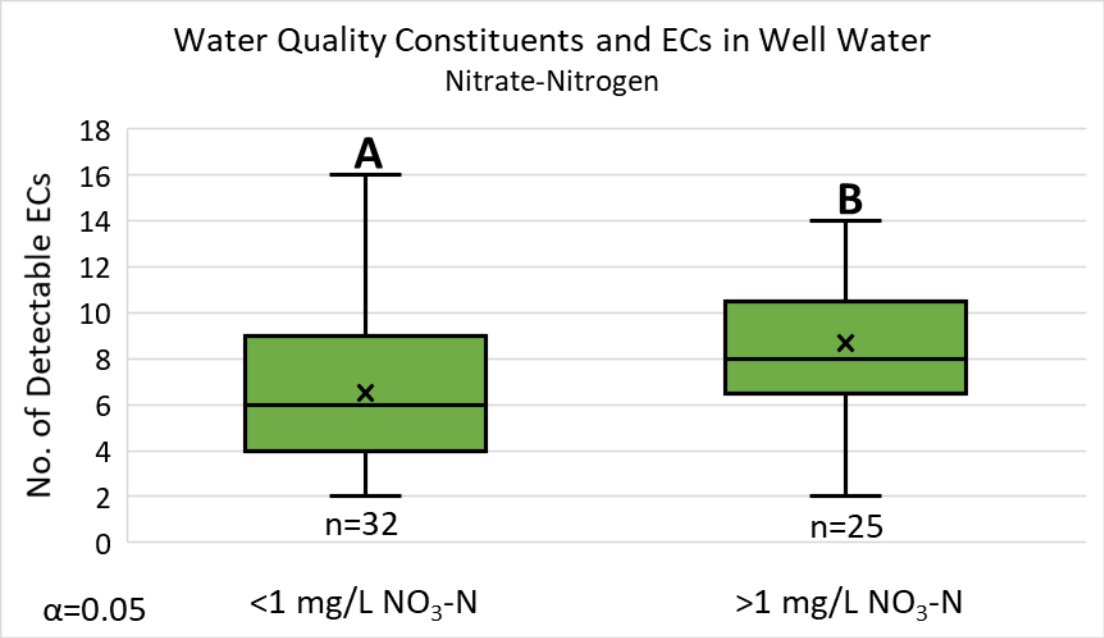


Figure 2.9: The relationship between nitrate concentration <1 mg/L or >1 mg/L and the number of detected ECs. The nitrate-nitrogen (NO_3-N) groups were chosen based on 1 mg/L of nitrate-nitrogen levels tenfold greater than typical background concentrations in a groundwater system (Schaider et al., 2011). Letters above column indicate statistical differences at $p<0.05$.

Total coliform bacteria relationship with occurrence of ECs was of great interest because it is an indicator of surface water intrusion in groundwater (Charrois, 2010). With respect to total coliform bacteria, more ECs were found in wells that had total coliform bacteria presence than wells without total coliform bacteria ($p<0.05$) (Figure 2.11).

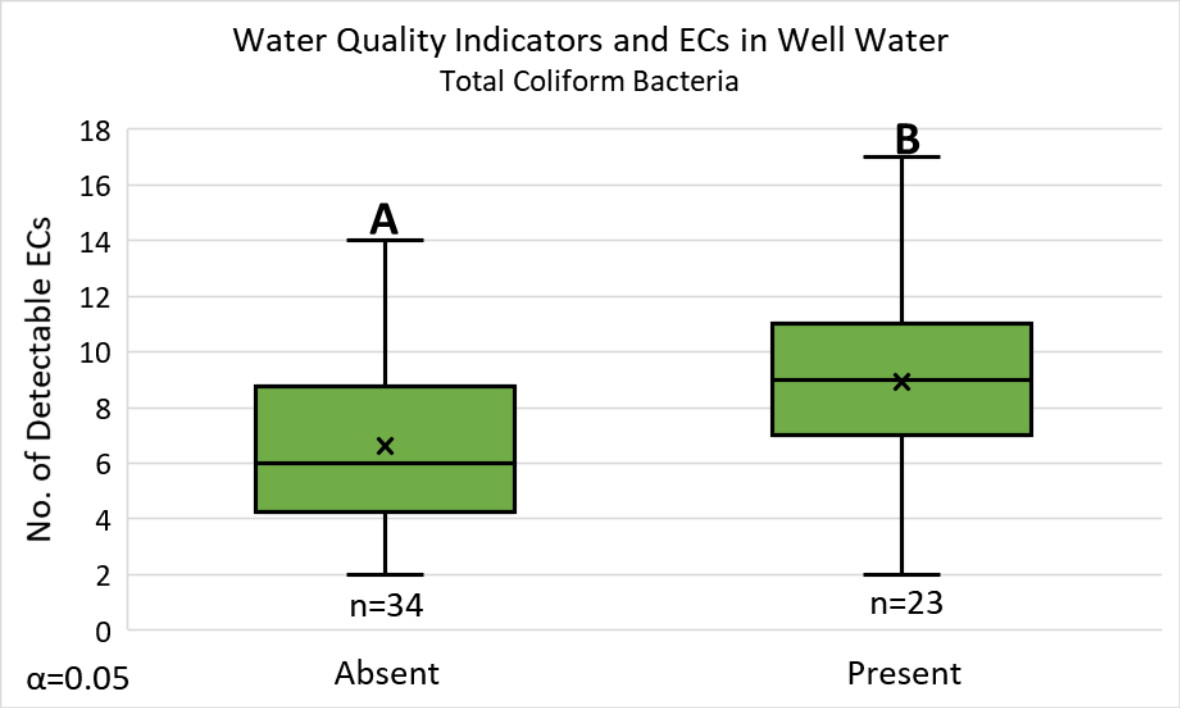


Figure 2.10: The relationship between the presence or absence of total coliform bacteria and the number of detected ECs in select Virginia well water. Letters above column indicate statistical differences at $p<0.05$.

A study of Nebraskan private well also analyzed for a relationship between total coliform bacteria presence and occurrence of ECs with no relationship was found (Verstraeten et al., 2005). Presence of total coliform bacteria can indicate the presence of pathogenic bacteria thus *E coli* was analyzed for. The presence of *E. coli* (indicator of human or animal waste) was not related with higher number of ECs detected. Private wells in this study with *E. coli* present had on average 6 more ECs present than wells with no *E. coli* present, but there were only three data points for wells with *E. coli* (Figure 2.11). Further sampling of private wells with *E. coli* for ECs

should considered in future studies because the presence of *E. coli* is an indicator that human or animal waste is influencing the water supply.

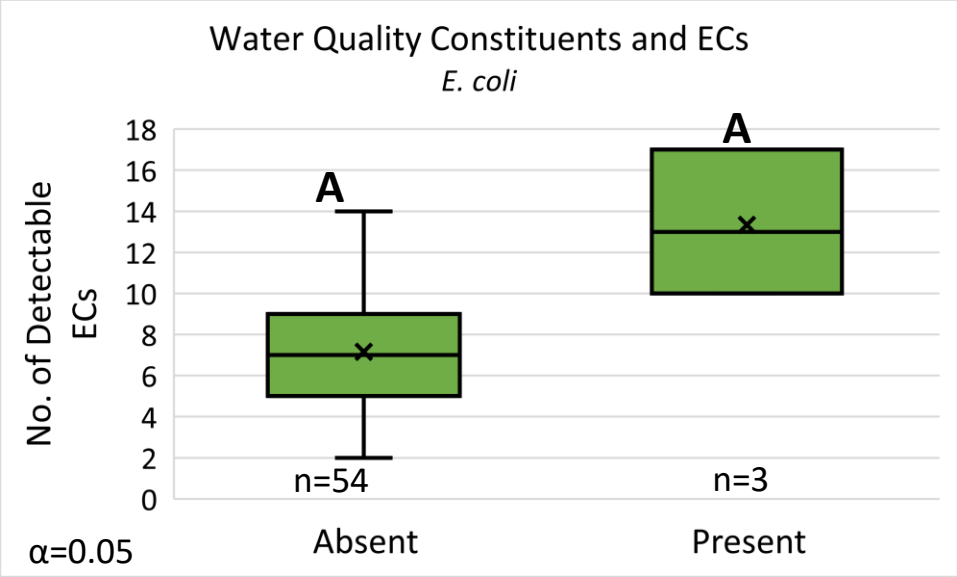


Figure 2.11: The relationship between the presence or absence of E. coli and the number of detected ECs in select Virginia private well water. Letters above column indicate statistical differences at p<0.05.

With respect to TDS, more ECs were found in wells that had TDS >250 mg/L than wells with <250 mg/L ($p<0.05$) (Figure 2.12).

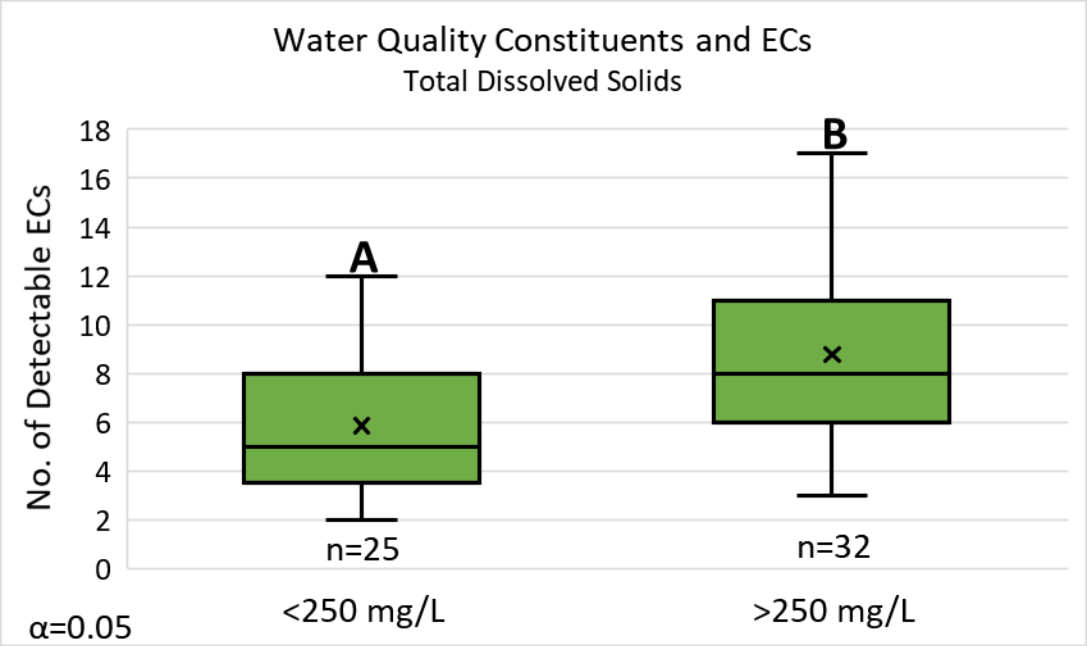


Figure 2.12: The relationship between TDS concentration (< 250 mg/L or >250 mg/L) and the number of detected ECs in select Virginia private well water. Letters above column indicate statistical differences at p<0.05.

To note, the EPA secondary water quality standard for TDS is 500 mg/L but 250 mg/L was used because it was a better population divide for the data. The influence that TDS has on the number of detected ECs in private well water is difficult to infer because TDS is made up of a variety of components (e.g. hardness ions, salts, etc.).

The pH of the well water was not related to number of ECs detected in the private well water for this study (Figure 2.13). pH levels were separated by <7 or >7 due to it being the best divide for the data rather than using the EPA recommended safe drinking pH of 6.5-8.5. However, literature findings have shown that pH can influence the transport of ECs (Kummerer, 2008). The pH can influence the charge of an EC which may impact its interactions with other charged species. Specifically, in groundwater, ECs interact with aquifer material such as clay that are charged and ECs can bind to these materials (Chen et al., 2011). The interactions with aquifer material can influence how EC travels with groundwater.

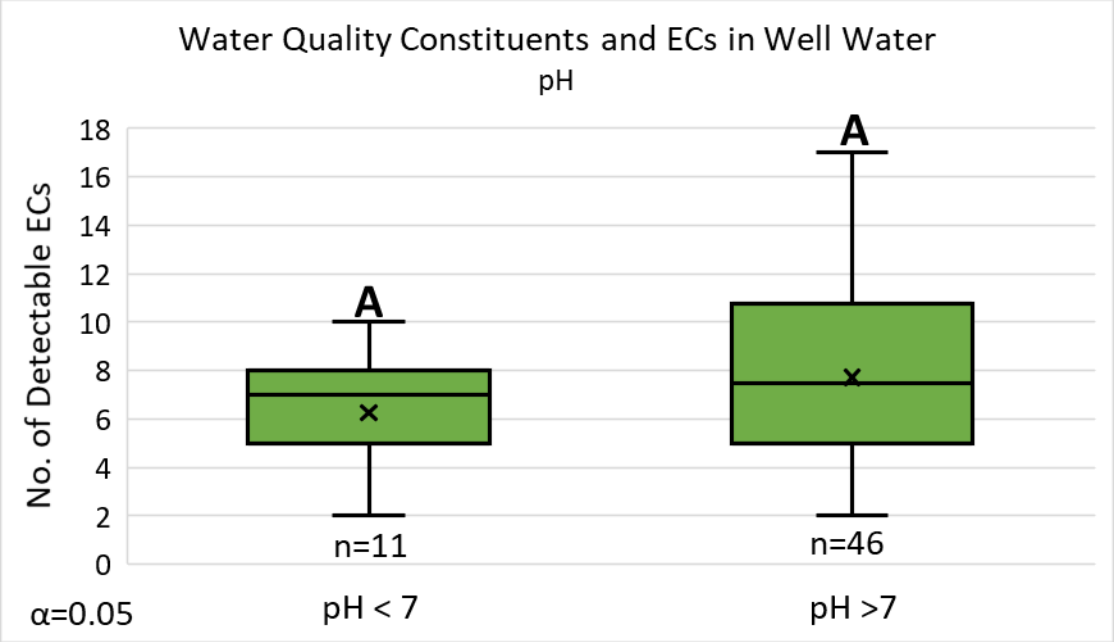


Figure 2.13: The relationship between pH (<7 or >7) and the number of detected ECs in select Virginia private well water. Letters above column indicate statistical differences at p<0.05.

3.5 Observation of EC Detection in Private Wells Before and After Household Treatment

The household treatment systems reported by homeowners via survey were water softeners (42% of samples), sediment filters (25% of samples), UV light systems (9% of

samples), acid water neutralizer (5% of samples), chlorinator (4% of samples), and iron removal system (2% of samples) (Figure 2.14).

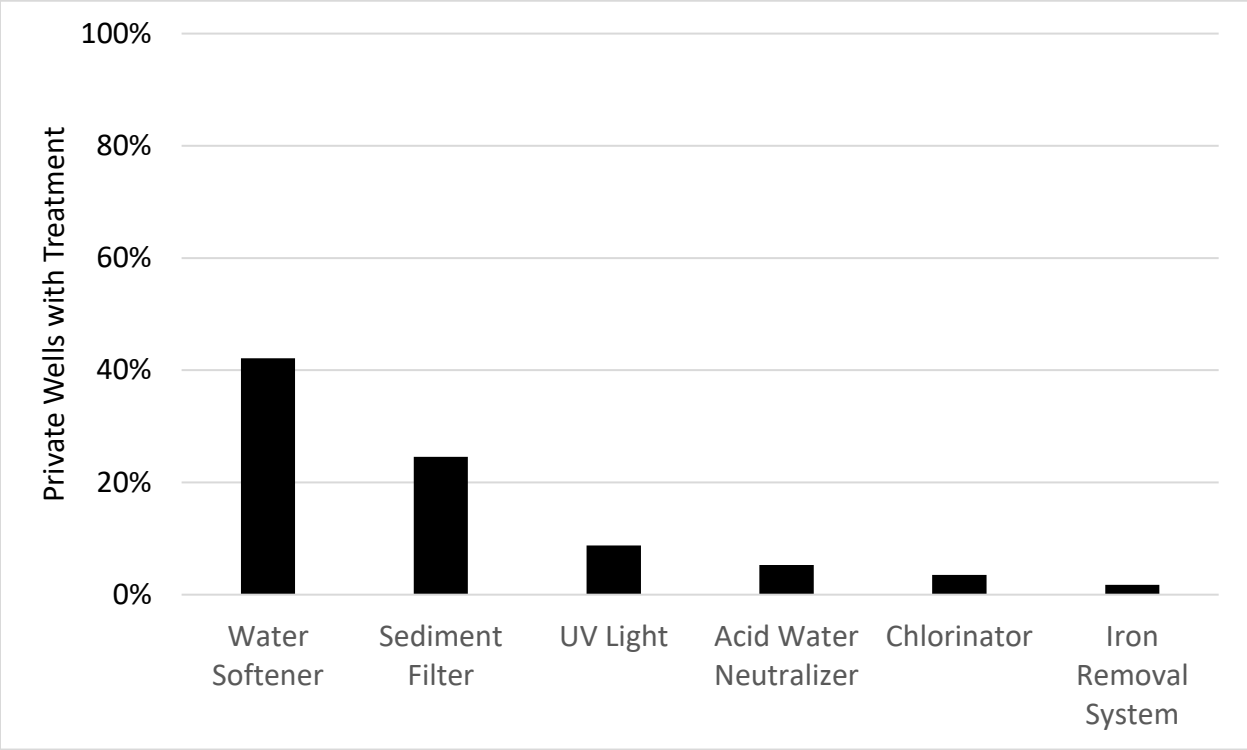


Figure 2.14: The percent of private well owners reporting treatment devices installed.

Water softeners were used frequently in these two counties in Virginia to address high water hardness levels, attributed to the carbonate rich aquifers, or to remove iron or manganese, also from the bedrock. Sediment filters are commonly used water treatment device for water derived to remove particulates and to improve taste and clarity. In the individual homes, UV light systems are usually used to prevent bacteria present from reproducing.

The household treatment systems appeared to have a varied effect on the removal of ECs but we cannot state this with certainty since detailed information regarding the systems were unavailable (Figure 2.15). The systems with multiple treatment types were in a specific order and

in conjunction with each other making it difficult to pinpoint how effective an individual system was.

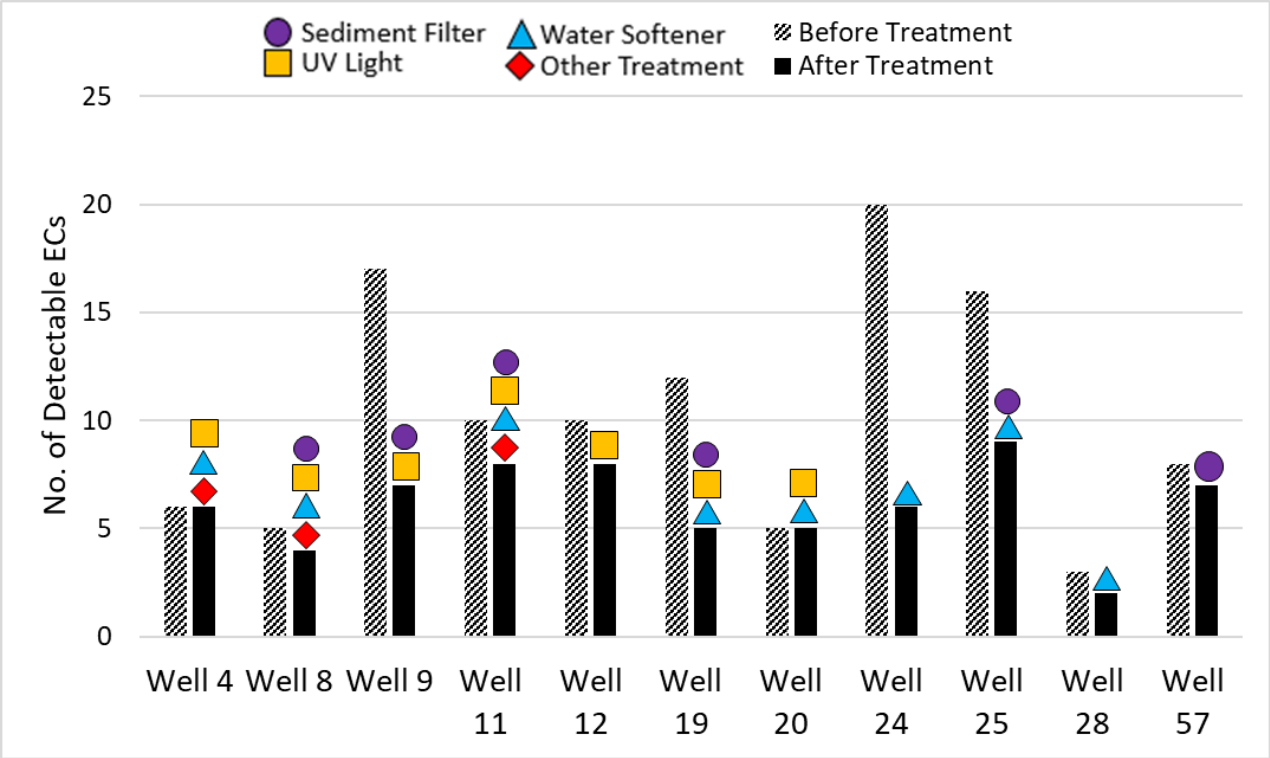


Figure 2.15: The number of ECs before and after treatment of 11 private well with different water treatment options as indicated by the colored symbols in the figure. The other treatments are acid-water neutralizer, chlorinator, iron removal system, and a PUR filter.

Treatment systems with a sediment filter had at least 10% less ECs present in the after treatment for every system. Water softeners had a varied observed impact on the number of ECs removed after treatment, with 14 ECs removed in Well 24 (14 ECs removed) and zero ECs removed in Wells 4 and 20 (Figure 2.15). Treatment systems with a UV light removed half of the ECs in the before treatment in well 9 but in well 4 and 20 no ECs were removed. The ability of the acid-water neutralizer, chlorinator, and iron removal system to remove ECs cannot be observed since there was only one to two sampled of each system (Figure 2.14).

4. Conclusions and Future Research

In this investigation, 73 ECs were detected in at least one private well of the 57 wells analyzed. Each well had at least 2 ECs present. The concentrations for caffeine were greater than

previously detected concentrations in other US private well water (Schaider et al., 2016; Seiler et al., 1999). Triclosan and tylosin concentration comparison to other US private well water is unknown because their concentrations have not been previously reported. The number of ECs detected in municipal drinking water and private well water was comparable. For caffeine, triclosan, and tylosin concentrations, the one municipal drinking water sample was comparable to the nine private well water samples, but more of both private well and municipal drinking water samples need to be quantified for better comparison. In this study, well age and well depth had no correlation with number of ECs detected. Additionally, the reported distance (<30 m or >30 m) of the well from septic systems had no relationship with number of ECs detected. Additional sampling of wells <30 m from septic system is needed to further analyze this relationship. Based on homeowner reporting of treatment systems installed, it is unclear what types of treatment devices may be most effective at removing ECs from water.

A higher number of ECs detected was related with nitrate >1 mg/L, TDS > 250 mg/L, and presence of total coliform bacteria. The nitrate relationship could be due to septic system leakage because of improper septic maintenance and/or construction. This is significant to potentially infer some ECs are coming from septic system leakage. However, a detailed isotopic analysis of nitrate is needed, to pinpoint the nitrate source because nitrate could also be coming from agricultural sources. Surface water could be a source of ECs into private well water based on the relationship with total coliform bacteria presence (indicator of surface water intrusion into groundwater). Detailed mapping of the well capture zone and its relation to surface water is needed to better understand the influence surface water intrusion may have. Further sampling of well water with *E. coli* present could better understand the relationship between number of ECs in a well and *E. coli*. This is significant because *E. coli* is an indicator of human and livestock waste. The occurrence of ECs in the private well water raise concern for human health, but it is difficult to know the risk with lacking health-based guidelines for most of these compounds.

This investigation documented the presence of ECs in select private well water in two southwest Virginia counties and future studies can contribute to these foundational results. There is great interest to determine the presence of antibiotic resistant bacteria and their correlation to the occurrence of ECs especially with the observed relationship between ECs and total coliform bacteria presence (indicator of pathogenic bacteria). This project would be meaningful due to the

increase in antibiotic resistant bacteria in the environment and its potential to cause persistent human health issues (Kim and Aga, 2007). Further health guidelines for these ECs would need to be developed to determine if the daily exposure is hazardous to human health. The determination of the exact source of ECs into private well water would help better understand an ECs distribution in the environment and to develop mitigation strategies to reduce the occurrence of ECs. The three most commonly used treatment systems (sediment filter, UV light system, and water softener) should be tested at the bench-scale to determine their EC removal effectiveness. There is still a need to better understand the risk of EC in drinking water on human health and a human risk study could focus on the tested private well water.

5. References

American Public Health Association, American Water Works Association, Water Environment Federation. (2012) Standard Methods for the Examination of Water and Wastewater. 22nd ed. American Public Health Association, Washington, DC.

Batt A.L., Snow D.D., Aga D.S. (2006) Occurrence of sulfonamide antimicrobials in private water wells in Washington County, Idaho, USA. Chemosphere 64:1963-1971.

Benham B., Ling E., Ziegler P., Krometis L.A. (2016) What's in Your Water? Development and Evaluation of the Virginia Household Water Quality Program and Virginia Master Well Owner Network. Journal of Human Sciences and Extension 4:15.

Benotti M.J., Trenholm R.A., Vanderford B.J., Holady J.C., Stanford B.D., Snyder S.A. (2009) Pharmaceuticals and Endocrine Disrupting Compounds in U.S. Drinking Water. Environmental Science & Technology 43:597-603.

Bradley P.M., Journey C.A., Button D.T., Carlisle D.M., Clark J.M., Mahler B.J., Nakagaki N., Qi S.L., Waite I.R., VanMetre P.C. (2016) Metformin and Other Pharmaceuticals Widespread in Wadeable Streams of the Southeastern United States. Environmental Science & Technology Letters 3:243-249.

Bruton T., Alboloushi A., de la Garza B., Kim B.-O., Halden R.U. (2010) Fate of Caffeine in the Environment and Ecotoxicological Considerations 1048:257-273.

Burkholder J., Libra B., Weyer P., Heathcote S., Kolpin D., Thorne P.S., Wichman M. (2007) Impacts of waste from concentrated animal feeding operations on water quality. Environ Health Perspect 115:308-12.

Charrois J.W.A. (2010) Private drinking water supplies: challenges for public health. CMAJ : Canadian Medical Association Journal 182:1061-1064.

Chen H., Gao B., Li H., Ma L.Q. (2011) Effects of pH and ionic strength on sulfamethoxazole and ciprofloxacin transport in saturated porous media. J Contam Hydrol 126:29-36.

Environmental Protection Agency. (2002) A Homeowner's Guide to Septic Systems.

Erickson M., Langer S., Roth J., Kroening S. (2012) Contaminants of Emerging Concern in Ambient Groundwater in Urbanized Areas of Minnesota, 2009-12, in: USGS (Ed.). pp. 38.

Focazio M.J., Kolpin D.W., Barnes K.K., Furlong E.T., Meyer M.T., Zaugg S.D., Barber L.B., Thurman M.E. (2008) A national reconnaissance for pharmaceuticals and other organic wastewater contaminants in the United States--II) untreated drinking water sources. Sci Total Environ 402:201-16.

Focazio M.J., Tipton D., Shapiro S., Geiger L. (2006) The Chemical Quality of Self-Supplied Domestic Well Water in the United States. Ground Water Monitoring and Remediation 26:13.

Fram M.S., Belitz K. (2011) Occurrence and concentrations of pharmaceutical compounds in groundwater used for public drinking-water supply in California. Sci Total Environ 409:3409-17.

Holm J., Rugge K., Bjerg P., Christenson T. (1995) Occurence and Distribution of Pharmaceutical Organic Compounds in the Groundwater Downgradient of Landfill Environmental Science & Technology 29:6.

IQVIA Institute. (2017) Medicines Use and Spending in the U.S.: A Review of 2016 and Outlook to 2021, IQVIA Institute, Parsippany, NJ.

Kasprzyk-Hordern B., Dinsdale R.M., Guwy A.J. (2008) The occurrence of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs in surface water in South Wales, UK. Water Research 42:3498-3518.

Kim S., Aga D.S. (2007) Potential ecological and human health impacts of antibiotics and antibiotic-resistant bacteria from wastewater treatment plants. J Toxicol Environ Health B Crit Rev 10:559-73.

Kummerer K. (2008) Pharmaceuticals in the Environment--A Brief Summary Springer

Lapworth D.J., Baran N., Stuart M.E., Ward R.S. (2012) Emerging organic contaminants in groundwater: A review of sources, fate and occurrence. Environ Pollut 163:287-303.

Lin A.Y., Tsai Y.T. (2009) Occurrence of pharmaceuticals in Taiwan's surface waters: impact of waste streams from hospitals and pharmaceutical production facilities. Sci Total Environ 407:3793-802.

Maupin M.A., Kenny J.F., Huston S.S., Lovelace J.K., Barber N.L., Linsey K.S. (2010) Estimated Use of Water in the United States in 2010, in: U. G. Survey and U. D. o. Interior (Eds.). pp. 56.

Postigo C., Barcelo D. (2015) Synthetic organic compounds and their transformation products in groundwater: occurrence, fate and mitigation. Sci Total Environ 503-504:32-47.

Schaider L., Ackerman J., Rudel R., Dunagan S., Brody J. (2011) Emerging Contaminants in Cape Cod Private Drinking Well Water Silent Spring Institute:13.

Schaider L.A., Ackerman J.M., Rudel R.A. (2016) Septic systems as sources of organic wastewater compounds in domestic drinking water wells in a shallow sand and gravel aquifer. Sci Total Environ 547:470-81.

Scheurer M., Michel A., Brauch H.J., Ruck W., Sacher F. (2012) Occurrence and fate of the antidiabetic drug metformin and its metabolite guanylurea in the environment and during drinking water treatment. Water Res 46:4790-802.

Seiler R.L., Zaugg S.D., Thomas J.M., Howcroft D.L. (1999) Caffeine and Pharmaceuticals as Indicators of Waste Water Contamination in Wells Groundwater 37:5.

Servos M., Smith M., McInnis R., Burnison K., Lee B., Seto P., Backus S. (2007) The Presence of Selected Pharmaceuticals and the Antimicrobial Triclosan in Drinking Water in Ontario, Canada Water Quality Resources Journal of Canada 42:8.

Stackelberg P.E., Furlong E.T., Meyer M.T., Zaugg S.D., Henderson A.K., Reissman D.B. (2004) Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water-treatment plant. Sci Total Environ 329:99-113.

Stuart M.E., Manamsa K., Talbot J.C., Crane E.J. (2011) Emerging Contaminants in Groundwater. British Geological Survey:112.

Verstraeten I.M., Fetterman G.S., Meyer M.T., Bullen T., Sebree S.K. (2005) Use of Tracers and Isotopes to Evaluate Vulnerability of Water in Domestic Wells to Septic Waste. Groundwater Monitoring and Remediation 25:11.

Virginia Department of Health. (1992) Private Well Regulations, in: V. D. o. Health (Ed.), 12.

Woodward H.P. (1932) Geology and Mineral Resources of the Roanoke Area, Virginia in: V. G. Survey (Ed.).

Chapter 3 Removal of Emerging Contaminants from Secondary Wastewater Treatment Effluents Using MicroEvap™

Abstract

Emerging contaminants (ECs) have been detected worldwide in surface and groundwater, and even drinking water primarily due to the inadequacy of conventional wastewater treatment plants (WWTPs) to remove them. There is an urgent need to develop cost-effective wastewater treatment technology that removes all ECs from contaminated water. This study investigated the effectiveness of an emerging water purification treatment device, MicroEvap™ (Aerial 2.0 system, Micronic Technologies, Wise, VA) to remove ECs from secondary wastewater effluent. Secondary wastewater effluent was collected from three wastewater treatment plants (WWTPs) in southwest Virginia. After sampling, the secondary wastewater effluent was processed through the MicroEvap™. The MicroEvap™ purifies a wastewater by employing a tornadic flow field that evaporates the wastewater stream at ambient temperatures and re-condenses 95% of it as clean water. During the evaporation of the wastewater stream, the contaminants remain in solution and are transferred into the waste brine. The secondary wastewater effluent, MicroEvap™ treated secondary wastewater effluent (product water), and waste brine were then extracted and cleaned up through solid phase extraction followed by screening for 36 ECs on an UPLC/MS/MS. Twenty-four ECs were positively identified in the secondary wastewater effluent. Only two ECs (diltiazem and sertraline) were detected in the product water generated by the MicroEvap™. However, there was >99% removal rates for the 26 detected ECs. A mass distribution showed most ECs were completely transferred into the waste brine. The results demonstrate that the MicroEvap™ is a promising water purification system for removal of ECs from partially treated wastewater.

1. Introduction

Wastewater reuse is essential to the long-term sustainability of drinking water with a growing demand and scarce water resources worldwide. There is a growing concern of ensuring clean drinking water due to the increased detection of chemical compounds at trace concentrations (i.e. ng/L-µg/L), that are not historically considered contaminants (Benotti et al., 2009b; Kim et al., 2007; Kolpin et al., 2002; Ternes, 1998). These compounds, termed emerging contaminants (ECs), are an increasing water pollution concern because they are continuously released into the environment through anthropogenic activities. Emerging contaminants are made

up of several chemical classes of compounds: human/veterinary antibiotics and pharmaceuticals and personal care products (PPCPs), as well as their transformation products (Kummerer, 2008). Emerging contaminants persist because they are not fully removed by wastewater treatment plants (WWTPs) and are released in WWTP effluent. Due to the potential long-term effects on human health, there is a great need to develop and implement effective water treatment technology that sufficiently removes all ECs from wastewater (Hazelton et al., 2014; Kim and Aga, 2007; Kummerer, 2008).

1.1 Effectiveness of Current Wastewater Treatment Technologies for Removal of Emerging Contaminants

The primary source of ECs in aquatic systems is the effluent of WWTPs. The inadequacy of WWTPs to account for the chemical heterogeneity of ECs during wastewater processing allows for EC residues to be released into water bodies (Benotti et al., 2009b). Even though WWTP effluent is typically discharged into large water bodies, natural attenuation is not sufficient enough to prevent ECs from entering drinking water (Kummerer, 2008). Conventional wastewater treatment technology can remove/reduce some ECs from wastewater, but these treatment processes were not specifically designed to remove ECs. Chemical coagulation/flocculation and chlorination disinfection are largely ineffective at removing ECs (Vieno et al., 2006). Disinfection using UV-light is a promising technology to degrade ECs with removal rates reported up to 60% (Kim et al., 2009). Ozonation (advanced oxidative treatment) is able to remove ECs from oxidative degradation and removal rates have been reported up to 60% removal (Huber et al., 2003). Activated sludge microbiological treatment, removed 40% of select ECs but the treatment needs greater bacterial growth time for further removal of ECs (Radjenovic et al., 2009). Carbon activated filters, nanofiltration, and reverse osmosis membranes (pressure-driven membrane purification processes) appear to be most effective at removing ECs (90% removal) due to their size and charge exclusion. There is a need to upgrade existing treatment to ensure WWTPs are more effective at EC removal.

Using unconventional wastewater treatment technologies and/or the pairing of unconventional technologies with conventional technologies present a potential solution to remove or degrade chemically diverse ECs. Clay minerals (montmorillonite, goethite, etc.) have shown to remove up to 88% of tested EC compounds primarily from charge exclusion and size

exclusion of ECs (Grassi et al., 2012). Zero valent iron particles are a promising approach to removes ECs from contaminated wastewater due to its ability to remove metronidazole (antibiotic) from wastewater in bench-scale experiments (Fang et al., 2011). Titanium nanoparticles (emerging photocatalytic treatment) paired with UV light removed 70% of 32 ECs in a pilot system study (Benotti et al., 2009a). Membrane bioreactors, the pairing of nanofiltration technology with activated sludge, led to a 14% increase in EC removal efficiency compared to activated sludge (Radjenovic et al., 2009). The EC removal effectiveness of UV light and ozonation treatment was increased by 40% when paired with hydrogen peroxide (Huber et al., 2003).

The chemical and physical properties (pH, organic matter content, temperature, etc.) of wastewater directly affect the ability of treatment systems to remove ECs. The pH of wastewater can alter the charge of an EC which can affect an ECs transport and reaction with physiochemical treatments (Hari et al., 2005). High organic matter content in wastewater leaves fewer binding sites for ECs to sorb to a filtration or membrane devices (Fan et al., 2001). An ECs physiochemical properties (biodegradability, cation-exchange potential, polarity, solubility, etc.) can be a major reason that residue of ECs can persist through WWTP treatment systems (Kummerer, 2008). An EC having a stronger sorption affinity to a filter may prevent other ECs from sorbing to it. If a wastewater treatment system is being designed to remove ECs, the persistence of an EC (resistance to UV-degradation, resistance to microbiological degradation, etc.) needs to be a focus parameter (Benotti et al., 2009b). There is a need for an all-encompassing wastewater treatment system, if possible, that can accommodate a range of chemically diverse ECs in a variety of wastewater streams.

1.2 MicroEvap™ Wastewater Treatment Technology

Micronic, a water treatment technology firm based in Wise, VA, has developed a novel wastewater treatment technology called the MicroEvap™ (Aerial 2.0 system, Micronic Technologies, Wise, VA). The MicroEvap™ aims for cost effectiveness for cleaning wastewater without using filters, membranes, or chemical additives. The MicroEvap™ was originally designed to remove minerals typically associated with “hard” water (calcium and magnesium), heavy metals (arsenic, lead, etc.), nutrients (nitrogen and phosphorus, and sodium chloride. The

two main components of the MicroEvap™ are mechanical evaporation and vapor compression/condensation technology.

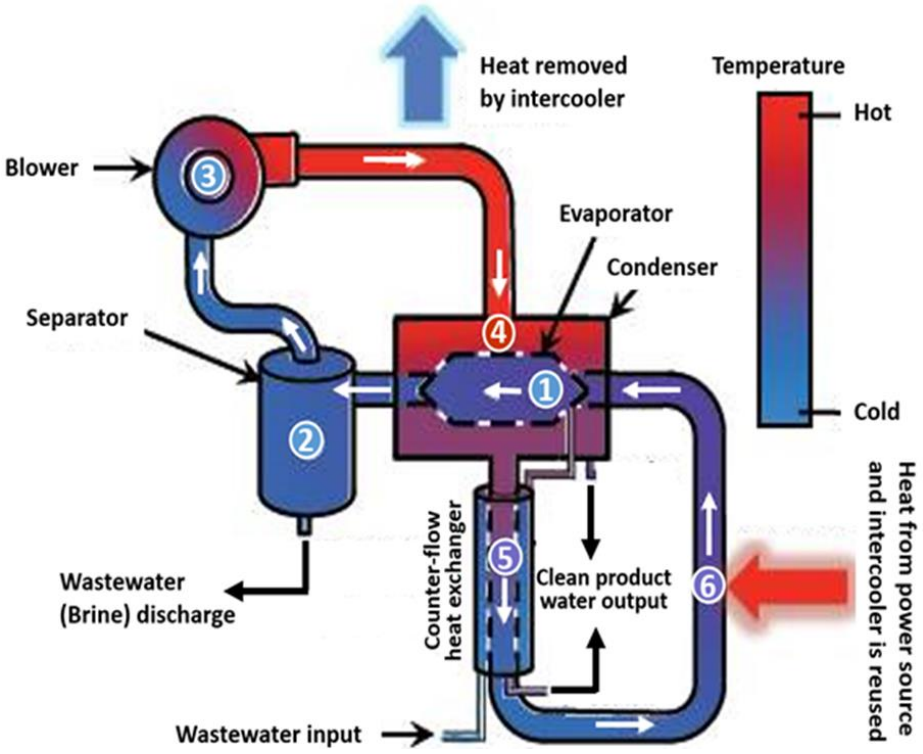


Figure 3.1: Schematic diagram of the water treatment flow (influent to effluent) through the MicroEvap™ system.

The air flow in the system utilizes a unique geometry (#5 in Figure 3.1) that creates a tornadic flow field. The wastewater stream combined with an incoming air field is pushed through a specialized flow-path device. The unique flow field creates a pressure gradient that allows for evaporation of the flow field (#1 in Figure 3.1) at ambient temperatures. During this evaporation process, the contaminants remain in solution due to high boiling points (#2 in Figure 3.1) than that of water. The contaminants remaining in the solution form a waste brine (5% of the original sample volume). The other 95%, evaporated wastewater stream, is blown into the condenser (#3) where it is re-condensed (#4 in Figure 3.1) and then reclaimed as clean water. The MicroEvap™ is a closed-loop system that reclaims air and heat for energy savings.

Researchers partnered with Micronic Technologies to test their MicroEvap™ technology for removal of ECs from wastewater. As of 2018, the MicroEvap™ would be one of the first technologies tested for EC removal that primarily uses water distillation and evaporation

techniques as the contaminant removal mechanism. The objectives of this investigation were: 1) to determine the occurrence of 36 ECs in the secondary wastewater effluent from three southwest Virginia WWTPs; 2) to calculate the EC removal efficiency of the MicroEvap™.

2. Methods and Materials

2.1 Wastewater Collection

Secondary wastewater effluent samples were collected from three smaller-scaled wastewater treatment plants (WWTPs) in southwest Virginia during fall 2016 (Table 3.1). WWTP 1 treats a mixture of municipal, coal mining, and agricultural wastewater. WWTP 2 services municipal and textile factory waste, and WWTP 3 services wastewater from predominantly suburban/urban area and a major university.

Table 3.1: The water treatment characteristics of the three sampled WWTPs secondary wastewater effluent in southwest Virginia.

WWTP #	People Served	Water Processed (millions of liters/day)	Coagulation, Sedimentation, & Flocculation	Disinfection Type
1	3,000	32,000	Yes	Chlorination
2	20,000	7,500	Yes	UV Disinfection
3	35,000	55,000	Yes	UV Disinfection

Approximately 20 L of secondary wastewater effluent were collected from each WWTP as grab samples in acid-rinsed plastic buckets using an acid-rinsed 1 L plastic bottle mounted on a sampling rod. Samples from WWTP 1 effluent were collected by the Micronic staff and immediately transported to the Micronic lab. Samples from WWTP 2 and 3 were collected by Virginia Tech environmental organic chemistry lab members and transported and stored at 4°C to Micronic.

2.2 Treatment of Secondary Wastewater Effluent Using MicroEvap™

Before processed through MicroEvap™, the secondary wastewater effluent samples were processed through a sediment excluding mesh screen filter (Figure 3.2).

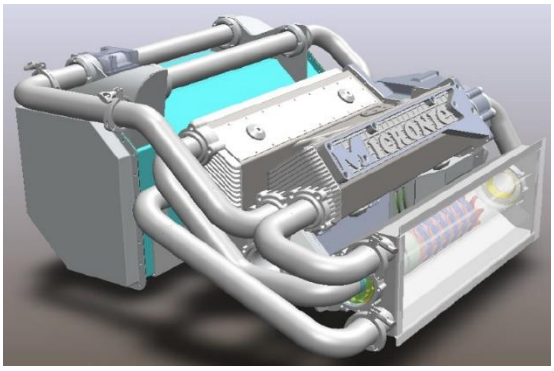


Figure 3.2: Bench scale prototype of the MicroEvap™ system.

All samples were processed through the MicroEvap™ several days after collection (**Error! Reference source not found.**; Figure 3.2). The MicroEvap™ system was flushed thoroughly with distilled water before each use to remove any remaining water and then was cooled to room temperature to remove any condensed water from previous runs. Approximately 7.5 L per WWTP secondary wastewater effluent were processed through the MicroEvap™. The 7.5 L per WWTP secondary wastewater effluent was processed through the MicroEvap™ in two separate runs per WWTP leading for a total of runs. Distilled water was processed through the MicroEvap™ before the secondary wastewater effluent samples to clean the system. After MicroEvap™ processing; the WWTP secondary wastewater effluent sample, product water (MicroEvap™ treated secondary wastewater effluent), and waste brine were collected in acid rinsed EPA grade 1 L amber bottles and then were transported at 4°C to the Virginia Tech organic environmental chemistry lab. Samples were stored at -20°C before analysis for ECs.

2.3 Analysis of Emerging Contaminants in Water

2.3.1 Water Sample Extraction and Cleanup Using Solid Phase Extraction

The water samples were processed through solid phase extraction (SPE) to concentrate and clean up the samples. For SPE processing, 100 mL of the secondary wastewater effluent, product water, and the control blanks were diluted with 150 mL of ultra-pure water (MilliQ, Millipore, Billerica, MA). Five mL of the concentrated waste brine was diluted with 245 mL of ultra-pure water. Ultra-pure water blanks and ultra-pure water spikes were included in the SPE processing for quality assurance and control (QA/QC) to determine how much of select ECs were being retained during SPE processing. A mixture of two high purity (>90%) antibiotic

standards (sulfamethazine and tylosin) purchased from Sigma Aldrich (St. Louis, MO) were used for the spiked samples.

Before SPE processing, all water samples including blanks and spikes were filtered through a 0.7-micron 55 mm glass fiber filter (Whatman, GE, Maidstone, UK). Samples were then processed through hydrophilic-lipophilic balance 6 cc cartridges (Oasis, Waters, Milford, MA) on a SPE manifold. Before processing, the cartridges were pre-conditioned with 3 mL of ultra-pure water and then 3 mL of HPLC-grade methanol (Fisher Scientific, Hampton, NH). The water samples were processed through the cartridges at ≈5 mL/min. The concentrated cartridges were dehydrated before elution to remove any remaining water. The cartridges were eluted with 3 mL of HPLC-grade methanol. The elutes were dried on a vacuum evaporation system (RapidVap, Labconco, Kansas City, MO) and then reconstituted with 1:1 LC-grade acetonitrile/ultra-pure water. The reconstituted concentrates were filtered through an 0.2-micron polytetrafluoroethylene syringe filter (Thermo Scientific, Rockwood, TN) into 2 mL amber vials (Agilent, Santa Clara, CA). The reconstituted concentrates were stored in a -20°C freezer before analysis.

2.3.2 Screening of Emerging Contaminants using UPLC/MS/MS

The SPE sample concentrates were screened for 36 ECs on an ultra-performance liquid chromatography tandem mass spectrometry (UPLC/MS/MS) (6490, Agilent, Santa Clara, CA). The instrument operating conditions are listed in Table 3.2. The MassHunter™ software (Agilent, Santa Clara, CA) controlled the operation of the UPLC/MS/MS and data collection and processing.

Table 3.2: The measurement conditions of the UPLC/MS/MS.

Agilent 6490 UPLC		
Column: Agilent Zorbax Extend C-18 (5 µm)		
Column Temp: 40°C		
Flow Rate: 0.3 mL/min		
Injection Volume: 20 µL		
Mobile Phase:		
	A: Water w/ 0.1% Formic Acid	B: 95% Acetonitrile/5% Water
Gradient:		
Time (min)	A (%)	B (%)
0	95	5

15	10	90
17.5	10	90
18	95	5
MS/MS: Agilent 6490 Triple Quad		
Ionization: Electrospray Ionization Positive		
Capillary Voltage: 3500 V		
Capillary Temp: 250°C -Source Temp: 200°C		

The 36 screened ECs were selected from an Agilent Technologies database, specifically designed for the Agilent 6490 UPLC/MS/MS model and provides analytical information including parent ion, daughter ions, and collision energy for 142 ECs (Yang et al., 2014). Agilent selected these 142 ECs to account for the most detected ECs in the environment. Our investigation reduced that number based on what was most frequently detected in testing of southwest Virginia wastewater. The recovery rates were calculated from the triplicate spikes in each SPE run to determine the precision and accuracy of the sample processing procedure.

The average QA/QC recovery rates for sulfamethazine and tylosin were 82% and 48%, respectively for the three SPE runs. DEET was present in all instrumental blanks and samples likely due to a false signal coming off the column or the UPLC/MS/MS itself. DEET contamination has been reported before in solvent and method blanks during EC sample analysis (Erickson et al., 2012). Otherwise, method blanks for all three WWTP SPE processing runs had no detected ECs.

2.3.3 UPLC/MS/MS Data Analysis

The chromatograms produced from the UPLC/MS/MS were analyzed on two software packages (Agilent, Santa Clara, CA): Masshunter Qualitative and Quantitative Analysis version 6.0. An EC was positively identified using the Qualitative Analysis software package by comparing the two daughter ions of an EC.

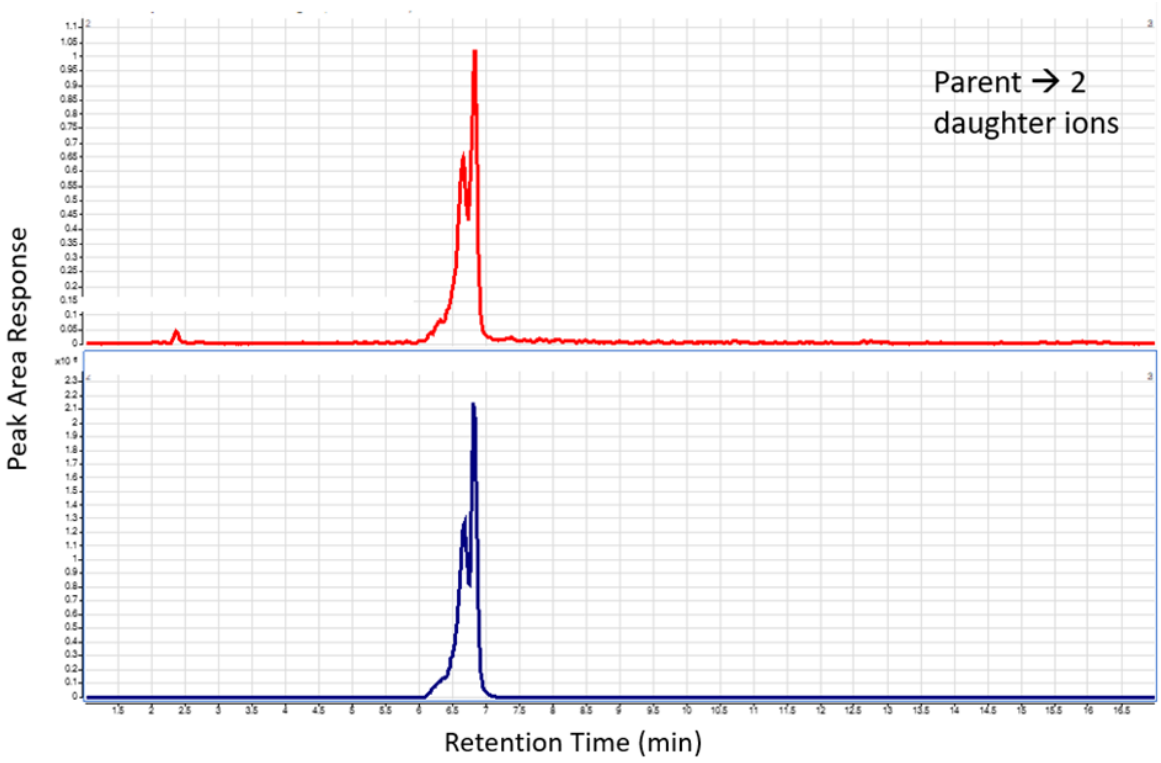


Figure 3.3: An example chromatogram showing a positive identification for tramadol (a narcotic pain reliever).

The positive identification of an EC in a water sample was determined by the identification of the same peak shape at the same retention time for both daughter ions of a compound and a signal to noise ratio >3 is needed (Figure 3.3). The retention time of an EC was determined from previous testing using wastewater and analytical standards. The detected ECs were quantified for peak area on the Quantitative Analysis software package. The determination of the occurrence of an EC and peak area quantification method was the same for the secondary wastewater effluent, product water, waste brine, and blanks.

2.4 MicroEvap™ Data Analysis

The EC removal efficiency (RE) of the MicroEvap™ was calculated as:

$$RE\ (\%) = 100\% * \frac{P_{swe} * V_{swe} - P_{pw} * V_{pw}}{P_{swe} * V_{swe}} \qquad (1)$$

The P_{swe} and P_{pw} are the peak area of the screened ECs in the secondary wastewater effluent and the product water, respectively. The V_{swe} and V_{pw} are the volumes of the secondary wastewater effluent and the product water, respectively.

A mass balance (MB) was performed to determine the mass distribution of an EC in the product water and waste brine following the MicroEvap™ treatment. A mass balance was calculated for WWTP 2 and WWTP 3 as follows:

$$MB\ in\ Brine\ (\%) = 100\% * \frac{P_b * V_b * C_f}{P_{swe} * V_{swe}} \quad (2)$$

where P_b is the peak area of the waste brine and V_b is the volume of the brine. C_f is the concentration factor used to adjust for the difference in dilution during the water sample extraction processing or the waste brine. The C_f was 20 in this case. A mass balance was not conducted for WWTP 1 because the waste brine was not provided by Micronic.

3. Results and Discussion

3.1 Occurrence of Emerging Contaminants in the Secondary Wastewater Treatment Plant Effluents

Of the 36 ECs that were screened for, 26 (72%) were detected in secondary wastewater effluent across the three WWTPs, with 16 ECs found in all three WWTPs detected (atrazine, carbamazepine, cotinine, dextromethorphan, diltiazem, EDDP, escitalopram, gabapentin, lidocaine, meprobamate, metformin, propranolol, sertraline, thiabendazole, triamterene, trimethoprim, and vancomycin) (Table 3.3).

Table 3.3: The 36 ECs screened for and detection frequency in three secondary WWTP effluent.

		Detected in Secondary Wastewater Effluent			Removal Efficiency
Emerging Contaminant	**Treatment Usage**	**WWTP 1**	**WWTP 2**	**WWTP 3**	**(%)**
Amitriptyline	antidepressant		√	√	100
Atrazine	pesticide		√	√	100
Buprenorphine	pain reliever	√	√		100
Carbamazepine	anticonvulsant	√	√	√	100
Cefotaxime	antibiotic				
Cocaine	recreational drug		√	√	100

Cotinine	nicotine metabolite	√	√	√	100
Chlortetracycline	antibiotic				
Clenbuterol	decongestant				
Dextromethorphan	cough suppressant	√	√	√	100
Diltiazem	beta blocker	√	√	√	99
EDDP	methadone metabolite	√	√	√	100
Erythromycin	antibiotic		√	√	100
Escitalopram	antidepressant	√	√	√	100
Gabapentin	pain reliever	√	√	√	100
Lidocaine	numbing agent	√	√	√	100
Lorazepam	sedative	√		√	100
MDMA	ecstasy				
Mefenamic Acid	pain reliever				
Meprobamate	anxiolytic	√	√	√	100
Metformin	antidiabetic	√	√	√	100
Ormetoprim	antibiotic				
Oxidized Nifedipine	nifedipine metabolite		√	√	100
Primidone	anticonvulsant		√	√	100
Propranolol	beta blocker	√	√	√	100
Sertraline	antidepressant	√	√	√	99
Sulfamethazine	antibacterial agent				
Tetracycline	antibiotic	√	√		100
Thiabendazole	fungicide	√	√	√	100
Triamterene	beta blocker	√	√	√	100
Trimethoprim	antibiotic	√	√	√	100
Tylosin	veterinary antibiotic				
Vancomycin	antibiotic	√	√	√	100
Venlafaxine	pain reliever		√		100

The general use or category of the detected ECs was wide-ranging and not specifically related to one category. The three most detected EC general use categories were antidepressants, anticonvulsants, and antibiotics (Figure 3.4). Two pesticides atrazine, a common pesticide used for corn production, and thiabendazole, a pesticide used to treat parasites in household pets, were found. Cotinine (metabolite of nicotine), EDDP (metabolite of methadone), and oxidized nifedipine (metabolite of nifedipine) were also detected.

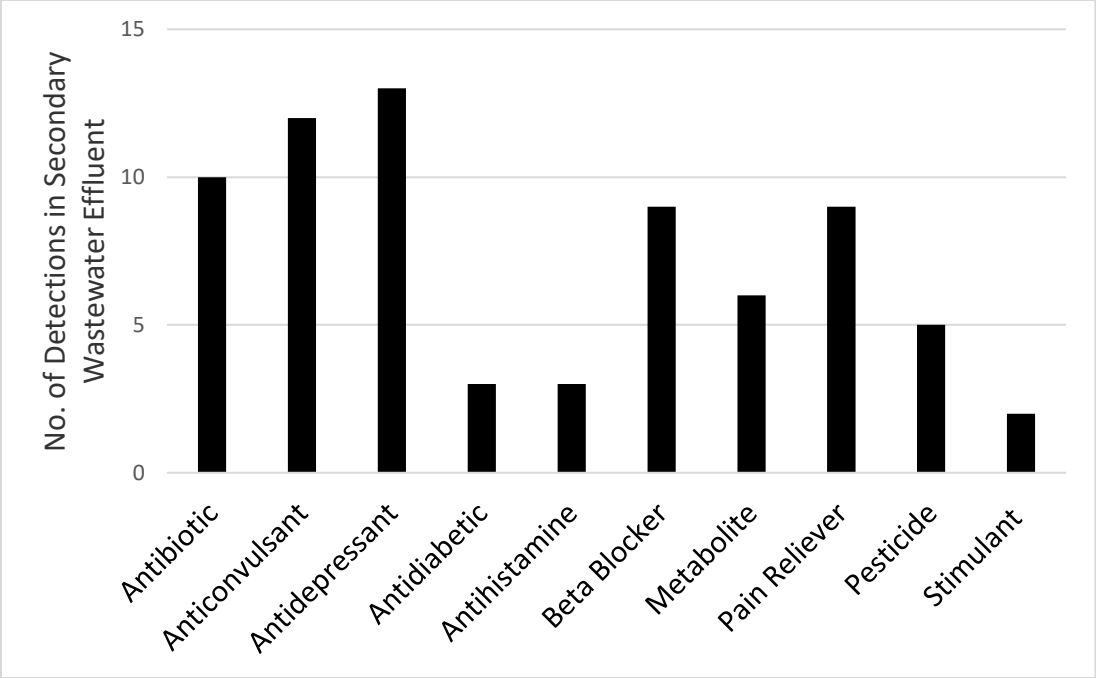


Figure 3.4: Number of detected ECs, grouped by general use categories in the secondary WWTP effluent.

There were a variety of commonly used ECs detected in the US: metformin (2016 7th most prescribed), gabapentin (2016 10th most prescribed), and sertraline (2016 13th most prescribed) and lesser used compounds: carbamazepine and oxidized nifedipine (IQVIA Institute, 2017). This pattern indicates how environmental persistence can be a better predictor of occurrence of ECs rather than its frequency of usage by humans (Benotti et al., 2009b). The persistence of an EC in the environment stems from its ability to resist degradation (resistance to biotic and abiotic degradation and sorption to sediment/soil.) and affinity to sorb to sediment. For example in a bench-scale persistence study, carbamazepine had an environmental half-life of 82 days, 81 days greater than the 2016 4th most prescribed compound in the US, acetaminophen (IQVIA Institute, 2017; Lam et al., 2004). This means even if acetaminophen has a higher input into a water body it may break down before it reaches drinking water whereas carbamazepine may have greater detection due to its persistence. To conclude, the detected ECs in the secondary wastewater effluent appear to be influenced by more than its frequency of usage by humans.

The detected ECs in the secondary wastewater effluent is similar to what has been detected in other treated and untreated wastewater and drinking water in the U.S. Carbamazepine

and cotinine, both of which were detected in all three secondary WWTP effluent in this investigation, were detected at trace concentrations in influent and effluent of four WWTPs in Nebraska (Bartelt-Hunt et al., 2009). Carbamazepine and meprobamate (detected in three WWTPs) were detected at trace concentrations in the source, finished, and distributed water of 19 US drinking water treatment plants (DWTPs) (Benotti et al., 2009b). Trimethoprim (detected in all three WWTPs) was detected in the source water of the 19 US DWTPs but was removed during treatment. The database, the EC screening method was developed from, accounts for the most detected ECs in the environment thus its sensible, the detected ECs have been commonly detected in other treated and untreated wastewater and drinking water in the US.

3.2 Removal of Emerging Contaminants from Secondary Wastewater Effluent by MicroEvap™

3.2.1 Removal Efficiencies

The MicroEvap™ removed 24 of the 26 detected ECs that were present in the secondary wastewater effluent. The peaks for those 24 ECs were not present in the product water meaning these ECs were 100% removed (Figure 3.5).

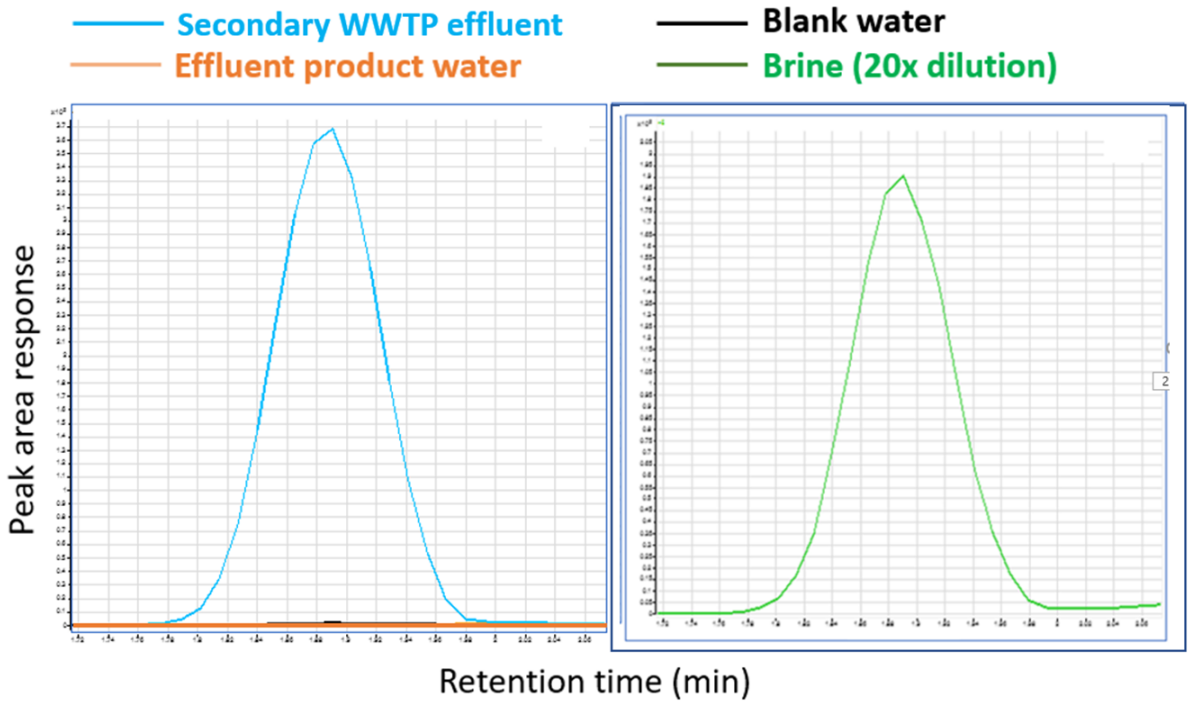


Figure 3.5: The metformin chromatogram for WWTP 2s secondary wastewater effluent, product water, control blank, and brine water.

As shown in Figure 3.5, the complete reduction of the secondary WWTP effluent peak area (blue) illustrated by the non-existent effluent product water peak area (orange) shows the MicroEvap™ fully removes an EC. Although small peaks were observed for diltiazem and sertraline for the product water, these 2 ECs still had >99% reduction in the peak area when compared to the incoming secondary WWTP effluent. The removal efficiencies demonstrate that the MicroEvap™ is effective at removing a variety of ECs from the sampled WWTPs secondary wastewater effluent (Figure 3.5).

Because the MicroEvap™ relies on ambient temperature water evaporation technology, the wastewater stream can be quickly evaporated. During evaporation of ECs, all of which have boiling points greater than ambient temperature, remain in the waste stream as the wastewater is evaporated. The ability of the flow field to create evaporation at ambient temperature is what makes the MicroEvap™, an innovative water treatment technology.

3.2.2 Mass Distribution of ECs After MicroEvap™ Processing

The next step was to determine what portion of each detected EC in the secondary wastewater effluent ended up in the product water and/or waste brine after MicroEvap™ processing. The 26 detected ECs in the secondary wastewater effluent, were also detected in the waste brine. Due to the described ratio of volume change during the recondensation phase, the waste brine was highly concentrated with ECs (Figure 3.5; Figure 3.6).

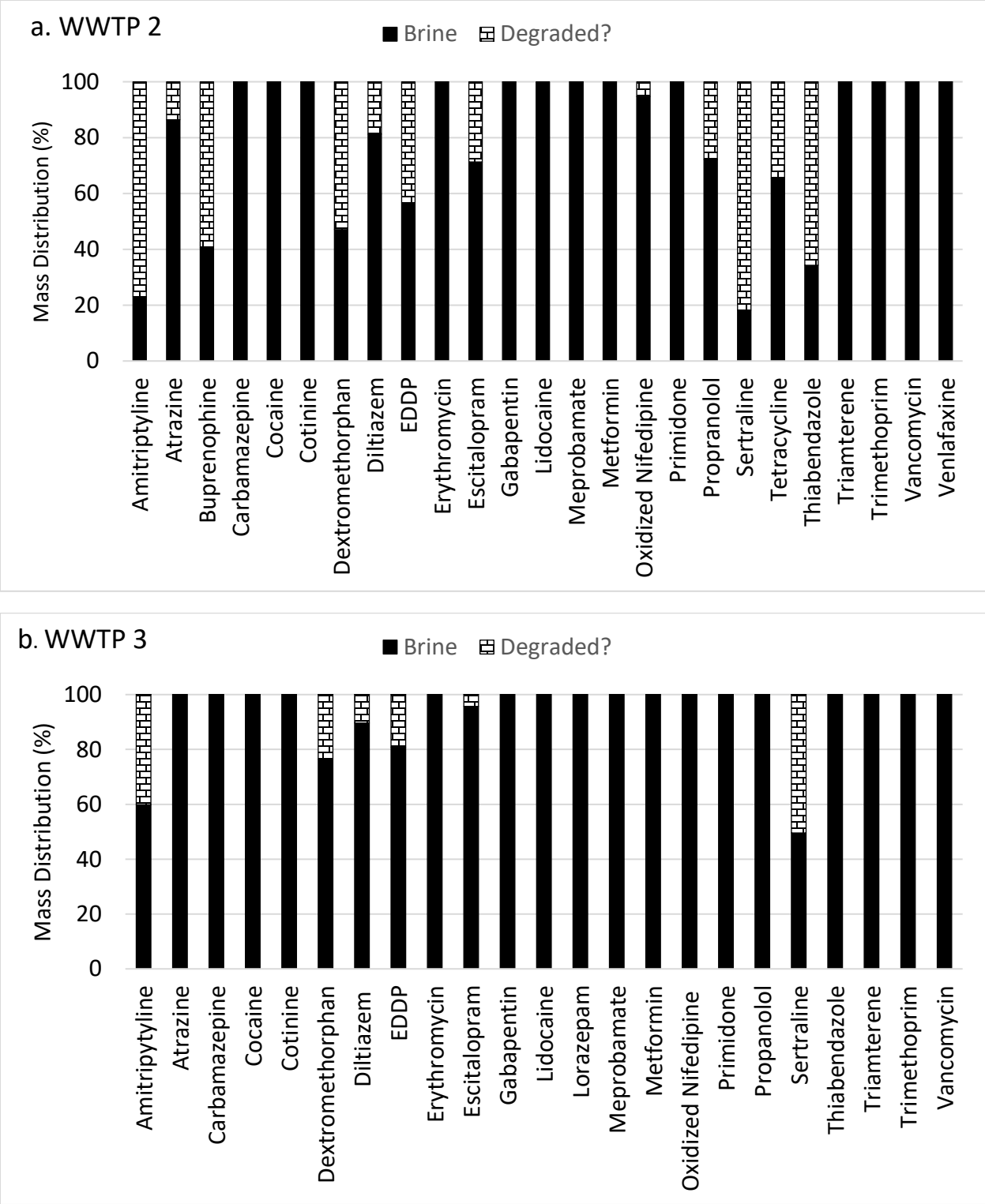


Figure 3.6: The mass distribution of ECs during treatment of WWTP effluents using the MicroEvap™ system, a. WWTP 2 and b. WWTP 3.

The waste brine could be considered a hazardous by-product and would need to be accounted for, for larger application of the MicroEvap™.

After MicroEvap™ processing, 52% of detected ECs in WWTP 2 and 74% of detected ECs in WWTP 3 were 100% transferred into the waste brine. This is likely because the ECs remain in solution after evaporation of the wastewater stream and exit the system as waste brine as the water to be cleaned is evaporated. Six EC detections (amitriptyline, dextromethorphan, diltiazem, EDDP, escitalopram, and sertraline) were not fully transferred into the waste brine. A portion of these compounds are not accounted during MicroEvap™ treatment, thus, they could be degrading. These six ECs are of interest for further investigation to test their degradation properties and determine if they are degraded during MicroEvap™ processing. This could be useful to understand if these ECs are degrading. As stated, the two ECs present in the product water constituted <1% of the mass distribution of the secondary wastewater effluent. In conclusion, the detected ECs are primarily being transferred into the waste brine.

4. Conclusions and Future Research:

Overall, the MicroEvap™ effectively removed >99% of detected ECs from three southwest Virginia secondary wastewater effluent streams. Of the 36 ECs screened, 26 ECs were detected in at least one WWTPs secondary wastewater effluent. Of these 26 detected ECs, 16 ECs were detected in all three WWTPs secondary wastewater effluent. The detected ECs represented a wide-variety of human medical uses. The removal efficiencies of the MicroEvap™ may be different dependent on the mixture of ECs targeted because of the unique physiochemical properties of an EC and an additional MicroEvap™ study should test more types of ECs (fire retardants, surfactants, etc.).

The ability of the MicroEvap™ to evaporate the wastewater stream at ambient temperature is likely the main reason why the MicroEvap™ removes >99% of tested ECs. The ECs have much greater boiling points than water, thus are not evaporate with the water. Greater than 50% of all ECs mass are being transferred into the waste brine after MicroEvap™ processing. However, several ECs were not 100% transferred into the waste brine, thus, degradation may be occurring. The degradation properties of these compounds and how the MicroEvap™ processing relates to the degradation should be further investigated. This

investigation demonstrates the MicroEvap™ is a potentially effective technology to treat wastewater contaminated with ECs.

5. References

Bartelt-Hunt S.L., Snow D.D., Damon T., Shockley J., Hoagland K. (2009) The occurrence of illicit and therapeutic pharmaceuticals in wastewater effluent and surface waters in Nebraska. Environ Pollut 157:786-91.

Benotti M.J., Stanford B.D., Wert E.C., Snyder S.A. (2009a) Evaluation of a photocatalytic reactor membrane pilot system for the removal of pharmaceuticals and endocrine disrupting compounds from water. Water Res 43:1513-22.

Benotti M.J., Trenholm R.A., Vanderford B.J., Holady J.C., Stanford B.D., Snyder S.A. (2009b) Pharmaceuticals and Endocrine Disrupting Compounds in U.S. Drinking Water. Environmental Science & Technology 43:597-603.

Erickson M., Langer S., Roth J., Kroening S. (2012) Contaminants of Emerging Concern in Ambient Groundwater in Urbanized Areas of Minnesota, 2009-12, in: USGS (Ed.). pp. 38.

Fan L., Harris J.L., Roddick F.A., Booker N.A. (2001) Influence of the Characterstics of Natural Organic Matter on the Fouling of Microfiltration Membranes. Pergamon 35:9.

Fang Z., Chen J., Qiu X., Qiu X., Cheng W., Zhu L. (2011) Effective removal of antibiotic metronidazole from water by nanoscale zero-valent iron particles. Desalination 268:60-67.

Hari A., Paruchuri R., Sabatini D., Kibbey T. (2005) Effects of pH and Cationic and Nonionic Surfactants on the Adsorption of Pharmaceuticals to a Natural Aquifer Material. Environ. Sci. Technol. 39:7.

Hazelton P.D., Du B., Haddad S.P., Fritts A.K., Chambliss C.K., Brooks B.W., Bringolf R.B. (2014) Chronic fluoxetine exposure alters movement and burrowing in adult freshwater mussels. Aquatic Toxicology 151:27-35.

Huber M.M., Canonica S., Park G.-Y., Gunten U.V. (2003) Oxidation of Pharmaceuticals during Ozonation and Advanced Oxidation Processes. Environmental Science & Technology 37:9.

IQVIA Institute. (2017) Medicines Use and Spending in the U.S.: A Review of 2016 and Outlook to 2021, IQVIA Institute, Parsippany, NJ.

Kim I., Yamashita N., Tanaka H. (2009) Performance of UV and UV/H2O2 processes for the removal of pharmaceuticals detected in secondary effluent of a sewage treatment plant in Japan. J Hazard Mater 166:1134-40.

Kim S., Aga D.S. (2007) Potential ecological and human health impacts of antibiotics and antibiotic-resistant bacteria from wastewater treatment plants. J Toxicol Environ Health B Crit Rev 10:559-73.

Kim S.D., Cho J., Kim I.S., Vanderford B.J., Snyder S.A. (2007) Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters. Water Res 41:1013-21.

Kolpin D.W., Furlong E.T., Meyer M., Thurman E.M., Zaugg S.D., Barber L.B., Buxton H.T. (2002) Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams,1999-2000: A National Reconnaissance. Environmental Science & Technology 36:10.

Kummerer K. (2008) Pharmaceuticals in the Environment--A Brief Summary Springer

Lam M., Young C., Brian R., Johnson D., Hanson M., Wilson C., Richards S., Solomon K., Mabury S. (2004) Aquatic Peristence of Eight Pharmaceuticals in Microosm Study Environmental Toxicology and Chemistry 23:10.

Radjenovic J., Petrovic M., Barcelo D. (2009) Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment. Water Res 43:831-41.

Ternes T. (1998) Occurrence of Drugs in German Sewage Treatment Plants and Rivers. Pergammon 32:16.

Vieno N., Tuhkanen T., Kronberg L. (2006) Removal of Pharmaceuticals in Drinking Water Treatment: Effect of Chemical Coagulation. Environmental Technology 27:183-192.

Yang D.-H.D., Murphy M.A., Zhang S. (2014) Highly Sensitive Detection of Pharmaceuticals and Personal Care Products (PPCPs) in Water Using an Agilent 6495 Triple Quadrupole Mass Spectrometer. Agilent 16.

Chapter 4 Conclusions and Future Research

This investigation examined the occurrence of ECs in private well water in Roanoke and Montgomery counties in southwest Virginia. Concentrations were determined for nine wells with the highest peak areas and one municipal water sample for comparison. Researchers used a novel method to quickly screen for 142 ECs in private well water. ECs detected was similar between private well water and municipal drinking water in the same counties. The concentrations of caffeine, tylosin, and triclosan were comparable between the nine private wells and one municipal drinking water quantified but more municipal drinking water samples are needed to further compare. The age and depth of the private well did not seem to be related to the number of ECs present for this study, but this information was not verified, only based on what the homeowner reported on the survey. The distance of the private well from the septic system did not influence the number of ECs detected. This investigation determined what ECs are occurring and how frequently, which is significant to determine the human risk assessment regarding ECs for consumption of this water.

Potential indicators of higher number of ECs detected in private well water were observed. A higher number of ECs detected was related with nitrate >1 mg/L and TDS <250 mg/L, and presence of total coliform bacteria. The pH of the well water was not related with occurrence of ECs, but the pH has shown to influence the fate and transport of an ECs in other studies (Chen et al., 2011). Further research and sampling are needed to get a better understanding of the relationship between *E. coli* and number of ECs detected.

The determination of the occurrence of ECs in select private well water provided foundational data to do additional research. A greater detailed analysis of the relationship of septic systems and occurrence of ECs should be done to determine if septic is a potential source of ECs into private wells. The exact distance of a septic system from the well rather than a range would better determine the influence the proximity of septic has on the occurrence of ECs. The most common household treatment systems (sediment filter, UV light, and water softeners) should be analyzed individually to determine their EC removal effectiveness. Three household water treatment pitchers (Zerowater, Vitapur, and EHM) are currently tested to determine their ability to remove ECs from the analyzed private well water. Another follow-up study would be to analyze the presence of antibiotic resistant bacteria and genes in private well water samples

The MicroEvap™ was able to remove >99% of ECs from the three Virginia WWTPs secondary wastewater effluent. The unique pressure gradient of the MicroEvap™ created by the tornadic flow field was able to evaporate wastewater at ambient temperature. ECs were primarily transferred into the brine after evaporation of 95% wastewater stream. A mass balance of detected ECs for two of the WWTPs confirmed ECs were primarily transferred into the waste brine. Some ECs were not fully transferred into the waste brine. Thus, these ECs are not accounted for in the waste brine and could be degraded during the MicroEvap™ processing. The degradation properties of these ECs should be further researched to determine why the MicroEvap™ is breaking them down.

The MicroEvap™ should be developed and tested further to increase its applicability to be utilized as a wastewater treatment system and applied to other purposes. The MicroEvap™ should be tested to remove a larger number of ECs. The MicroEvap™ would need to add a more rigorous filtration process to increase its ability to process wastewater with high solid content. Determining a way to clean the waste brine would allow for the brine water to be reutilized. The reutilization of nitrogen and phosphorus is becoming of great interest due to the declining sources of these nutrients worldwide. Nutrients could be reutilized from the MicroEvap™ brine by processing waters rich in nutrients (animal waste lagoon water, agricultural runoff, etc.). The nutrients could then be regenerated from the waste brine as struvite to be reutilized as fertilizer.

Appendix:

Appendix A. Emerging Contaminants Tested for in Chapter 2

Compound Name	Treatment Usage	Compound Name	Treatment Usage
10,11-dihydro-10-hydroxycarbamazepine	carbamazepine metabolite	Mefenamic acid	anti-inflammatory
6-acetylmorphine	heroin metabolite	Meperidine	pain reliever
9carboxy-THC	marijuana metabolite	Meprobamate	can treat anxiety
Acebutolol	beta blocker	Metformin	antidiabetic
Acetaminophen	pain reliever	Methadone	pain reliever
Albuterol	bronchodilator	Methamphetamine	treats ADHD
Amitriptyline	antidepressant	Methotrexate	chemotherapy drug
Amitriptyline metabolite	amitriptyline metabolite	Methylparaben	anti-fungal agent
Amphetamine	central nervous stimulant	Methylphenidate	can treats ADHD
Aripiprazole	antipsychotic	Metoprolol	beta blocker
Atenolol	beta blocker	Mevastatin	cholesterol-lowering agent
Atorvastatin	treats high cholesterol	m-Hydroxybenzoylecogonine	cocaine metabolite
Atrazine	herbicide	Modafinil	treat narcolepsy
Benzoylecgonine	cocaine metabolite	Modafinil acid	modafinil metabolite
Bezafibrate	lipid-lowering agent	Montelukast	treats allergies
Buprenorphine	pain reliever	Morphine	pain reliever
Bupropion	antidepressant	Naproxen	pain reliever
Caffeine	psychoactive drug	N-Butylparaben	cosmetic preservative
Carbamazepine	anticonvulsant	Nifedipine	treat high blood pressure
Carbamazepine 10,11 epoxide	carbamazepine metabolite	Norfentanyl	fentanyl metabolite
Carisoprodol	muscle relaxant	Norfluoxetine	fluoxetine metabolite
Celecoxib	pain reliever	Norlidocaine	lidocaine metabolite

Chloramphenicol	antibiotic	Normeperidine	meperidine metabolite
Chlorpheniramine	antihistamine	Norquetiapine	quetiapine metabolite
Clenbuterol	decongestant	Norsertraline	sertraline metabolite
Clopidogrel carboxylic acid	clopidogrel metabolite	Norverapamil	verapamil metabolite
Cocaethylene	cocaine metabolite	Omeprazole	treats heartburn
Cocaine	recreational drug	Oxazepam	antidepressant
Codeine	decongestant	Oxcarbazepine	anticonvulsant
Cotinine	nicotine metabolite	Oxidized Nifedipine	nifedipine metabolite
DEET	insect repellant	Oxycodone	pain reliever
Dehydroaripiprazole	aripiprazole metabolite	Oxymorphone	pain reliever
Desmethylcitalopram	citalopram metabolite	Oxymorphone glucuronide	oxymorphone metabolite
Desmethylvenlafaxine	antidepressant	Paroxetine	antidepressant
Dextromethorphan	cough medicine	Phenmetrazine	appetite suppressant
Diclofenac	anti-inflammatory	Phenobarbital	antidepressant
Diclofenac 4-hydroxy	diclofenac metabolite	Phentermine	weight loss drug
Diltiazem	treats high blood pressure	Phenylpropanolamine	decongestant
Diphenhydramine	antihistamine	Phenytoin	anticonvulsant
Disopyramide	treats irregular heartbeats	Pioglitazone	antidiabetic
Donepezil	treat Alzheimer's disease	Pravastatin	cholesterol lowering agent
Duloxetine	antidepressant	Pregabalin	pain reliver
Ecgonine methyl ester	cocaine metabolite	Primidone	anticonvulsant
EDDP	methadone metabolite	Propranolol	beta blocker
Erythromycin	antibiotic	Pseudoephedrine	antihistamine
Erythromycin-anhydro	antibiotic	Quetiapine	antipsychotic
Escitalopram	antidepressant	Ritalinic acid	methylphenidate metabolite

Famotidine	antacid and antihistamine	Sertraline	antidepressant
Fenbufen	anti-inflammatory	Sildenafil	vasodilator
Fentanyl	can treat severe pain	Simvastatin	treats high cholesterol
Fluoxetine	antidepressant	Sotalol	treats heart rhythm problems
Fluticasone propionate	treat nasal symptoms	Sulfamethazine	antibacterial agent
Furosemide	treats fluid retention	Sulfamethoxazole	antibiotic
Gabapentin	pain reliever	Sumatriptan	treats migraines
Gemfibrozil	lowers cholesterol	Tadalafil	vasodilator
Glyburide	antidiabetic	Temazepam	sedative
Hydrochlorothiazide	treats high blood pressure	Thiabendazole	pesticide
Hydrocodone	opioid pain medication	Tramadol	pain reliever
Hydromorphone	pain reliever	Trazadone	antidepressant
Hydroxybupropion	bupropion metabolite	Triamterene	diuretic
Ibuprofen	pain reliever	Triclocarban	antibacterial agent
Ketoprofen	anti-inflammatory	Triclosan	antibacterial agent
Lamotrigine	anticonvulsant	Trimethoprim	antibiotic
Levorphanol	pain reliever	Tylosin	antibiotic
Lidocaine	anesthetic	Valsartan	antihypertensive drug
Loratadine	antihistamine	Venlafaxine	antidepressant
Lorazepam	anticonvulsant	Verapamil	antihypertensive drug
MDA	ecstasy	Warfarin	blood thinners
MDEA	psychoactive drug	Zolpidem	treats insomnia
MDMA	ecstasy	Zolpidem phenyl-4-carboxylic acid	zolpidem metabolite

Appendix B. Emerging Contaminants Tested in Chapter 3

Compound Name	Treatment Usage	Compound Name	Treatment Usage
Amitriptyline	antidepressant	MDMA	ecstasy
Atrazine	pesticide	Mefenamic acid	pain reliever
Buprenorphine	pain reliever	Meprobamate	antidepressant
Carbamazepine	anticonvulsant	Metformin	antidiabetic
Cefotaxime	antibiotic	m-Hydroxybenzoylecgonine	cocaine metabolite
Chlortetracycline	antibiotic	Ormetoprim	antibiotic
Clenbuterol	decongestant	Oxidized Nifedipine	nifedipine metabolite
Cocaine	strong stimulant	Primidone	anticonvulsant
Cotinine	nicotine metabolite	Propranolol	beta blocker
DEET	insect repellant	Sertraline	antidepressant
Dextromethorphan	cough medicine	Sulfamethazine	antibacterial agent
Diltiazem	antihypertensive drug	Tetracycline	antibiotic
EDDP	methadone metabolite	Thiabendazole	pesticide
Erythromycin	antibiotic	Triamterene	antihypertensive drug
Escitalopram	antidepressant	Trimethoprim	antibiotic
Gabapentin	pain reliever	Tylosin	veterinary antibiotic
Lidocaine	numbing agent	Vancomycin	antibiotic
Lorazepam	anticonvulsant	Venlafaxine	antidepressant

Appendix C. Concentrations of Caffeine, Triclosan, and Tylosin in Select Private Well Water

Well ID	Caffeine (µg/L)	Triclosan (µg/L)	Tylosin (µg/L)
Well 2	1.32	3.27	0.30
Well 3	0.99	3.99	1.54
Well 5	1.01	2.74	0.17
Well 11	0.79	2.38	1.20
Well 12	0.69	19.00	0.13
Well 15	0.97	11.87	0.65
Well 24	0.64	53.55	1.15
Well 43	1.33	0.78	0.83
Well 54	1.53	2.39	0.49
Avg.	1.03	11.11	0.72
St. Dev.	0.31	16.58	0.50

Appendix D. Chapter 2 Detailed Emerging Contaminant Sampling Analysis Procedure

Procedure:

1. Remove samples from the -20°C freezer and let thaw for 8-12 hours at room temperature in a dark environment.
2. Pour 200 mL of well water sample into a mason jar and include triplicates for each household. Include 200 mL of ultra-pure water blanks and spikes as needed. Spike 50 µL of an antibiotic mixture (two high purity (>90%) antibiotic standards (sulfamethazine, and tylosin) into ultra-pure water for a set of triplicates for each run.
3. Filter the 200 mL sample for all samples using the vacuum pump with a filtration setup with a ceramic cup through a GF/F Whatman 0.70-micron glass filter.
4. Setup the new Oasis HLB cartridges (60mg, 3cc) on the SPE module. Condition the cartridges with 3 mL of 100% HPLC-grade methanol and then 3mL of ultra-pure water. Allow the solvent to pass through the cartridge with gravity.
5. Attach hoses to the pre-conditioned cartridges and then attach to their respective sample. Run the samples through the cartridge using the vacuum pump at ≈5mL/min.
6. After the samples have run through, leave the vacuum on for 2 mins and then turn pump off and let the cartridges continue to dry for 10 mins.
7. Place 6 mL test tubes under each sample cartridge.
8. Elute the cartridge with 3 mL of 100% HPLC-grade methanol at gravity speed with the vacuum on
9. Dry down the elutes for 60 mins at 50°C at 115 mbar on the RapidVap and be very cautious about splashing. Splashing can be avoided through starting at a higher vacuum (350-400 mbar) then lower to 115 mbar slowly and making sure there is a tight vacuum seal before starting.
10. Reconstitute samples with 1 mL of the mobile phase (1:1 LC-grade acetonitrile: ultra-pure water) for the Agilent UPLC/MS-MS method and vortex at speed 8 for 30 seconds.
11. Extract the sample from the test tube using a disposable green syringe with a disposable needle. Once the sample is extracted remove the needle and attach a PTFE 0.2-micron filter on the same place as where the needle used to be. Then pass the sample through the PTFE 0.2-micron filter into a 2 mL amber vial.

12. Analyze samples on the Agilent UPLC/MS/MS using the updated 142 EC and two pesticide positive and negative polarity screening methods.

Appendix E. Chapter 3 Detailed Emerging Contaminant Sampling Analysis Procedure

Procedure:

1. Remove samples from the -20°C freezer and let thaw for 8-12 hours at room temperature in a dark environment.
2. For the secondary wastewater effluent, MicroEvap™ treated secondary wastewater effluent, and the control blank samples: 100 mL of sample was used and placed into a mason jar then 150 mL of ultra-pure water was added to have a total of 250 mL of sample water. For the method blank and water spikes. 250 mL of ultra-pure water was added to the mason jars and for the water spikes, 50 µL of 1 ppm high purity (>90%) antibiotic mixture (sulfamethazine, and tylosin) standard were added to the ultra-pure water. For the waste brine, 5 mL of sample was added and then 245 mL of ultra-pure water was added into a mason jar.
3. Filter the 250 mL of sample using the vacuum pump with a ceramic filtration setup through a Whatman GF/F 0.7-micron glass filter.
4. Setup new Oasis HLB cartridges (60 mg, 3 cc) on the SPE module. Condition the cartridges with 3 mL of 100% HPLC-grade methanol and then 3 mL of ultra-pure water.
5. Attach hoses to the pre-conditioned cartridges and then attach to their respective sample. Run the samples through the cartridge using the vacuum pump at ≈5 mL/min.
6. Once all the sample has run through, clean the cartridge with approximately 5 mL of ultra-pure water and up to 10 mL of ultra-pure water if the samples are extremely dirty.
7. After the samples have fully been processed through, leave the vacuum on for 2 mins and then turn pump off and let the cartridges continue to dry for 8 mins.
8. Place 6 mL test tubes under each sample cartridge.
9. Elute the cartridge with 3 mL of 100% HPLC-grade methanol at gravity speed with the vacuum on.
10. Dry down the elutes for 60 mins at 50°C at 115 mbar on the RapidVap and be very cautious about splashing. Splashing can be avoided through starting at a higher vacuum (350-400 mbar) then lower to 115 mbar slowly and making sure there is a tight vacuum seal before starting.

11. Reconstitute samples with 1 mL of the mobile phase (1:1 LC-grade acetonitrile: ultra-pure water) for the Agilent UPLC/MS-MS method and vortex at speed 8 for 30 seconds.
12. Extract the sample from the test tube using a disposable green syringe using a disposable needle. Once the sample is extracted remove the needle and attach a PTFE 0.2-micron filter on the same place as where the needle used to be. Then pass the sample through the PTFE 0.2-micron filter into a 2 mL amber vial.
13. Analyze samples on the Agilent UPLC/MS/MS using the 34 EC and 2 pesticide screening method.

Appendix F. Chapter 2 Recruitment Letter

Hello,

Thank you for participating in the Virginia Cooperative Extension Drinking Water Clinic in the past. I am writing to see if you would be interested in participating in a Virginia Tech research project to investigate the presence of pharmaceuticals and personal care products (PPCPs; e.g., compounds in soaps, shampoos, detergents and other household products), and pesticides in Virginia private well water supplies. The goal of this study is to better understand the occurrence of PPCPs and pesticides in private well water and the different factors that may affect their occurrence and levels. A recent study from the United States Geological Survey surveyed for 108 pharmaceuticals in 59 US streams and detected at least one PPCP compound in every stream. To the best of our knowledge, at this point there is a lack of knowledge of what compounds may be present in the private well water supplies in Virginia, the United States, and worldwide. Your support would contribute greatly to the enhancement of our understanding on this matter.

You are invited to participate in the study mentioned above because we have selected two focus counties in Virginia (Montgomery and Spotsylvania). These counties were chosen to allow researchers to answer research questions about how geological conditions, well type, well age, and land use practices affect what we find in the water. **Participation for this additional study is completely voluntar**y. A certain number of volunteers will be selected once we hear from the people who are interested.

If you participate, we will work with you to find a convenient time over the next 6-8 months for an onsite visit by our graduate student, Will Vesely. This visit will take about 20-30 minutes. During the visit, Mr. Vesely will conduct a short interview and will collect several water samples from your well water system. The interview will include questions about the use of medications for humans, pets, and livestock on the property, the use of pesticides and herbicides, and septic system history (if applicable). The samples will be transported back to Virginia Tech for analysis. All information will be kept strictly confidential, and your identifying information will never be associated with your water test results.

As compensation for your participation in this study, you will receive a complementary water test free of charge (value: $55). Your confidential results from this complementary water test will be mailed to you in a sealed envelope. The analytical result of PPCPs and pesticides for the samples from your household will be provided to you upon your request.

If you are interested in participating in this study, please contact Will Vesely at veselywc@vt.edu or at 404-862-5629 to express your interest. If you have general questions about your water quality or water system, please feel free to contact me. Thank you.

Sincerely,

Erin Ling, Coordinator, Virginia Household Water Quality Program
155 Ag Quad Lane, Seitz Hall 400
Blacksburg, VA 24060
540-231-9058
www.wellwater.bse.vt.edu.

Appendix G. Chapter 2 Private Well Consent Form

Survey of Pharmaceuticals and Personal Care Products (PPCPs) and Pesticides in Virginia Well Water Supplies

The objective of the Virginia Household Water Quality Program (VAHWQP) is to improve the water quality and health of Virginians reliant on private water supplies, such as wells, springs, and cisterns. Researchers from the Department of Crop and Environmental Soil Sciences and Biological Systems Engineering at Virginia Tech are doing an additional volunteer study with participants from VAHWQP to better understand the occurrence of PPCPs and pesticides in private well water supplies.

Participation in this study is voluntary and should you choose to participate, your responses or data generated from your well water samples will not be linked with your contact information at any time. The results of this study may be published. Please read over the attached consent form and feel free to contact us with any questions or concerns.

Graduate Student:
Will Vesely veselywc@vt.edu 404-862-5629

Investigators:
Dr. Brian Benham benham@vt.edu 540-231-5705
Ms. Erin Ling ejling@vt.edu 540-231-9058
Dr. Kang Xia kxia@vt.edu 540-231-9323

Methods/Procedures
The method of data collection for this study will include completion of a short survey, onsite collection of well water samples from your residence at a scheduled, convenient time, and sample analysis at Virginia Tech. The survey will include questions about the demographics of those living in your home, and the type and frequency of use of different PPCPs and pesticides in and outside the home. We will also verify some of the information you provided on your questionnaire when you participated in the VAHWQP drinking water clinic (e.g. well age and depth). During the scheduled visit, samples will be collected from your well water supply at your residence and the graduate student will transport the samples to Virginia Tech. Analysis of the water samples for PPCPs and pesticides will be done in the Environmental Organic Chemical Analysis Laboratory at Virginia Tech by a trained graduate student and supervised by a faculty member. In appreciation of your participation, you will be offered a full water quality analysis (same as VAHWQP drinking water clinic) free of charge ($55 value). Analytical data on PPCPs and pesticides for the sample from your household will be provided to you upon your request.

Confidentiality
All the confidentiality measures for the VAHWQP will be applied to this study. There will be no identifying information used in any written reports or publications resulting from this study. Your participation in this evaluation will be strictly confidential. All findings used in any written reports or publications that result from this project will be reported in aggregate form with no

identifying information. The Virginia Tech Institutional Review Board and federal regulatory agencies may look at records related to this study for quality improvement and regulatory functions.

Risks and Inconveniences
There are no anticipated physical risks to participants. Visits for sample collection will only be scheduled at a convenient time for you, and participation is completely voluntary.

Benefits
Potential benefits of participating in this study include: the opportunity to assist researchers to better understand the occurrence of PPCPs and pesticides in Virginia private well water supplies, and receipt of a free well water quality analysis (value $55).

Questions
If you have any questions about this study at any time, you may contact Will Vesely at Virginia Tech (email: veselywc@vt.edu; phone: 404-862-5629) or any of the faculty investigators listed above.
Should you have any questions or concerns about the study's conduct or your rights as a research participant, or need to report a research-related injury or event, you may contact the Virginia Tech Institutional Review Board at irb@vt.edu or (540) 231-3732.

Subject's Consent
You will be given a copy of this consent form to keep for your records. Once again, we thank you for taking time out of your busy schedule to assist with this study.
I have read the Consent Form and conditions of this project. I have had all my questions answered. I hereby acknowledge the above and give my voluntary consent:

Printed Name of the Participant _____

Signature of the Participant _____

Date_____

Printed Name of the Investigator _____

Signature of the Investigator _____

Appendix H. Chapter 2 Private Well Water Survey

Script: Thank you for your interest in participating in our study: Pharmaceuticals and Personal Care Products (PPCPs) and Pesticides in Virginia Well Water Supplies. I would like to ask you a few questions to help us better understand your household, your well water system, and use of certain products of interest in and around your home. You may decline to answer any question if you like but having this information will greatly contribute to our understanding of how certain compounds make their way into well water supplies in the State of Virginia. All your answers and water quality results will be kept strictly confidential and will never be associated with your identifying information. The summarized results of this survey, and/or your water analysis will be provided to you upon your request. As compensation for your willing participation in this study, you will be offered a complementary water test identical to the test you've received through the Virginia Tech drinking water clinic (value: $55).

1. How many people live in your home in each age category?

Category	Number of people
0-5 years	
6-18 years	
19-50 years	
51-65 years	
66 or older	

2. How many people in the home use the following? If so, how often?

	# of people	How often? (circle)		
Antibiotics		Daily	Weekly	Occasionally
Antidepressant		Daily	Weekly	Occasionally
Beta-blocker		Daily	Weekly	Occasionally
Anticonvulsant		Daily	Weekly	Occasionally
Antianxiety		Daily	Weekly	Occasionally
Anti-inflammatory		Daily	Weekly	Occasionally
Lipid regulator		Daily	Weekly	Occasionally
Pain Relievers		Daily	Weekly	Occasionally
Diabetes medicine		Daily	Weekly	Occasionally
Tobacco		Daily	Weekly	Occasionally
Caffeine		Daily	Weekly	Occasionally

3. How many pets (cats and dogs) do you have, and what medications are used for them?

	# of pets	How often? (circle)

Antibiotics		Daily	Weekly	Monthly
Antiparasitics		Daily	Weekly	Monthly
De-wormer		Daily	Weekly	Monthly
Flea/Tick Prevention		Daily	Weekly	Monthly
Heart Worm Prevention		Daily	Weekly	Monthly
Pain Relievers		Daily	Weekly	Monthly
Anti-fungal		Daily	Weekly	Monthly
Other		Daily	Weekly	Monthly

4. Do you own livestock?

□ Yes □ No (move to question # 8)

5. What type(s) of livestock do you own? Please indicate about how many in the blank.

- ☐ Horse (_____)
- ☐ Poultry (_____)
- ☐ Cattle (_____)
- ☐ Pigs (_____)
- ☐ Other (_____)

6. What is the approximate distance where livestock are kept from your well?

□ <100 feet □ 101-500 feet □ 501-999 feet □ > 1000 feet

7. What medications are used for your livestock?

	type of livestock	How often? (circle)		
Antibiotics		Daily	Weekly	Monthly
Antiparasitics		Daily	Weekly	Monthly
Ionophores		Daily	Weekly	Monthly
Topical antiseptics		Daily	Weekly	Monthly
Bactericides/ Fungicides		Daily	Weekly	Monthly
Pain Relievers		Daily	Weekly	Monthly
Other		Daily	Weekly	Monthly

8. How do you dispose of expired or obsolete medication? Check all that apply

- ☐ Return to a verified disposal site (drug take-back, pharmacy)
- ☐ Dispose of in the garbage (fill with dirt, cat litter, or used coffee grounds)
- ☐ Do not dispose of; keep stored in the home
- ☐ Flush down the toilet or pour down the drain
- ☐ Other: _____

9. Do you plant or maintain crops, lawns, or gardens, or does your neighbor?

You/Participant:	Neighbor:
☐ Flower garden ☐ Lawn ☐ Crops ☐ Corn ☐ Soybean ☐ Cotton ☐ Other	☐ Flower garden ☐ Lawn ☐ Crops ☐ Corn ☐ Soybean ☐ Cotton ☐ Other

10. What is the approximate distance of your or your neighbor's cropland from your well?
□ <100 feet □ 101-500 feet □ 501-999 feet □ > 1000 feet

11. Do you use any of the following pesticides, herbicides, or fungicide products?

	Atrazine	Roundup	Karate/Demand	Other
Do you use?	Yes No	Yes No	Yes No	Yes No
How many times a year?				
During what season(s)?	Spr Summ Fall Winter	Spr Summ Fall Winter	Spr Summ Fall Winter	Spr Summ Fall Winter

List other: _____

12. Do you have a septic system?
- ☐ Yes. If yes, what is the approximate distance to your well?
  - ☐ <100 feet
  - ☐ 100-500 feet
  - ☐ 500 – 1000 feet
  - ☐ > 1000 feet
- ☐ No. If no, are you connected to public sewer?
  - ☐ Yes
  - ☐ No

13. Approximate age of your septic system?
- ☐ <5 year
- ☐ 5-10 years
- ☐ 10-20 years
- ☐ >20 years

14. When was the last time you had the septic system pumped out or maintained?
- ☐ In the last year
- ☐ In the last 3 years
- ☐ In the last 5 years
- ☐ In the last 10 years
- ☐ Never

15. Have you ever had your septic system fail or had to have major repairs performed on it?
    - ☐ Yes
    - ☐ No

16. Are you still using the same well you had tested through the most recent VAHWQP well testing program?
    - ☐ Yes
    - ☐ No, I had a new well drilled
        - What year? _____
        - Depth? _____

17. Do you have any other comments or questions?

Appendix I. Chapter 2 Municipal Drinking Water Consent Form:

Survey of Pharmaceuticals and Personal Care Products (PPCPs) and Pesticides in Virginia Well and Municipal Tap Water Supplies

The objective of the Virginia Household Water Quality Program (VAHWQP) is to improve the water quality and health of Virginians reliant on private water supplies, such as wells, springs, and cisterns. Researchers from the Department of Crop and Environmental Soil Sciences and Biological Systems Engineering at Virginia Tech have undertaken an additional volunteer study with participants from VAHWQP to better understand the occurrence of PPCPs and pesticides in private well water supplies. For comparison, researchers will also collect and analyze municipal source (regulated) tap water from the same counties where well water samples are being collected.

Participation in this study is voluntary. Should you choose to participate, your responses and data generated from your samples will kept confidential, and will not be linked with your contact information at any time. Summary results of this study may be published. Please read over the attached consent form and feel free to contact us with any questions or concerns.

Graduate Student:
Will Vesely veselywc@vt.edu 404-862-5629

Investigators:
Dr. Brian Benham benham@vt.edu 540-231-5705
Ms. Erin Ling ejling@vt.edu 540-231-9058
Dr. Kang Xia kxia@vt.edu 540-231-9323

Methods/Procedures
The method of data collection for this study will include completion of a short survey, onsite collection of tap water samples from your residence at a scheduled, convenient time, and sample analysis at Virginia Tech. The survey will include questions about the demographics of those living in your home and the taste of the water. During the scheduled visit, samples will be collected from your water supply at your residence and the graduate student will transport the samples to Virginia Tech. Analysis of the water samples for PPCPs and pesticides will be done in
the Environmental Organic Chemical Analysis Laboratory at Virginia Tech by a trained graduate student and supervised by a faculty member. Analytical data about PPCPs and pesticides for the sample from your household will be provided to you upon your request.

Confidentiality
All the confidentiality measures for the VAHWQP will be applied to this study. There will be no identifying information used in any written reports or publications resulting from this study. Your participation in this evaluation will be strictly confidential. All findings used in any written reports or publications that result from this project will be reported in aggregate form with no identifying information. The Virginia Tech Institutional Review Board and federal regulatory

agencies may look at records related to this study for quality improvement and regulatory functions.

Risks and Inconveniences
There are no anticipated physical risks to participants. Visits for sample collection will only be scheduled at a convenient time for you, and participation is completely voluntary.

Benefits
Potential benefits of participating in this study include: the opportunity to assist researchers to better understand the occurrence of PPCPs and pesticides in Virginia municipal water.

Questions
If you have any questions about this study at any time, you may contact Will Vesely at Virginia Tech (email: veselywc@vt.edu; phone: 404-862-5629) or any of the faculty investigators listed above.

Should you have any questions or concerns about the study's conduct or your rights as a research participant, or need to report a research-related injury or event, you may contact the Virginia Tech Institutional Review Board at irb@vt.edu or (540) 231-3732.

Subject's Consent
You will be given a copy of this consent form to keep for your records. Once again, we thank you for taking time out of your busy schedule to assist with this study.
I have read the Consent Form and conditions of this project. I have had all my questions answered. I hereby acknowledge the above and give my voluntary consent:

Printed Name of the Participant _____

Signature of the Participant _____

Date_____

Printed Name of the Investigator _____

Signature of the Investigator _____

Appendix J. Chapter 2 Municipal Drinking Water Survey

Script: Thank you for your interest in participating in our study: Pharmaceuticals and Personal Care Products (PPCPs) and Pesticides in Virginia Well and Municipal Tap Water Supplies. I would like to ask you a few questions to help us better understand your household and the taste of the water. You may decline to answer any question if you like. All of your answers and water quality results will be kept strictly confidential and will never be associated with your identifying information. The summarized results of this survey, and/or your water analysis will be provided to you upon your request.

1. How many people live in your home in each age category?

Category	Number of people
0-5 years	
6-18 years	
19-50 years	
51-65 years	
66 or older	

2. Does water have an unpleasant taste?

□ Yes. If yes, what does it taste like?

□ Bitter

□ Metallic

□ Oily

□ Salty

□ Soapy

□ Sulfur

3. Who supplies your water?

4. Do you have any other comments or questions?