ABSTRACT

Title of Thesis: OCCURRENCE OF PHARMACEUTICALS AND PERSONAL CARE PRODUCTS (PPCP) & ARTIFICIAL SWEETENERS (AS) IN SURFACE WATERS OF MARYLAND'S CHESAPEAKE BAY WESTERN SHORE

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In the United States, nutrient, personal care products (PPCP) and artificial sweeteners (AS) pollution in lakes, rivers, and estuaries is a problem that has been recognized for decades and is of special concern for many in coastal Maryland. PPCP are used on a daily basis, and include prescription analgesics, antibiotics, over-the-counter medications, fragrances, and cleansers. AS are synthetic sugar substitutes, ubiquitous in everyday food and drink, including soft drinks, baked food and dairy products. The widespread use of PPCP and AS by human populations results in their sustained contribution to surface waters via wastewater treatment. This study used 13 PPCP and 2 AS to describe their sources and temporospatial patterns in Maryland's Western Shore. Sampling was conducted over three seasons in 2021 at 79 sites, including headwater streams, groundwater, and rivers feeding into the Chesapeake Bay. Sites were influenced by a

mix of wastewater treatment plants (WWTP) and onsite wastewater treatment systems (OWTS). The detection frequency of the study compounds ranged from 2% to 100% in large catchments and 31% to 100% in headwater catchments. Six PPCP and AS were measurable at 80% or more of the sites, illustrating their ubiquitous presence throughout the study area. During the study, individual PPCP and AS concentrations were highly variable temporally, ranging from non-detectable to 6.58 µg/L. Major factors controlling concentrations were proximity to wastewater treatment, discharge and season. Four compounds—Ace-K, carbamazepine, sucralose and caffeine—were used as tracers to identify wastewater sources as they have distinct removal efficiencies during wastewater treatment and have anthropogenic origins. Caffeine to sucralose/Ace-K/carbamazepine ratios were used to identify discharges of untreated wastewater. Finally, PPCP and AS concentrations were explored in one headwater stream during storm events. Stormflow discharge was shown to impact the water quality of the receiving waters. The combination of discharge data, OWTS distribution data, an extensive suite of PPCP and AS and varied catchment types used in this thesis contributes to the understanding of human sourced wastewater pollution in coastal communities.

# OCCURRENCE OF PHARMACEUTICALS AND PERSONAL CARE PRODUCTS (PPCP) & ARTIFICIAL SWEETENERS (AS) IN SURFACE WATERS OF MARYLAND'S CHESAPEAKE BAY WESTERN SHORE

by

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# Dedication

I want to dedicate this thesis to my grandmothers, Margret Gibbs and Deborah Bradsher, and all BPOIC women who have worked extremely hard to help themselves, their families, and their communities.

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# List of Abbreviations

| | |
|---|---|
| **Ace-K** | Acesulfame potassium |
| **AS** | Artificial sweeteners |
| **BDL** | Below detection limit |
| **BOD** | Biochemical oxygen demand |
| **BQL** | Below quantification limit |
| **CASIF** | The Central Appalachians Stable Isotope Facility |
| **CBL** | Chesapeake Biological Laboratory |
| **DO** | Dissolved oxygen |
| **DOC** | Dissolved organic carbon |
| **EPA** | United States Environmental Protection Agency |
| **EU** | European Union |
| **IPA** | Isopropyl alcohol |
| **MDE** | Maryland Department of the Environment |
| **n.d.** | Non-detect |
| **NASL** | Nutrient Analytical Services Laboratory |
| **$NH_4$** | Ammonium |
| **$NO_2$** | Nitrite |
| **$NO_3$** | Nitrate |
| **NSAID** | Nonsteroidal anti-inflammatory drug |
| **ON** | Organic Nitrogen |
| **OWTS** | Onsite Wastewater Treatment Systems |
| **PC** | Particulate carbon |
| **PN** | Particulate nitrogen |
| **$PO_4$** | Phosphate |
| **PP** | Particulate phosphorus |
| **PPCP** | Pharmaceuticals and Personal Care Products |
| **PPL** | Priority PolLutant |
| **SPE** | Solid-Phase Extraction |
| **TDN** | Total dissolved nitrogen |
| **TDP** | Total phosphorus |
| **TOC** | Total Organic Carbon |
| **TSS** | Total suspended solids |
| **UMCES** | University of Maryland Center for Environmental Science |
| **USGS** | United States Geological Survey |
| **UV** | Ultraviolet |
| **WHO** | World Health Organization |
| **WWTP** | Wastewater Treatment Plant |

# Chapter 1: Introduction

## 1.1 Motivation and background

Pharmaceuticals and personal care products (PPCP) and artificial sweeteners (AS) are a class of emerging contaminants used for the health and cosmetic upkeep of humans and livestock. The most common PPCP groupings include antibiotics, hormones, nonsteroidal anti-inflammatory drugs (NSAIDs), preservatives, fragrances, and sunscreens. The grouping can also include food additives like caffeine and natural and synthetic hormones like estrone. These PPCP and AS are typically released into the environment through septic leach fields, aging municipal sewer lines, landfills, and the reuse of wastewater for irrigation [Shala and Foster, 2010].

PPCP were first identified outside of their expected range (i.e., not in their target organisms or environment) in the 1970s with the detection of clofibric acid (metabolite of the lipid-lowering pharmaceuticals) in the effluent of a wastewater treatment plant (WWTP) in Kansas City, US [Garrison, 1976]. By the early 2000s, PPCP and AS were detected WWTP effluents and aquatic environments worldwide. Growth in the use of PPCP and AS and advancements in analytical techniques have contributed to an increase in the detection frequency of PPCP and AS [Wang and Wang, 2016; Nash Jett et al., 2021; Wilkinson et al., 2022].

PPCP and AS have been suggested as tracers for human waste in water bodies, substituting traditional metrics like fecal coliform, stable isotope ratios or excess nitrogen [Glassmeyer et al., 2005; Hlavinek et al., 2008]. Because PPCP and AS are solely anthropogenic in origin, they allow the differentiation between human and mammalian animal waste on their own [Burns et al., 2009] and allows for more accurate reporting of wastewater [Buerge et al., 2009; Yang et al., 2013; Yang et al., 2017; Tran et al., 2019]. PPCP and AS are consistently associated with sewage due to their rate of excretion in solid and liquid waste (30 to 90%) and

their poor removal in the wastewater treatment process [Owens, 2015; Meyer et al., 2019]. Such association has become useful tool in detecting the presence and quantifying the magnitude of wastewater pollution in the environment [Meyer et al., 2019].

Insufficiently treated municipal wastewater discharge has been identified as the major source of surface water PPCP and AS contamination [Meyer et al., 2019]. As shown in table 1, compounds not significantly degraded by WWTP are often detected in higher concentrations in the aquatic environment than more readily degraded compounds. For example, acetaminophen is readily degradable and typically found in concentrations several orders of magnitude lower in freshwater streams than their initial concentration in wastewater effluent [Sun et al., 2015; Cantwell et al., 2018]. However, a compound such as sucralose, which is not as easily degraded is readily found in streams as concentrations remain stable even after the wastewater treatment process [Tran et al., 2015; Yang et al., 2017; Cantwell et al., 2018]. Yet, less degradable (conservative) compounds can be found in surface water at the same concentration as more readily degradable compounds (Table 1). Such concentrations cannot be solely attributed to degradation in WWTP as multiple factors, contribute to their presence , which will be discussed in this chapter.

**Table 1 PPCP and AS measured in this study and their occurrence in WWTP and freshwater**

| Compound | Class [Name Brand] | WWTP influent (µg/L) | WWTP effluent (µg/L) | Source | Surface water (µg/L) | Source |
|---|---|---|---|---|---|---|
| Acesulfame-K (Ace-K) | Artificial sweetener | 0.336 | 0.0235 | [Yang et al., 2017] | 2.9 | [Belton et al., 2020] |
| Acetaminophen | Analgesic & Antipyretic [Tylenol] | 1.64 | BDL | [Sun et al., 2015] | 0.008 to 0.0175 | [Cantwell et al., 2018] |
| Atorvastatin | Statin [Lipitor] | 0.033 | 0 | [Padhye and Huang, 2012] | 0.102 | [Tete et al., 2020] |
| Caffeine | Stimulant | 0.368<br>2.02 | BDL<br>0.0082 | [Yu and Chu, 2009]<br>[Sun et al., 2015] | 0.0491 to 0.0703 | [Cantwell et al., 2018] |
| Carbamazepine | Anticonvulsant & Mood-Stabilizer [Tegretol] | 0.00854 | 0.0277 | [Yang et al., 2017] | 0.0039 to 0.0056 | [Cantwell et al., 2018] |
| Cotinine | Biomarker [Metabolite of nicotine] | 1.492<br>0.92–2.65 | 0.004<br>0.023–0.112 | [Padhye and Huang, 2012]<br>(Buerge et al., 2008) | 0.0026 to 0.0154 | [Buerge et al., 2008] |
| DEET | Insect Repellent [OFF!] | 45.7 | 45 | [Yang et al., 2017] | 0.29 | [Veach and Bernot, 2011] |
| Dichlorvos | Insecticide [Vapona] | NO DATA | NO DATA | NO DATA | 0.0263 | [Gao et al., 2012] |
| Diclofenac | NSAID [Voltaren] | 0.0494 | 0.0394 | [Sun et al., 2015] | 0.031 | [Huebner et al., 2015] |
| Estrone | Estrogen [Estragyn] | 0.05 | 0.013 | [Manickum and John, 2014] | $8*10^{-5}$ to 0.00075<br>0.004 | [Vaicunas et al., 2013]<br>[Manickum and John, 2014] |
| Ibuprofen | NSAID [Advil] | 0.00324<br>1.217 | BDL<br>0.341 | [Yang et al., 2017]<br>[Yu and Chu, 2009] | 0.022 | [Shala and Foster, 2010] |

| Compound | Class [Name Brand] | WWTP influent (µg/L) | WWTP effluent (µg/L) | Source | Surface water (µg/L) | Source |
|---|---|---|---|---|---|---|
| Paraxanthine | Stimulant [Metabolite of caffeine] | 0.00273 | 0.0487 | [He et al., 2018] | 0.004 | [Valcárcel et al., 2011] |
| Sucralose | Artificial sweetener [Splenda] | 0.0638 | 0.076 | [Yang et al., 2017] | 0.8702 to 0.1182 | [Cantwell et al., 2018] |
| Sulfamethoxazole | Antibiotic [Gantanol] | 0.082.5<br><br>0.0175 | 0.039<br><br>0.0091 | [Yang et al., 2017]<br><br>[Sun et al., 2015] | 0.0123 to 0.0191<br><br>0 to 0.00082 | [Cantwell et al., 2018]<br><br>[Vaicunas et al., 2013] |

Note: All concentrations are median/mean. BDL=below detection limit

In the United States, the US Geological Survey (USGS) has conducted a recent national study that quantified the presence of PPCP in a wide range of lotic ecosystems, spanning from major rivers to headwater streams. In an extensive survey of American headwater streams, the USGS detected PPCP in 99% of the 308 stream sites sampled [Bradley et al., 2020]. The only two sites where no PPCP were detected were located in rural areas with low population densities. In another study, PPCP concentrations and detection frequency were equally high in agricultural and urban areas, suggesting that PPCP concentrations are associated with land use [Vaicunas et al., 2013]. The same study revealed PPCP higher concentrations during spring than summer and attributed the higher values to runoff from the application of manure in agricultural communities.

PPCP and AS have been found to be ubiquitous in the aquatic environment due to their common use and persistence. Consequently, PPCP and AS research has rapidly increased over the last two decades, especially regarding potential sources and environmental fate [Caliman and Gavrilescu, 2009; Boxall Alistair et al., 2012; Lapworth et al., 2012; Ebele et al., 2017; Meyer et al., 2019; Wilkinson et al., 2022]. Commonly detected PPCP and AS can be classified as

persistent, pseudo persistent and intermittent, with persistent compounds not being well degraded in wastewater treatment [Brausch and Rand, 2011; Barber et al., 2013]. While not all PPCP and AS are persistent, their continuous use and release to the environment means many are considered “pseudo-persistent”.

### *1.1.1 Advancements in PPCP & AS detection*

Liquid chromatography with tandem mass spectroscopy (LC-MS/MS) has become the dominant form of PPCP detection in wastewater with 64% of academic papers published from 2013 to 2018 utilizing the technique (n=67) [Pérez-Lemus et al., 2019]. Gas chromatography with mass spectrometry (GC-MS) decreased in popularity for PPCP detection in the late 2000s due to LC-MS/MS’ ability to analyze a larger spectrum of compounds without the derivatization needed for GC-MS [Pérez-Lemus et al., 2019]. Prior to LC-MS/MS’ popular use, GC-MS was used due to its sensitivity [Ohoro et al., 2019]. However, many PPCP and AS like carbamazepine and sucralose are not volatile making them poor candidates for GC-MS without further derivatization steps to improve sensitivity following GC analysis [Won, 2017; Ohoro et al., 2019]. These additional steps are labor intensive and lead to the need for a transition to LC-MS/MS. LC-MS/MS offers the ability to identify and measure a broader range of compounds with less sample preparation when compared to GC-MS [Perez et al., 2016]. In a 2016 study comparing LC-MS/MS and GC-MS recoveries and detection limits for wastewater samples in a North Carolina river and WWTP effluent, LC-MS/MS was found to have lower detection limits than GC-MS [Rushing, 2016]. With a broader range of compounds detectable at low concentrations, LC-MS/MS technology is superior and more commonplace than previous instrumentation.

Advances in mass spectrometry techniques such as ion trap and triple quadrupole mass filters have allowed for detection of environmental contaminants in the ng/L or lower concentration range [Nikolaou, 2013; Rasheed et al., 2019; Meng et al., 2021]. In conjunction with constantly evolving analytical methods, the process for isolating compounds from the raw water sample has also improved. These methods include liquid-liquid extraction and the more often used solid-phase extraction (SPE) procedures, which allowed the transformation of raw sample to a stable extract for contaminant quantification. The switch from liquid-liquid phase extraction to SPE has allowed samples to be processed more efficiently and provide more reproducible results [Rasheed et al., 2019]. Without further review it is not possible to know how many sites have been found to be contaminated at low concentration levels due to improvements in PPCP and AS detection technology, but these improvements have significantly advanced the field of PPCP and AS detection.

1.2 Distribution of PPCP in freshwater systems (Current state of knowledge)

According to a recent comprehensive review and synthesis of PPCP in the environment, the prevalence of contaminants is higher in freshwater lotic systems (63%) than in freshwater lentic (24%) and terrestrial (20%) systems [Meyer et al., 2019]. Figure 1 shows a general overview of the path that PPCP and AS take through the built and natural environment to reach water bodies. PPCP generally originate from wastewater treatment plants, septic systems, sewer overflows, or broken sewer pipes [Ebele et al., 2017] (Figure 1). Hence, water bodies receiving more WWTP effluent often have elevated concentrations due to many PPCP and AS not being entirely removed from wastewater during treatment [Conn, 2009; Barber et al., 2013; Dai et al., 2014; Tran et al., 2015]. In areas without sewer systems, the two main pathways for PPCP and

AS to enter the natural environment and reach water bodies include waste lagoons and onsite wastewater treatment systems (OWTS).

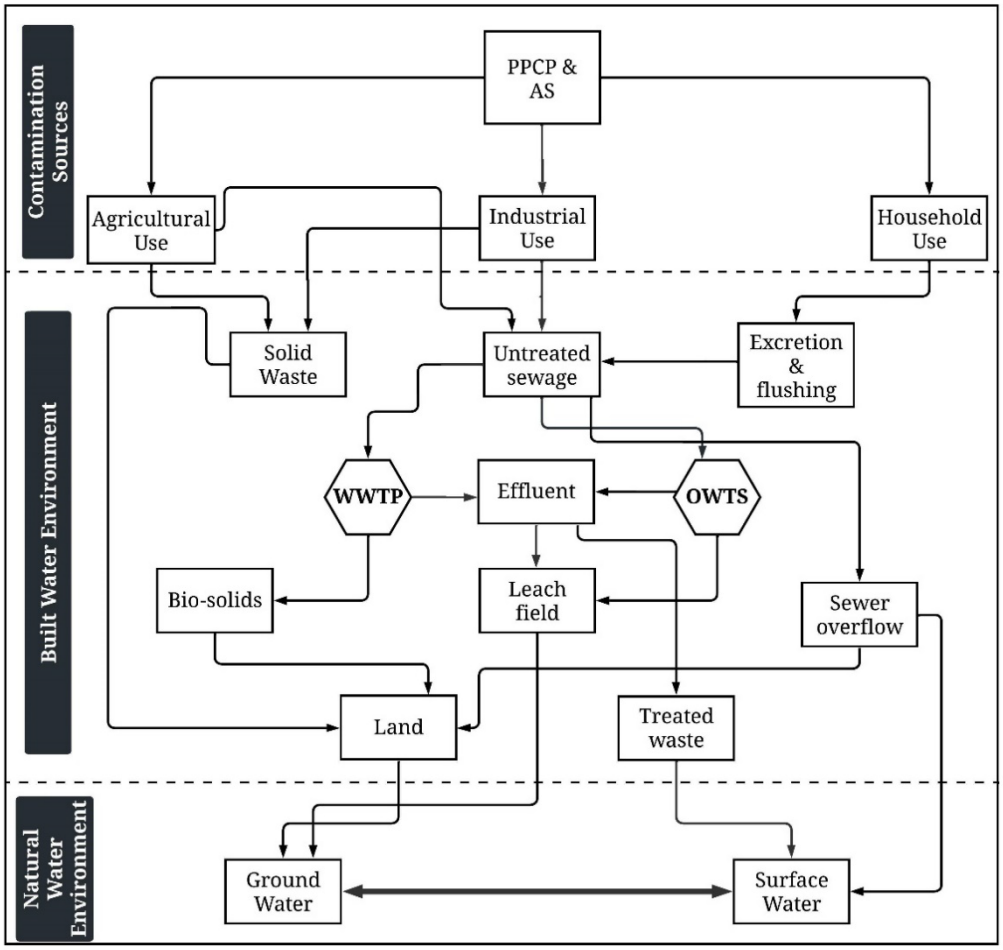



**Figure 1 Schematic showing interconnectivity inputs of PPCP and AS in the build and natural water environment**

Waste lagoons are particularly common in agricultural areas, they are used for the disposal and decomposition of animal waste by anaerobic bacteria [Hoque et al., 2014; Panthi et al., 2019]. The leftover solids from this process are subsequently dried and applied to land as a natural fertilizer (Figure 1), becoming a potential source of contaminants to water bodies. In areas with a human population but without sewer systems, waste is commonly treated via an OWTS. OWTS are the combination of a septic tank and dispersion system, also referred to as a

septic system. They are typically an underground waste treatment system for one or more homes and businesses. The septic tank provides waste treatment while the dispersal system (leach field) allows the flow of the treated waste into soils for additional microbial treatment, eventually connecting the effluent to groundwater [EPA, 2008; Heufelder, 2012] (Figure 1).

PPCP and AS are found in various aquatic environments, not just in WWTP receiving waters [Kallenborn et al., 2017]. PPCP and AS contamination in waters not receiving waste can be sourced to discharge from septic systems, run-off from agricultural land uses and groundwater [Fairbairn et al., 2016]. While PPCP and AS have various pathways to surface water, the interconnectedness of the aquatic environment results in pollution. Concentrations of PPCP and AS in the aquatic environment are generally small in relation to those in wastewater effluents but significant, in both surface and ground water they range from parts-per-trillion (ng/L) to parts-per-billion (μg/L). Concentrations also vary among regions, while the detection frequency depends on the type of PPCP, the analytical method used, and detection limits [Kolpin et al., 2002]. Coastal mixing zones are at high risk for anthropogenic contamination from both point and non-point sources due to high human population densities, close proximity to impervious surfaces, and residential and commercial development [Quigg et al., 2009; Hedgespeth et al., 2012]. The US Atlantic coast is particularly at risk for PPCP and AS pollution sourced from septic systems. For instance, in New England, as ~51% of new homes and ~36 of existing homes have septic systems compared to 8% of new homes and ~22 of existing homes in the Pacific region [Bureau, 1990; Siniavskaia, 2014].

The most commonly detected PPCP in surface waters are carbamazepine, sulfamethoxazole, and caffeine; concentration ranges can be found in table 1 [Kolpin et al., 2002; Batt et al., 2016; Ebele et al., 2017]. Sulfamethoxazole is a widely used antibiotic that

treats urinary tract infections and bronchitis [Roth et al., 2018] and was the most frequently detected compound in a nationwide survey conducted by the USGS between 2008 and 2009 [Batt et al., 2016]. Therefore, sulfamethoxazole has been commonly used as an indicator of wastewater contamination in freshwater [Glassmeyer et al., 2005; Panthi et al., 2019]. Similarly, the anticonvulsant drug carbamazepine, which is also used to treat bipolar disorder, depression and addiction is one of the most frequently detected compounds in freshwater ecosystems, with a detection frequency of 85% in the US and worldwide [Neppe et al., 1998; Jarvis et al., 2014]. Carbamazepine is poorly degraded in conventional activated sludge and membrane bioreactor WWTP due to molecular structure and hydrophilic properties [Hai et al., 2018].

Caffeine is a natural and artificial stimulant found in many foods and beverages, an estimated 85% US population consumes at least one caffeinated beverage per day [Mitchell et al., 2014]. Consequently, caffeine was found in concentrations above 70 ng/L in the national survey that included streams draining minimally impacted sites, urban and agricultural areas [Bernot et al., 2016]. The presence of caffeine in water is an indicator of untreated human fecal matter as the compound is readily degradable in WWTP [Potera, 2012]. Caffeine has a strong correlation with fecal coliform counts, which are a traditional method of wastewater detection [Sauvé et al., 2012].

Artificial sweeteners such as acesulfame-K (Sweet One®), aspartame (Equal®), saccharin (Sweet'n Low®), and sucralose (Splenda®) are food additives commonly associated with human wastewater due to their solely anthropogenic use. Acesulfame-K (Ace-K) is an artificial sweetener found in many foods and beverages including protein shakes, soft drinks, baked goods and dairy products. The sweetener has been detected in both untreated and treated wastewater (12-46 μg/L), surface waters, septic drainage fields and in Swedish drinking water in

concentrations up to 2.6 μg/L [Buerge et al., 2009; Robertson et al., 2013]. The water soluble compound is poorly removed in biological sludge WWTP due to a low $K_d$ sorption coefficient [Tran et al., 2015; Belton et al., 2020]. The compound can not be degraded using direct photolysis via sunlight but has shown improved removal in aerobic sequential batch reactors [Falås et al., 2016; Perkola et al., 2016]. Due to the generally poor removal, treated waste is likely to contain Ace-K, making it a conservative human wastewater tracer.

Sucralose is another common artificial sweetener found in baked goods, beverages, chewing gum, gelatins, and frozen dairy desserts. The sweetener has been detected in both untreated and treated wastewater (0.0638- 0.076 μg/L) and surface waters in concentrations up to 0.1182 μg/L [Yang et al., 2017; Cantwell et al., 2018]. Concentrations of sucralose have been shown to remain consistent during the wastewater treatment process with no to negative degradation as a result of sorption to sludge [Soh et al., 2011; Cantwell et al., 2019].

In summary, while concentrations and detection frequencies of carbamazepine, sulfamethoxazole, and caffeine are considered relatively high, increased consumption of new and existing PPCP and improved detection methods are likely to increase detection frequencies even further [Deo and Halden, 2013]. Less frequently found/studied compounds such as Ace-K, acetaminophen, atorvastatin, cotinine, DEET, dichlorvos, diclofenac, estrone, ibuprofen, paraxanthine, and sucralose have been detected and quantified in wastewater and other highly impacted waters [Deo and Halden, 2013; Kim et al., 2014; Roberts et al., 2016]. Some of these compounds have been less frequently reported due to quantification limitations, but they are examined in this study.

### *1.2.1 Factors affecting concentrations and detection frequencies of PPCP in surface waters*

Studies have shown that PPCP and AS are present in streams, lakes, and rivers where wastewater is discharged, e.g. Spoelstra et al., [2020], and that spatial variability in contaminant concentrations is correlated with proximity to wastewater sources [Roberts et al., 2016]. For example, in Ohio freshwater streams, concentrations and detection frequencies of sucralose, sulfamethoxazole, and triclosan generally increase with the number of septic systems in the drainage area, with sucralose having the strongest positive correlation [Schenck et al., 2015]. A possible cause for this correlation is the low removal rates of sucralose in septic systems, with a 6-24% removal rate depending on the type of septic system [Du et al., 2014]. In contrast, no correlation has been observed between estrone and septic density [Schenck et al., 2015], likely due to sources of estrone are unrelated to septic systems, like animal waste.

The spatial variability in PPCP concentrations has also been associated with the proximity of the water body to point sources such as WWTP effluent. Cantwell et al., [2018], surveyed the length of the Hudson River, NY, which has several WWTP outfalls and found significant increases in PPCP levels near WWTP effluents, likely due to incomplete removal and degradation in the treatment plant. In a survey of multiple WWTP in an urban UK watershed, similar trends were found, with concentrations generally highest immediately downstream of the WWTP effluent and decreasing downstream [Burns et al., 2018]. The decrease in downstream concentrations was variable between compounds, indicating that in-stream attenuation is compound specific. The reduction in concentrations moving downstream suggests in-stream removal processes such as photolysis or microbial degradation while fluctuating concentrations could be due to a complex dynamic between dilution and other PPCP sources such as aging

sewer systems, septic effluents, and tributaries [Benotti and Brownawell, 2007; Daneshvar et al., 2010; Heufelder, 2012; Burns et al., 2018; Zhang et al., 2022].

In addition to spatial variability, seasonal variability in PPCP concentrations have been shown in long-term PPCP studies [Kolpin et al., 2004; Conley et al., 2008; Tete et al., 2020; Zhang et al., 2022]. In some cases, PPCP concentrations were lower in the winter than in other seasons [Jones-Lepp et al., 2012; Burns et al., 2018], but in other cases, winter showed the highest concentrations. One of explanation for such discrepancies is that PPCP usage has trends, which significantly impact seasonal PPCP levels during a year [Patel et al., 2019]. Usage trends are hard to predict as they vary from region to region. In rural and dominant agricultural watersheds, PPCP concentrations often increase in spring, which corresponds to the period of manure fertilizer application [Vaicunas et al., 2013]. In urban settings, PPCP concentrations in WWTP effluent can vary by population served. Sun et al., [2015] found significantly higher PPCP concentrations in WWTP effluent, which mainly processes domestic wastewater compared to an even mix of domestic and industrial wastewater. In urban domestic wastewater effluent with higher PPCP levels correlate with colder weather [Sui et al., 2011; Sun et al., 2015]. The higher consumption of antibiotics, NSAIDs, and antilipidemic[1] during the cold seasons has been linked to the increase in PPCP levels in WWTP receiving waters [Ockene et al., 2004; Davey et al., 2008]. Similarly, DEET, an insect repellent, has higher usage rates in summer months and was detected at higher rates in WWTP in Minnesota during summer months [Santos et al., 2019].

Seasonal variation has also been observed between surface and ground waters. Gray et al., [2010], found significantly higher concentrations of antibiotics sulfamerazine (antibacterial)

[1] Used to lower low-density lipoprotein (LDL) cholesterol levels.

and danofloxacin (veterinary antibiotic) in North Carolina surface water than groundwater in the fall season, which was hypothesized to be due to biodegradation and photodegradation, and stream hydrology.

Discharge has been considered a driver of temporal variability in PPCP concentrations [Kolpin et al., 2004; Kasprzyk-Hordern et al., 2008]. This is particularly observed of urban settings, where relatively high concentrations of PPCP were observed during low flow periods and become diluted during precipitation events [Kolpin et al., 2004; Kasprzyk-Hordern et al., 2008]. Kolpin et al., [2004], also found a significant correlation between urban population, stream discharge ratio and total concentrations of deodorants, disinfectants, antibiotics, and plasticizers.

Land use has been considered a better predictor of some PPCP concentration/detection than human population [Veach and Bernot, 2011; Bernot et al., 2016]. Specifically, areas with high human use of PPCPs, i.e. rural area with high agriculture, a suburban area with a high population density, often have significant contributions of PPCP and AS. Areas with intensive agriculture also have high concentrations of PPCP originating from animal husbandry [Vaicunas et al., 2013]. AS are less commonly found in agricultural areas due to their strong association with human waste, while PPCP can be associated with both human and animal waste.

Two commonly used classes of antibiotics for animal feeding operations are sulfonamides and tetracyclines. These PPCP types are strongly associated with animal husbandry and were not examined in the present study [Arikan et al., 2008]. Veach and Bernot [2011] found comparable concentrations of PPCP in streams in agricultural and urban-influenced sites. However comparable concentrations were not found temporally, with urban areas having higher concentrations of cotinine, sulfamethoxazole and caffeine in summer months, up to fourfold

higher than agricultural areas. Differentiation between animal sourced PPCP and human sourced can be enhanced by understanding differences in PPCP classes, seasonal trends and incorporating AS detection.

## 1.3 Impacts of PPCP and AS contamination to surface waters

PPCP and AS are not currently included in the ambient water quality criteria for the United States Clean Water Act. Yet, many are considered contaminants of emerging concern due to their widespread uses, persistence, effect on aquatic systems, and public concern [Swackhamer and Meyer, 2008]. Detection does not necessarily indicate that a PPCP or AS compound can cause harm, but there is a wealth of evidence that PPCP and AS impact wildlife and potentially people [Rosi-Marshall and Royer, 2012; Cizmas et al., 2015].

### *1.3.2 Impacts on aquatic life*

Though PPCP and AS are not regulated in freshwater, pharmaceutical pollution can negatively impact aquatic life including changes in reproduction, abnormal growth behavioral effects, and oxidative stress. Compounds such as carbamazepine, caffeine, and ibuprofen, have been shown to bioaccumulate in algae*, Pseudokirchneriella subcapitata*, crustaceans, *Thamnocephalus platyurus* and mosquitofish, *Gambusia holbrooki* [Vernouillet et al., 2010; Wang and Gardinali, 2013]. While these studies did not determine the impacts of bioaccumulation, the authors did raise concern about unknown side effects. In addition to bioaccumulation, more direct impacts of PPCP can be seen in the endocrine system of aquatic life. Several studies have shown negative endocrine impacts in association with pharmaceutical pollution, including reduced reproduction rates (white suckerfish, *Catostomus commersoni*, exposed to estrogenic WWTP effluent), slowed and reduced growth (invertebrates, *Gammarus*

*fasciatus* & *Psephenus herricki*, exposed to cimetidine[2]), and may cause mortality (*Daphnia* exposed to diphenhydramine[3]) [Vajda et al., 2008; Hoppe et al., 2012; Rosi-Marshall and Royer, 2012]. Many PPCP, particularly NSAIDs, can disrupt the endocrine system of their non-target organisms producing side effects that interfere with egg production, post-embryonic development, and disrupt thyroid hormone metabolism in North American Bullfrog tadpoles (*Rana catesbeiana*) and Japanese medaka fish (*Oryzias latipes*) [Han et al., 2010; Veldhoen et al., 2014]. Estrogens, disinfectants, antibiotics, anti-inflammatory drugs, and anti-depressants have all been shown to impact the endocrine system of multiple aquatic organisms [Ebele et al., 2017]. Rainbow trout liver cells exposed to a pairing of PPCP were more likely to negatively impact cell viability compared to the compounds individually, with increased harm found in cells exposed to PPCP from multiple chemical classes [Schnell et al., 2009]. The authors raised concern as PPCP are almost always found in conjunction with other PPCP.

## 1.4 Wastewater Treatment Techniques and PPCP & AS

### *1.4.1 The fate of PPCP in WWTP*

The contamination of surface water and groundwater with PPCP is most often a result of wastewater effluent. PPCP and AS enter the environment via excretion, washing and disposal of surplus drugs into sewage systems [Batt et al., 2016; Nash Jett et al., 2021]. The excreted material may also contain metabolized parent compounds such as paraxanthine, caffeine's primary degradation product. The waste is processed in a WWTP or septic system for treatment, where PPCP and AS are released to water bodies via their effluent [Ebele et al., 2017]. PPCP appear in aquatic environments due to their generally low volatility, high polarity, hydrophilic

[2] Antihistamine and antacid
[3] Antihistamine, Brand name: Benadryl

properties, and disposal route which allow for poor removal in wastewater treatment [Caliman and Gavrilescu, 2009].

Recent reports show that the elimination of PPCP and AS in WWTP is often incomplete with treatment efficiencies ranging from less than 50 % - 99 % (Table 2). The degree of treatment is greatly dependent on the WWTP treatment type and less on initial contaminate load [Blair et al., 2015; Cardenas et al., 2016; Dwivedi et al., 2017].

**Table 2 PPCP and AS analyzed in this study and their removal rates in WWTP**

| Compound | Removal efficiency | Treatment process | Sources | Degradability in WWTP |
|---|---|---|---|---|
| Acesulfame-K | 11–16% | Settling tanks + Chemical flocculation + ultraviolet disinfection | [Van Stempvoort et al., 2020] | Conservative |
| | 90% | Settling tanks + Chemical flocculation + aeration, activated sludge, sand filtration, ultraviolet disinfection | [Van Stempvoort et al., 2020] | |
| Acetaminophen | 100% | Bar screens + aerated grit chambers + flocculators + chemical clarification + aeration basins + secondary gravity clarifiers + sand filtration + chlorination + dichlorination | [Padhye and Huang, 2012] | Labile |
| Atorvastatin | 88 ±22% | Bar screens + aerated grit chambers + flocculation + chemical clarification + aeration basins + secondary gravity clarifiers + sand filtration + chlorination + dichlorination | [Padhye and Huang, 2012] | Labile |
| Caffeine | 83±30% | Bar screens + aerated grit chambers + flocculation + chemical clarification + aeration basins + secondary gravity clarifiers + sand filtration + chlorination + dichlorination | [Padhye and Huang, 2012] | Labile |
| Carbamazepine | -16– -2.3% | Grit tanks + primary sedimentation + bioreactor + clarifiers | [Roberts et al., 2016] | Conservative |

| Compound | Removal efficiency | Treatment process | Sources | Degradability in WWTP |
|---|---|---|---|---|
| Cotinine | 54% | Grit channels + primary clarifies + conventional activated Sludge | [Blair et al., 2015] | Semi-Conservative |
| DEET | 69 ± 21% | Settling tanks + secondary biological treatment + anaerobic/anoxic/oxic activated sludge | [Sui et al., 2010] | Semi- Labile |
| Dichlorvos | NO DATA | NO DATA | NO DATA | NO DATA |
| Diclofenac | 10–60&* varies by initial concentration | Settling tanks + Chemical flocculation + oxidation ditch + UV disinfection | [Sui et al., 2010] | Conservative |
| Estrone | 93.7% | Grit channels + primary clarifies + conventional activated sludge | [Blair et al., 2015] | Labile |
| Ibuprofen | 70±46%<br><br>100% | Bar screens + aerated grit chambers + flocculation + chemical clarification + aeration basins + secondary gravity clarifiers + sand filtration + chlorination + dichlorination<br><br>Mesh screen + primary clarification + bioreactor (anoxic zone and aeration zone) + membrane tank | [Padhye and Huang, 2012]<br><br>[Kim et al., 2014] | Labile |
| Paraxanthine | 100% | Mesh screen + primary clarification + bioreactor (anoxic zone and aeration zone) + membrane tank | [Kim et al., 2014] | Labile |
| Sucralose | -41.3–19%<br><br>-26.5% | Settling tanks + Chemical flocculation + ultraviolet disinfection<br><br>Settling tanks + Chemical flocculation + aeration + activated sludge + sand filtration, ultraviolet disinfection | [Van Stempvoort et al., 2020]<br><br>[Van Stempvoort et al., 2020] | Conservative |

| Compound | Removal efficiency | Treatment process | Sources | Degradability in WWTP |
|---|---|---|---|---|
| Sulfamethoxazole | 74±32% | Bar screens + aerated grit chambers + flocculation + chemical clarification + aeration basins + secondary gravity clarifiers + sand filtration + chlorination + dichlorination | [Padhye and Huang, 2012] | Semi-Conservative |
| | 66 | Mesh screen + primary clarification + bioreactor (anoxic zone and aeration zone) + membrane tank | [Kim et al., 2014] | |

Note: Labile tracers have high removal rates (90%) in WWTP, whereas conservative tracers have low removal rates (<50%) [Yang et al., 2017]. See table 1 for removal efficiency

Once in the WWTP, some PPCP, including acetaminophen and caffeine, are totally or partially degraded, while others remain unaltered (Table 2). The artificial sweetener Ace-K is known to be persistent as it passes unaltered through WWTP systems, making it a conservative tracer for human waste [Buerge et al., 2009] (Table 2). Several recent studies have challenged the idea of Ace-K as a conservative human waste tracer going so far as to call it "obsolete" due to their findings that it was primarily removed during treatment, but this appears to be variable on treatment type [Cardenas et al., 2016; Falås et al., 2016; Castronovo et al., 2017; Kahl et al., 2018; Kleinsteuber et al., 2019]. However, a recent study showed more nuance, finding a significant difference in Ace-K concentrations in the influent and effluent of 8 out of 12 WWTP studied [Van Stempvoort et al., 2020]. This difference was not definitive in establishing Ace-K as a conservative tracer but highlighted that degradation of Ace-K is variable depending on treatment type (average removal 12 to 99%) [Van Stempvoort et al., 2020]. Pairing the detection of Ace-K with the detection of sucralose, which is universally poorly removed in WWTP, provides a more robust detection of AS in wastewater [Arbeláez et al., 2015; Shreve and Brennan, 2019].

Carbamazepine is frequently found in all stages of WWTP [Nash Jett et al., 2021], indicating its resistance to natural attenuation and elimination via microbial wastewater treatment [Clara et al., 2004; Glassmeyer et al., 2005; Benotti and Brownawell, 2009]. The mood stabilizer has also been found in several studies to have negative removal efficiency in WWTP due to its poor biodegradability and low sorption to sludge used in treatment [Zhang et al., 2008; Xu et al., 2013; Hoque et al., 2014].

In contrast, acetaminophen and caffeine are readily removed by traditional WWTP, act as a "freshness" indicator of human waste and are among the most commonly detected PPCP [Sun et al., 2016; Nash Jett et al., 2021]. Acetaminophen and other NSAIDs have been found in high concentrations in WWTP influent (1.9 μg/L), which is expected as it is one of the two most commonly used NSAIDs in the United States [Sun et al., 2015; Nash Jett et al., 2021]. Activated sludge WWTP effectively removes acetaminophen with concentrations in effluents below detection limits [Sun et al., 2015]. Effective removal has been attributed to oxidoreductase enzymes (i.e. laccase) produced from microorganisms on the acetaminophen's electron-donating groups [Tran et al., 2010; Tran and Gin, 2017]. Ibuprofen is removed in activated sludge using the same microbial process [Tran et al., 2010; Tran and Gin, 2017].

Sulfamethoxazole is resistant to microbial degradation that is commonly used as a method of WWTP treatment, but can be easily photodegraded (Benotti and Brownawell, 2009). Removal efficiencies vary greatly from no removal in a high carbon and nitrogen sludge to low removal (22 to 39%) and fair removal (66%) [Drillia et al., 2005; Li and Zhang, 2010; Kim et al., 2014]. The cause for the variability has been attributed to variability in microbial communities and varying carbon sources [Larcher and Yargeau, 2012].

Currently, there are no wastewater treatment steps explicitly designed to remove PPCP and AS, but several processes can remove/degrade some of these compounds that are more resistant to traditional methods [Karnjanapiboonwong et al., 2011]. The most common wastewater treatment type is activated sludge, which uses microorganisms to remove organics from wastewater under aerobic conditions [Ting and Praveena, 2017].

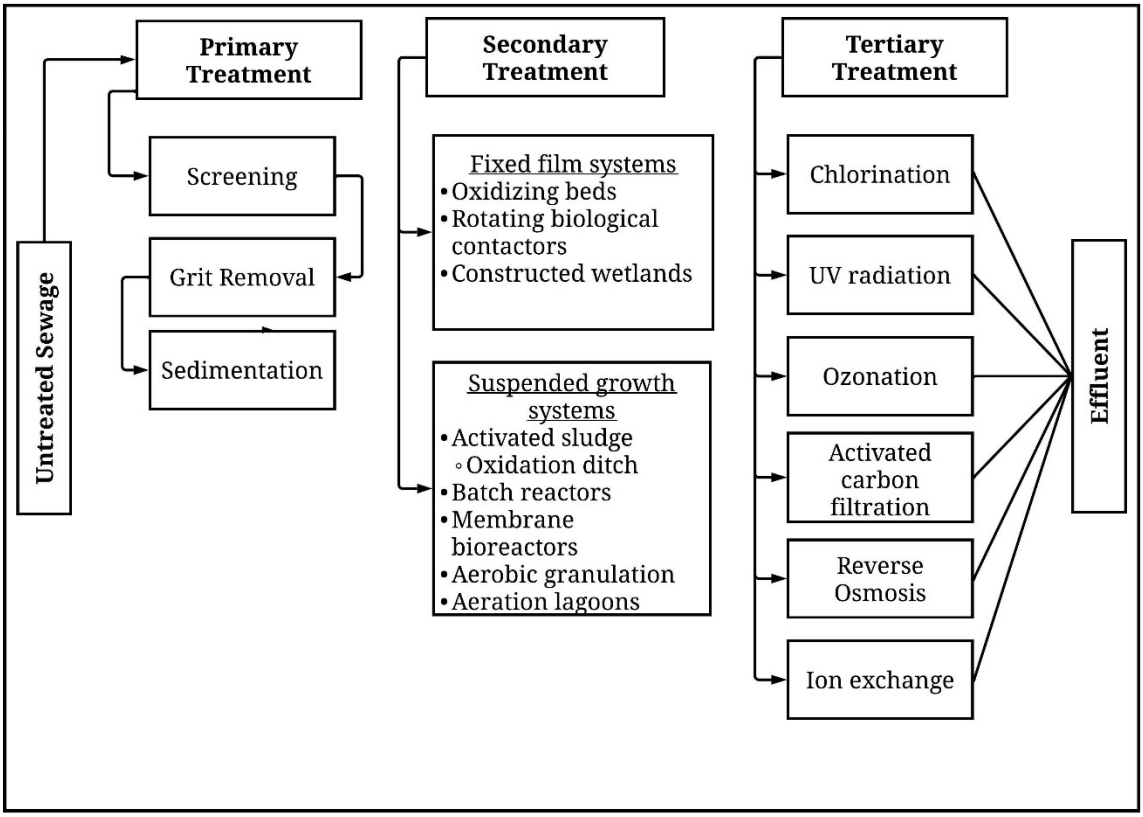



**Figure 2 Types of Wastewater Treatment Plants**

A WWTP typically has three stages of treatment: primary, secondary, and tertiary [Sui et al., 2010] (Figure 2). In primary treatment, the main goal is to settle solids out of solution via grit chambers, sedimentation, and skimming. Sorption of PPCP to sediment that makes up the settled matter removed in this step mostly removes compounds with hydrophobic properties. Many PPCP are not highly hydrophobic and will not be removed with this mechanism [Sedlak and

Pinkston, 2001]. The purpose of secondary treatment is to reduce total suspended solids (TSS), pathogens, turbidity, odor, biological oxygen demand (BOD), and nutrients (e.g., nitrogen and phosphorus compounds), which is often the above-mentioned activated sludge treatment, where oxygen is actively supplied to maintain fast aerobic respiration. Benchtop activated sludge experiments showed that primary and secondary treatments are ineffective at eliminating clofibric acid, carbamazepine, and diclofenac [Zupanc et al., 2013]. Biodegradable dissolved organic matter is removed using this aerobic biological treatment. Removal rates are typically low for amide-type pharmaceuticals such as ketoprofen[4], and naproxen[4], studied in survey of 18 different PPCP (anti-inflammatories, phenolic antiseptics, amide pharmaceuticals, phenolic endocrine-disrupting chemicals, and natural estrogens) in a WWTP that used primary and secondary treatment with activated sludge [Norihide et al., 2006]. Secondary treatment includes trickling filters or biofilters, oxidation ditches, membrane bioreactors and rotating biological contactors (Figure 2). Following biological treatment, clarification through settling and filtering helps remove any additional solids. The resulting effluent is disinfected using chlorine, ozone or UV treatments to kill any remaining pathogens (Figure 2). Some advanced treatment plants implement nutrient removal treatments prior to disinfection.

Blair et al., [2015] found that various PPCP, including carbamazepine, norfloxacin (antibiotic), and sulfamethoxazole, have negative removal efficiencies (Table 2). Their study of a WWTP that serves the Milwaukee, WI, area uses bar screens/grit channels, primary clarifiers, and conventional activated sludge treatment as a secondary treatment. Blair et al., [2015] suggest that a cause of the increased PPCP concentrations was PPCP enclosure in fecal matter particles being released during treatment by aerobic microbes [Göbel et al., 2007; Blair et al., 2015]. They

[4] NSAID

also suggested the cause for the increases in PPCP after treatment were metabolites reverting into their parent compound. This pattern has been observed with estrone, with its metabolite estradiol reverting to estrone through oxidation in WWTP aeration tanks [Carballa et al., 2004; Ting and Praveena, 2017]. The removal efficiency of PPCP seems to be strongly dependent on the technology implemented in WWTP, as seen in Table 2.

As an alternative to biological treatment, WWTP may implement other treatment technologies. Membrane bioreactor treatment combines activated sludge treatment with membrane filtration and has been shown to have a 20% increase in removal efficiency of sulfamethoxazole compared to activated sludge alone [Göbel et al., 2007]. Combining membrane bioreactor treatment with reverse osmosis or nanofiltration are more effective at reducing PPCP concentrations by 41 to 95% [Wang et al., 2018].

Ozone and chemical treatments can also be used to enhance the removal of PPCP. Ozone treatment can remove many PPCP, including diclofenac, estrone, ibuprofen, sulfamethoxazole, and triclosan, with removal efficiencies greater than 90% [Wang and Wang, 2016]. The use of ozone following conventional treatment to remove PPCP is effective due to its strong non-selective oxidizing activity of hydroxyl radicals which causes chemical breakdown [Wang and Wang, 2016]. While a strong contender for PPCP removal, ozone treatment is less popular for effluent treatment in the US [Oneby et al., 2010]. Chemical wastewater treatment is often used on waste from sources toxic to microorganisms needed for activated sludge treatment [Wang and Wang, 2016]. Chemical treatment may include chemical coagulants that combine smaller waste particles to form larger particles that can settle out of the solution. This treatment process can be used as a precursor to sludge treatment or individually. The success of PPCP and AS removal is dependent on WWTP technology.

*1.4.2 Septic treatment*

Groundwater and surface water are intertwined in the hydrogeologic cycle. Many assume that groundwater is "clean" due to natural filtration through sediment, but several studies have shown that groundwater is just as susceptible to pollution [Buerge et al., 2009; Bradley et al., 2016; Kibuye et al., 2019]. In a study conducted by Gray et al., [2010] comparing levels of PPCP contamination in surface water and groundwater, the authors found no significant differences. Septic tanks, whose final treatment step is leaching into the soil in an underground drain field, pose a substantial risk for groundwater pollution [Schaider et al., 2013].

Denitrifying bacteria are essential to reducing nitrogen loads in groundwater and are affected by pharmaceutical intrusion from WWTP and septics. Underwood et al., [2011] showed that the presence of sulfamethoxazole, even at low concentrations of 1.38 µg/L in groundwater, has direct negative correlations to the microbial community transforming nitrogen and decreased the potential for nitrate reduction up to 47% depending on concentration.

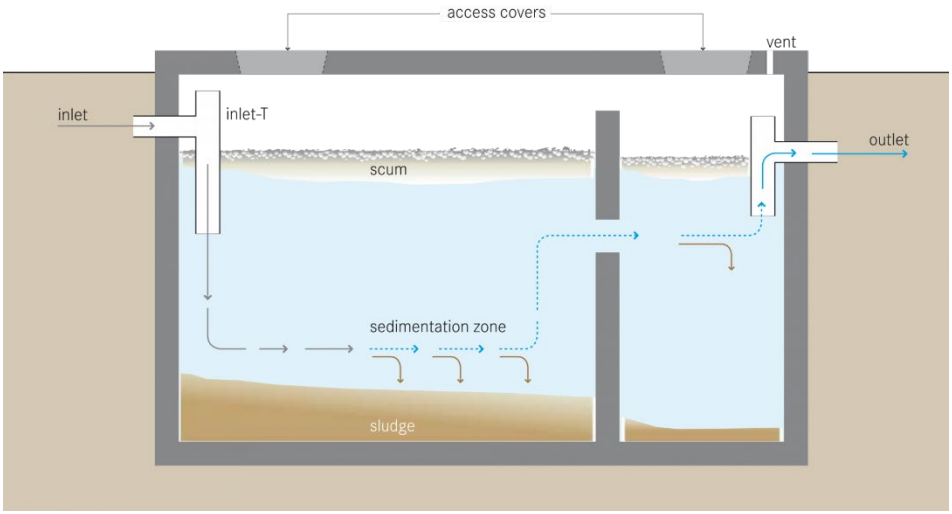



**Figure 3 Septic tank schematic**

Many homes depend on septic systems for waste disposal (Figure 3) with treatment occurring at individual houses rather than a large, centralized plant. In the US, 20% of

households use septic systems, with 97% in suburban and rural areas [EPA, 2008]. A conventional septic system is an underground structure containing one or more compartments and an effluent dispersal system (Figure 3). Traditional septic systems use settling and degradation by way of anaerobic bacteria. Septic effluent from the septic tank will travel to a leach field to facilitate infiltration into the home's soil and shallow groundwater, where subsequent treatment is performed by bacteria (Figure 3), but this is highly dependent on soil type, infiltration rate and oxygen supply. This step acts as a natural filtration that removes any remaining particulate matter and allows for additional microbial degradation in the leach field, removing nutrients and some PPCP [Underwood et al., 2011]. These systems are not intended to replace a WWTP but offer an option for waste removal in areas where sewers have not been connected either due to cost, location, or the municipality's choice. The efficiency of septic systems can vary based on their design and functionality. Du et al., [2014] found that in a model septic tank with a simulated improperly functioning drainage field, removal efficiencies for acetaminophen (28 to 65%), caffeine (40 to 52%), carbamazepine (6 to 7%), sucralose (6 to 13%), and sulfamethoxazole (8 to 11%) varied. The U.S. Environmental Protection Agency (EPA) estimates that 10 to 20% of septic systems are malfunctioning, with failure rates in some parts of the U.S. reaching 50 to 70% [Hogye et al., 2001; USEPA, 2002; Schaider et al., 2017]. Poorly maintained and aging septic systems threaten waterways due to increased risk for PPCP, AS and nutrient pollution.

Little PPCP removal occurs in the anaerobic conditions of traditional septic tank with the removal depending on the drain field [Schaider et al., 2017]. In a 2013 study of PPCP in septic systems in Cape Cod, MA, median concentrations of nonylphenol[5], DEET, sulfamethoxazole,

[5] Used in manufacturing antioxidants, laundry and dish detergents.

and triclosan were found in similar concentrations (0 to 30 μg/L) in septic effluent and septic drain fields, indicating little treatment in the drain field [Schaider et al., 2013]. Like WWTP, septic systems are not capable of removing or degrading all PPCPs. Septic system design is variable, with the age of the septic system also affecting PPCP removal efficiency [Schaider et al., 2017]. For example, drip dispersal systems work by distributing septic tank effluent through leach lines closer to the soil surface have been shown to provide a high degree of PPCP removal, especially with the addition of an aeration system. This is likely due to a combination of enhanced microbial activity from aeration and sorption in the carbon-rich root zone.

Nutrient contamination from septic systems is a well-studied field, but few studies investigate a septic systems ability for nutrient removal and PPCP and AS removal [Valiela et al., 1992; Jonathan et al., 2003; Lapointe et al., 2017]. Proximity, soil type, and season have been shown to impact nutrient pollution sourced from septic systems [Postma et al., 1992; Arnade, 1999; Reay, 2004; Lapointe et al., 2017]. Relatively high nitrate concentrations in groundwater wells have been correlated with PPCP concentrations [Ohr, 2016], suggesting that groundwater with nitrate above 4 mg/L is an indication of septic-impacted water. Additionally, nitrate and Ace-K concentrations have been used to identify sources of groundwater contamination, with higher levels of Ace-K and of nitrate often originating from wastewater [Robertson et al., 2016].

In a traditional septic system waste flows from the home to the airtight septic tank where the waste is broken down by anaerobic bacteria. The incoming raw waste nitrogen composition is approximately 73% organic nitrogen and 24% ammonium [Lowe, 2007]. The initial treatment in the septic tank involves the settling of solids in the tank and degradation of waste by anaerobic bacteria. During this process, the majority of the organic nitrogen is mineralized to ammonium (ammonification). The resulting treated effluent is 70 to 90% ammonium and 10 to 30% organic

nitrogen [Heatwole and McCray, 2007; Lowe, 2007]. This effluent is further treated in the drain field of the septic system. In the drain field the effluent is exposed to air and oxygenated microbial processes can occur. The majority of the ammonium from the effluent will be converted to nitrate (nitrification), given that the soil is unsaturated, and air is accessible in the soil pores. The resulting nitrate may be leached into groundwater or used by plants. In areas where the drain field, is saturated with water nitrification is not possible. If the septic effluent ammonium has been converted into nitrate by the time it reaches an anoxic area in the drain field denitrification may occur and result in the production of nitrogen gas. The conversion of nitrogen can vary dependent on the drain field and microbial conditions. The presence of certain PPCP, like the antibiotic sulfamethoxazole, can hinder the nitrogen cycle and result in poor to no microbial treatment of septic effluent in the drain field.

### 1.5 Use of Ace-K, caffeine, sucralose as wastewater tracers

Ace-K, caffeine, and sucralose have been used as freshness indicators of wastewater. Ace-K and sucralose act as stable tracers for wastewater as they are not easily degraded in WWTP or the environment [Soh et al., 2011; Yang et al., 2017]. Conversely, wastewater treatment easily degrades caffeine, and its presence in WWTP effluent can indicate that wastewater is being released untreated [Padhye and Huang, 2012] A high ratio of caffeine to sucralose can indicate relatively high untreated wastewater compared to treated wastewater [Cantwell et al., 2018]. While this ratio was initially introduced to determine discharges of untreated sewage occurring during combined sewage overflow events, one of the objectives of this project was to assess the efficacy of using this ratio to identify untreated treated waste discharge originating from septic systems and WWTP effluent.

1.6 Wastewater pollution in Maryland

Water pollution in Maryland has been a focus of environmental regulation due to the state's reliance on the health of the Chesapeake Bay and its tributaries for jobs and tourism. In the mid-1950s and 1960s, recurring deep-water hypoxia and loss of diverse submersed vascular plants was first reported, which resulted in the decline of the popular blue crab fishery (*Callinectes sapidus*) (Kemp et al., 2005). Further investigations into the cause of the decline found several factors contributing to the degradation of the Bay. Increased fertilizer use and human population growth from 1945 to 1990 resulted in a 2.5-fold increase in total nitrogen loads in the Chesapeake Bay area [Sprague et al., 2000]. This increase in fertilizer use aligned with several studies [Karlsen et al., 2000; Adelson et al., 2001; Willard et al., 2003] that found biotic and geochemical indicators of hypoxia during a similar time period. High inputs of in the Bay has been directly correlated with algal blooms in the spring and summer [Gallegos and Jordan, 2002]. These blooms contribute to hypoxia and poor conditions for aquatic life.

In the 1980s, excess nutrient pollution was identified as the primary source of the Bay's degradation [Liner et al., 2017]. Since then, a multi-state Chesapeake Bay Program partnership has been established to restore the health of the Bay. In 1985, wastewater represented 28% of total nitrogen loading to the Bay and 39% of total phosphorus loading [Liner et al., 2017]. Upon the realization that wastewater was a significant source of nutrients to the Bay, nutrient limits were proposed for WWTP effluents. In 2005, states in the Chesapeake Bay region began to implement a new permitting process that limited the amount of nitrogen and phosphorus that WWTP could discharge [Program, 2014].

In 2004, the Maryland senate enacted the Chesapeake Bay Restoration Fund to tax homeowners intending to use the money to modernize the state-owned WWTP [Haines et al.,

2004]. The goal of modernization was to reduce the amount of nitrogen and phosphorus pollution sourced from WWTP. According to the Maryland Department of the Environment (MDE), between 2004 and 2017, 53 of the 67 sewage plant upgrade projects have been completed, eliminating 6.3 million pounds of nitrogen and half a million pounds of phosphorus entering the Bay annually [Bernhardt and Pelton, 2017]. While the program has made strides in nutrient pollution reduction, improvements still need to be made to wastewater pollution in general. For example, Maryland's two largest WWTP (Baltimore's Back River WWTP & Patapsco WWTP) have consistently released nitrogen and phosphorus pollution at volumes up to 4 times their permitted limit [Bernhardt and Pelton, 2017]. Regrettably, nutrient pollution is not the only pollution originating from WWTP in Maryland. The two plants were knowingly discharging millions of gallons a day of partially treated sewage for several months in the summer of 2021 [Condon and Dance, 2021]. In addition to these discharges, aging sewer lines, improperly functioning septic drain fields and sewage overflows pose a threat to Maryland waterways. Maryland's two largest counties, Montgomery and Prince George, have ~5,500 miles of aging sewer lines with thousands more miles throughout the state, posing a risk of wastewater intrusion into groundwater and surface water [Hogan and Petitte, 2016]. In 2021 there was a 6% increase in nitrogen pollution with the majority of that increase sourced from wastewater [Azhar, 2022]. In order to combat this in the spring of 2022, Maryland House Bill 649 was passed to increase MDE staff to address the backlog of expired wastewater treatment permits and increase inspections of wastewater facilities flagged for violations [Love et al., 2022]. With these changes, Maryland can continue to protect and improve the Chesapeake Bay.

Many metrics for monitoring the Chesapeake Bay are based on excess nutrients removal, but nutrients are only part of the wastewater pollution challenge. Previously, $\delta^{15}N\text{-}NO_3^-$ values

have been used to distinguish $NO_3$-N derived from ammonium fertilizer, soil organic matter, and animal manure/septic waste [Yang and Toor, 2016]. However, abiotic (e.g., volatilization) and biotic (e.g., nitrification and denitrification) processes transform nitrogen moving from land to water, making it difficult to distinguish the contributing nitrogen sources in suburban and urban systems [Stumm and Morgan, 1981]. To circumvent this problem $\delta^{18}O\text{-}NO_{3-}$ and $\delta^{15}N\text{-}NO_{3-}$ ratios have been used to distinguish wastewater from other nitrogen sources [Kendall et al., 2007; Kaushal et al., 2011].

Studies investigating PPCP sourced from wastewater in Maryland have been few, but there is ample public and academic interest [Condon and Dance, 2021; Fork et al., 2021]. Early studies saw sulfamethoxazole in low concentrations (0.001 μg/L) in the Choptank River's septic-dominated agricultural watersheds [Arikan et al., 2008]. Investigations of Chesapeake Bay sediment near Baltimore's Back River WWTP found triclosan concentrations of 0.07 mg/kg [Miller et al., 2008]. A more recent investigation of sediment in the Patuxent River found triclosan ranging from 21 to 44 ng/g [Cantwell et al., 2010]. In streams feeding into the Anacostia River ibuprofen and triclosan have been found at concentrations of 22 and 25 ng/L [Shala and Foster, 2010]. The concentrations of ibuprofen and triclosan were similar in the NE and NW branches of the Anacostia River, even though the NW Branch receives no WWTP discharge. The authors propose septic leaching, aging sewer infrastructure, and landfills as sources of wastewater contamination.

Despite years of trying to improve water quality in the Chesapeake Bay, Maryland continues to struggle with nutrient pollution originating from wastewater. Discerning the magnitude of human wastewater from septic versus WWTP makes mitigation strategies difficult, especially with aging septic and sewer infrastructure and WWTP that are repeatedly releasing

untreated wastewater into the Bay. Based on the evidence of increasing detection and distribution of PPCP and AS and the lack of information about their extent in Maryland, this thesis aims to improve the current knowledge about sources of PPCP and AS and their distribution. PPCP and AS do not appear in waterbodies independently of nutrients and other pollutants but are part of the wastewater matrix that infiltrates surface and groundwater. By understanding their sources and fate, PPCP and AS may prove to be an important player in the goal to improve water quality in Maryland.

## 1.7 Goals and objectives

In this thesis, I aim to 1) assess the occurrence of PPCP and AS in urbanized catchments of Maryland's Western Shore, 2) determine potential factors controlling the spatiotemporal distribution of these contaminants in surface waters, and 3) investigate potential correlations between PPCS and AS with traditional water quality parameters such as nitrogen. These goals were accomplished in a 3-part study conducted in Maryland analyzing fifteen PPCP and AS commonly found in streams of the US.

The occurrence of PPCP and AS was investigated in tidal and non-tidal streams and groundwater. Non-tidal streams were sampled to examine the spatio-temporal variability of contaminants in streams draining urban catchments with a predominance of septic systems, and explore the relationships between concentrations and landscape and demographic characteristics. One of these streams was also sampled during stormflow events to examine how hydrological conditions affect PPCP and AS concentrations.

The goal of sampling tidal catchments was to assess the contribution, of WWTP and septic systems as sources of PPCP and AS to estuarine waters in Maryland and to examine the potential

link between PPCP and AS and other solutes commonly associated with water pollution such as nutrients.

### *1.7.1 Hypotheses*

1. PPCP and AS are ubiquitous in Coastal Plain streams draining urbanized catchments.
2. Biophysical characteristics such as land use, demographics and hydrology are major factors controlling PPCP and AS pollution from these catchments.

## 1.8 Chapter summaries

Chapter 2, provides an overview of the history of methodology used in this research project, including a description of how PPCP, AS and major ions were measured, and outlining general sampling procedures. Detailed descriptions of the instruments used, and methods of analysis are discussed.

Chapter 3, describes the research focused on headwater non-tidal streams to assess the presence and distribution of PPCP and AS in urban and suburban catchments. during baseflow, nutrient analysis, stormflow data collection and watershed land use. Stream flow samples were collected during baseflow and stormflow conditions and analyzed for PPCPs, ASs, nutrients, and major ions. Baseflow samples were collected monthly in ten streams for a period of 7 months, while stormflow samples were collected on an event basis in one selected stream. Catchment characteristics such as total area, land use, septic density, minimum and mean distances between septic systems and stream sampling sites were also determined in addition to stream characteristics such as depth and flow velocity as a proxy for discharge. This study is among the first to quantify PPCP and AS in headwater streams in Maryland.

Chapter 4, describes a synoptic monitoring study carried out in two sampling areas, one suburban and one rural to compare PPCP and AS contamination in septic dominated and sewer dominated catchments. Additionally groundwater was sampled in one catchment to access PPCP and AS contamination in comparison surface water.

# Chapter 2: Methodology

## 2.1 Introduction

This study provides an overview of methods used to determine multiple PPCP and AS concentrations in freshwater, outlines the approach developed to identify the most common contaminants in sewage waste, and describes all the other analytical methods and sampling procedures used in this research. In the past few decades, PPCP and AS have been identified to have connections to human waste [Evgenidou et al., 2015; Pérez-Lemus et al., 2019] but after extensive review, two LC-MS/MS methods have been developed to efficiently identify several of the most commonly identified PPCP and AS associated with sewage waste. These methods are outlined in detail in this chapter but, each chapter contains supplemental information and a discussion of any alterations to the methods described here.

## 2.2 Field Methods

The initial stages of sample collection and analysis for PPCP and AS were developed in Dr. Michael Gonsior's lab at the Chesapeake Biological Laboratory by himself and Dr. Katherine R. Martin.

Triplicate 250 mL grab water samples were collected in pre-combusted glass bottles (500 °C for 5 hours) for PPCP/AS analysis and sample-rinsed three times in the field before sample collection. Bottle lids were base washed (NaOH), rinsed with Milli Q ultrapure water, rinsed with isopropyl alcohol (IPA), and then rinsed again 3x with Milli Q ultrapure water (MilliporeSigma, Burlington, MA (. Samples were taken in the center of the water column with care taken to avoid collecting sediment. Collected samples were placed on ice and acidified within 24 hours of collection.

Sample collection design and frequency varied in each chapter and are detailed in each chapter's methods section. In chapter 3 surface water samples were collected monthly and analyzed for PPCPs, ASs and major ions. In addition to monthly sampling, one site (Chartwell Creek) was sampled 3 times during rain events of varying sizes. Samples during rain events were collected via an ISCO 6712 automated sampler (Teledyne, Lincoln, Nebraska). In chapter 4 surface water samples were collected on shore or via boat/kayak. Sites in Anne Arundel County were sampled once, sites in Charles County were sampled twice. All sites were sampled for PPCPs, ASs and nutrients. In addition to surface water sampling, groundwater water was sampled in Charles County.

All nutrient samples were collected in 30 mL Nalgene polypropylene bottles were rinsed with DI water, then soaked in 0.1 M HCl solution overnight. The bottle was then triple rinsed with Milli Q ultrapure water (resistivity 18.2 MΩ·cm) and allowed to dry. Samples were taken in the center of the water column with care taken to avoid collecting sediment. Collected samples were placed on ice and filtered within 24 hours of collection.

Environmental parameters studied, such as waterbody depth, and velocity, varied from chapter to chapter, see individual method sections in each chapter for further description.

## 2.3 Laboratory methods

### *2.3.1 Water sample processing for PPCP/AS analysis*

In the laboratory, samples were vacuum filtered through combusted 0.7 μm glass microfiber filters (Grade FT/F) (Whatman, Maidstone, United Kingdom) into combusted glass bottles. Filtered samples were then acidified to pH 2 using hydrochloric acid, concentrated by solid-phase extraction using solid phase extraction Bond Elut Priority PolLutant (PPL) cartridges (200 mg, 3 mL) (Agilent Technologies, Santa Clara, CA) and Oasis WAX cartridges (mixed-

mode, Weak Anion-eXchange)(150 mg, 6mL) (Waters Corporation, Milford, MA). PPL cartridges were activated with 2 mL of HPLC grade methanol (Fisher Chemical, Pittsburg, PA) followed by 2 mL 0.1% (v/v) formic acid (FA) water. Samples were added to 150 mL reservoirs atop the cartridges and loaded onto the cartridge. A flow rate of no more than 20 mL per minute was maintained using a vacuum pump. After sample loading, 5 mL of FA water was added to the cartridge. Cartridges were partially dried using the vacuum pump and eluted with 5 mL HPLC grade MeOH. The WAX cartridges were activated with 2 mL of LC-MS grade methanol amended with 2% HPLC grade $NH_4OH$ followed by 2 mL 0.1% FA water. Samples flowed directly from the PPL to the WAX cartridges via tubing connectors. After sample loading, 5 mL of FA water was added. WAX cartridges were partially dried using a vacuum pump and eluted with 5 mL 2% HPLC grade $NH_4OH$ methanol. Elution extract was collected in combusted glass vials and stored at -18° C.

*2.3.2 Analysis of solid-phase extraction samples for PPCP & AS*

Acetaminophen, Ace-K, atorvastatin, caffeine, carbamazepine, cotinine, DEET, dichlorvos, diclofenac, estrone, ibuprofen, paraxanthine, sucralose, sulfamethoxazole were quantified by high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS-MS) using an Agilent 1260 Infinity II LC interfaced with an Agilent 6420 Triple Quadrupole MS (Agilent Technologies, Santa Clara, CA). Standard sources and purity are summarized in table 1. PPCP/AS samples were diluted 5 to 1 with HPLC grade methanol; storm flow samples were not diluted due to lower contaminant concentrations. Instrument control and data processing was conducted using the Agilent MassHunter software suite.

*2.3.3 PPL and WAX analysis*

An Agilent 1260 Infinity II Vial sampler autosampler was used to inject each sample with an isopropanol needle wash step between injections. Ace-K was measured separately from the other PPCP to account for the $NH_4OH$ MeOH matrix. An ACE C18-PFP 150 x 2.1 mm ID column was used for both methods. For all compounds exuding Ace-K, the autosampler injection volume was 8 µL, the column temperature was set to 35 °C, and the flow rate was 0.200 mL $min^{-1}$. Mobile phase A was LC-MS grade methanol, and mobile phase B was 0.1% (v/v) LC-MS grade FA water. The separation gradient began at 80% mobile phase A, increased to 96% mobile phase A for 1–10 minutes, and returned to 80% mobile phase A at 11 minutes for a total run time of 22 minutes per sample. For MS settings, the carrier gas was high purity nitrogen from a Peak Scientific Genius NM32LA nitrogen generator. The capillary voltage was 4,800 V in positive mode, 4800 V in negative mode, the gas temperature was 350 °C, the gas flow was 10 L/min, nebulizer gas pressure was 35 psi, and delta electron multiplier voltage (+ & -) was 300 V. An internal standard (ISTD) quantification method was used to account for fluctuations in instrument performance and interfering matrix components, standards and ISTD can be found in table 1. As shown in table 2, target transition and stable isotope-labeled (SIL) ISTD transitions were used for standard curve quantification. The SIL ISTD spike was added at 25 µg/L to all blanks, calibration standards, and quality control standards. Quantification was done in triplicate and averaged. Results were corrected for SPE concentration factors and analysis dilution factors. Results were not corrected for SPE recovery.

For Ace-K quantification, the autosampler injection volume was 3 µL, the column temperature was 35 °C, and the flow rate was 200 µL $min^{-1}$. Mobile phase A was LC-MS grade methanol, and mobile phase B was 0.1% (w/w) ammonium acetate water made by adding ≥99.0% purity ammonium acetate to Milli Q ultrapure water. The isocratic elution is 90% mobile

phase A for 4 minutes for a total run time of 6 minutes per sample. For MS settings, the carrier gas was high purity nitrogen from a Peak Scientific Genius NM32LA nitrogen generator. The capillary voltage was 4000 V in positive mode, 2,500 V in negative mode, the gas temperature was 350 °C, the gas flow was 10 L/min, nebulizer gas pressure was 40 psi, and delta electron multiplier voltage (-) was 400 V.

For both methods, an internal standard (ISTD) quantification method was used to control for fluctuations in instrument performance and ion suppression. All blanks, calibration standards, quality control standards, and samples were spiked with ISTDs.

**Table 3 Sources and purities of PPCP & AS standards and ISTDs**

| Compound | Standard | Purity (%) | ISTD | Isotopic Purity (%) |
|---|---|---|---|---|
| Acesulfame-K | Acesulfame-K[a] | 99.9 | Acesulfame-d4 Potassium Salt | 98 |
| Acetaminophen | Acetaminophen | 99.9 | Acetaminophen-d3 | 98 |
| Atorvastatin | Atorvastatin Calcium[a] | 95.3 | Atorvastatin-d5 Sodium Salt [b] | 99.1 |
| Caffeine | Caffeine[a] | 99.1 | Caffeine-d9[b] | 99.7 |
| Carbamazepine | Carbamazepine[a] | | Carbamazepine-d10[d] | 98 |
| Cotinine | (-)-Cotinine[a] | 99.5 | S-(-)-Cotinine [b] | 97 |
| DEET | DEET[a] | 98.5 | DEET-d10[10] | 98 |
| Dichlorvos | Dichlorvos[b] | 95 | Dichlorvos-6 | 99.5 |
| Diclofenac | Diclofenac sodium salt[a] | 99.98 | Diclofenac-d4 | 98 |
| Estrone | Estrone[a] | 99.5 | Estrone-d2[b] | 95 |
| Ibuprofen | Ibuprofen[a] | 99.7 | Ibuprofen-$^{13}$C,d3 | 98.6 |
| Paraxanthine | Paraxanthine | 99.14 | Paraxanthine-d3[b] | 97 |
| Sucralose | Sucralose[a] | 99.2 | Sucralose-d6 [b] | 97 |
| Sulfamethoxazole | Sulfamethoxazole[a] | 100 | Sulfamethoxazole-d4 [b] | 98 |

Note: a=Sigma-Aldrich, b=TRC Canada, c= Honeywell International ISTD=internal standard

**Table 4 Multiple Reaction Monitoring settings**

| Compound | Transition Type | Ion Mode | Transition | RT (min) | FV (V) | CE (V) | CAV (V) |
|---|---|---|---|---|---|---|---|
| Ace-K | Target | Negative | 162 → 82 | 1.54 | 80 | 10 | 7 |
| Ace-K | Qualifier | Negative | 162 → 78 | 1.54 | 80 | 34 | 7 |
| Ace-K-d4 | ISTD | Negative | 166 → 86 | 1.54 | 80 | 10 | 7 |
| Acetaminophen | Target | Positive | 152 → 110.2 | 4.2 | 110 | 16 | 2 |
| Acetaminophen | Qualifier | Positive | 152 → 65 | 4.2 | 110 | 35 | 2 |
| Acetaminophen-d3 | ISTD | Positive | 155.2 → 111 | 4.2 | 110 | 16 | 2 |
| Atorvastatin | Target | Positive | 559.2 → 440.2 | 9.2 | 130 | 22 | 1 |
| Atorvastatin | Qualifier | Positive | 559.2 → 250.1 | 9.2 | 130 | 49 | 1 |
| Atorvastatin-d5 | ISTD | Positive | 564.3 → 445.2 | 9.2 | 130 | 22 | 1 |
| Caffeine | Target | Positive | 195.1 → 138 | 7.22 | 108 | 19 | 3 |
| Caffeine | Qualifier | Positive | 195.1 → 110.1 | 7.22 | 108 | 25 | 3 |
| Caffeine-d9 | ISTD | Positive | 204.2 → 144 | 7.22 | 108 | 19 | 3 |
| Carbamazepine | Target | Positive | 237 → 194 | 8.34 | 120 | 18 | 4 |
| Carbamazepine | Qualifier | Positive | 237 → 179 | 8.34 | 120 | 39 | 4 |
| Carbamazepine-d10 | ISTD | Positive | 247.2 → 204.2 | 8.32 | 120 | 18 | 4 |
| Cotinine | Target | Positive | 177.2 → 80.2 | 2.2 | 90 | 22 | 3 |
| Cotinine | Qualifier | Positive | 177.2 → 98.1 | 2.2 | 90 | 22 | 3 |
| Cotinine-d3 | ISTD | Positive | 180.2 → 101 | 2.2 | 90 | 22 | 3 |
| DEET | Target | Positive | 192.1 → 119 | 8.61 | 110 | 16 | 4 |
| DEET | Qualifier | Positive | 192.1 → 100.1 | 8.61 | 110 | 15 | 4 |
| DEET-d10 | ISTD | Positive | 202.2 → 119 | 8.6 | 110 | 16 | 4 |
| Dichlorvos | Target | Positive | 221 → 109 | 8.31 | 100 | 10 | 4 |
| Dichlorvos | Qualifier | Positive | 221 → 145 | 8.31 | 100 | 15 | 4 |
| Dichlorvos-d6 | ISTD | Positive | 227.1 → 115 | 8.29 | 100 | 15 | 4 |
| Diclofenac | Target | Positive | 296 → 215 | 10.14 | 85 | 19 | 1 |
| Diclofenac | Qualifier | Positive | 296 → 250 | 10.14 | 85 | 10 | 1 |
| Diclofenac-d4 | ISTD | Positive | 300 → 254 | 10.14 | 85 | 10 | 1 |
| Estrone | Target | Positive | 271 → 159 | 9.64 | 100 | 20 | 3 |
| Estrone | Qualifier | Positive | 271 → 157 | 9.64 | 100 | 20 | 3 |
| Estrone-d2 | ISTD | Positive | 273 → 159 | 9.64 | 100 | 20 | 3 |
| Ibuprofen | Target | Positive | 207.2 → 161.1 | 9.84 | 100 | 3 | 3 |
| Ibuprofen-13C, d3 | ISTD | Positive | 211.3 → 165.3 | 9.83 | 100 | 7 | 3 |
| Paraxanthine | Target | Positive | 181.1 → 124.1 | 3 | 90 | 23 | 3 |
| Paraxanthine | Qualifier | Positive | 181.1 → 96 | 3 | 90 | 29 | 3 |
| Paraxanthine-d3 | ISTD | Positive | 184.1 → 127.1 | 3 | 90 | 23 | 3 |
| Sucralose | Target | Negative | 443 → 397 | 7.2 | 90 | 7 | 4 |
| Sucralose | Qualifier | Negative | 441 → 395 | 7.2 | 90 | 7 | 4 |
| Sucralose-d6 | ISTD | Negative | 447 → 401 | 7.2 | 90 | 7 | 4 |
| Sulfamethoxazole | Target | Positive | 254 → 92 | 7.45 | 110 | 25 | 4 |
| Sulfamethoxazole | Qualifier | Positive | 254 → 156 | 7.45 | 110 | 15 | 4 |

| Compound | Transition Type | Ion Mode | Transition | RT (min) | FV (V) | CE (V) | CAV (V) |
|---|---|---|---|---|---|---|---|
| Sulfamethoxazole-d4 | ISTD | Positive | 258.1 → 160.1 | 7.45 | 110 | 15 | 4 |

Note=CAV=cell accelerator voltage, CE=collision energy, FV=fragmentor voltage, RT=retention time

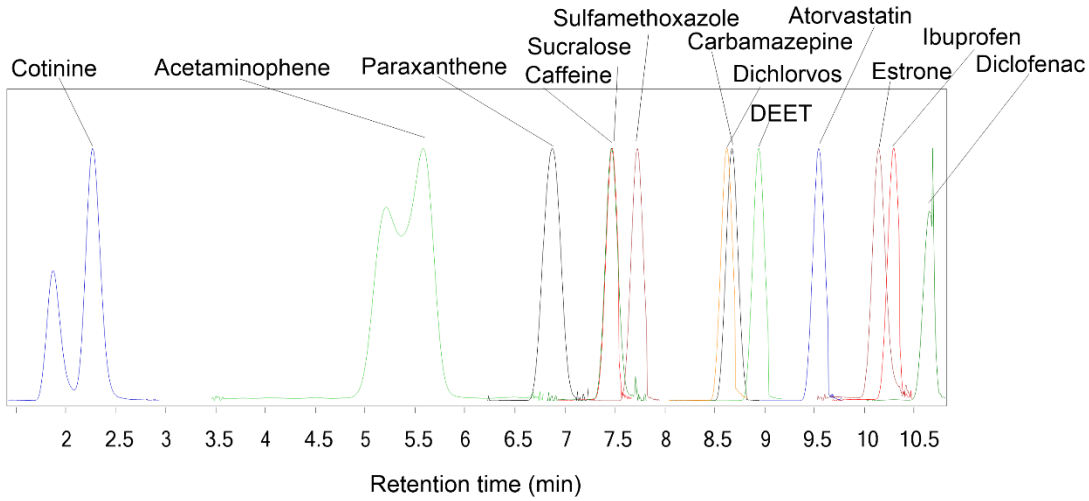



**Figure 4 Smoothed chromatogram of HPLC-MS-MS in MRM mode**

2.4 Analyses of nutrients and major ions

Water samples collected for analysis of nutrients and major ions were vacuum filtered through combusted 0.7 µm glass microfiber filters (Whatman GF/F) and stored in 30 mL Nalgene polypropylene bottles at 0°C until analysis. Nutrient and major ions analyses were undertaken both in the lab of Dr. Laura Lapham's lab at CBL and by UMCES CBL Nutrient Analytical Services Laboratory (NASL) in Solomons, MD. Water quality sampling parameters vary in each chapter and will be outlined in each methods section of each chapter.

Major ions (cations and anions) were analyzed using ion chromatography with a Dionex ICS-5000+ Reagent-Free Ion Chromatography System (Thermo Fisher Scientific, Waltham, MA) equipped with a KOH eluent generator and ion suppressor. Compounds were separated on an Dionex IonPac AS19 IC Column (2 x 250 mm; Thermo Fisher Scientific, Waltham, MA, Part # 062886) preceded by an AS11G guard column (2 x 50 mm, Thermo Fisher Scientific,

Waltham, MA, Part #046076). Ion components sampled can be found in table 3. The sampling needle was rinsed before each sample with Milli Q water. For anion quantification, the flow rate was 0.250 mL $min^{-1}$, and the column oven temperature was 30 °C. The elution gradient comprised an initial 10-minute equilibration at 10 mM KOH, followed by 0 to 10 min: 10 mM KOH, 10 to 25 minutes: ramp to 45 mM KOH, 25 to 28 minutes: 45 mM KOH, 28 minutes: decline to 10 mM KOH, 28 to 32 minutes: 10 mM KOH. A Dionex Seven Anion-II Standard was analyzed in a reference standard curve with each batch of Anion samples to ensure accuracy (Thermo Fisher Scientific, Product No. 057590). The cations elution gradient is as follows. The flow rate was 0.250 mL $min^{-1}$, and the column oven temperature was 35 °C. The elution gradient comprised an initial 5 minute equilibration at 10 mM KOH, followed by 0 to 5 minutes: 10 mM KOH, 5 to 6 minutes: 12 mM KOH, 6 to 7 minutes: 14 mM KOH, 7 to 8 minutes: 16 mM KOH, 8 to 9 minutes: 18 mM KOH, 9 to 21 minutes: ramp to 20 mM, 21 to 25 minutes: 10 mM KOH. A Dionex Six Cation-II Standard was analyzed in a reference standard curve with each batch of cation samples to ensure accuracy (Thermo Fisher Scientific, Product No. 210818). Each run follows the order of three blanks, a duplicate standard curve, two blanks, 20 samples in triplicate, one calibration check standard, one blank, 20 samples in triplicate, one calibration check standard, and two blanks. Chromatograms were analyzed in Chromeleon 7.2 (Thermo Scientific).

**Table 5 Ions measured by Dionex ICS-5000+**

| Anions | Cations |
|---|---|
| Fluoride | Lithium |
| Bromide | Sodium |
| Chloride | Ammonium |
| Nitrite | Potassium |
| Nitrate | Magnesium |
| Sulfate | Calcium |
| Phosphate | |

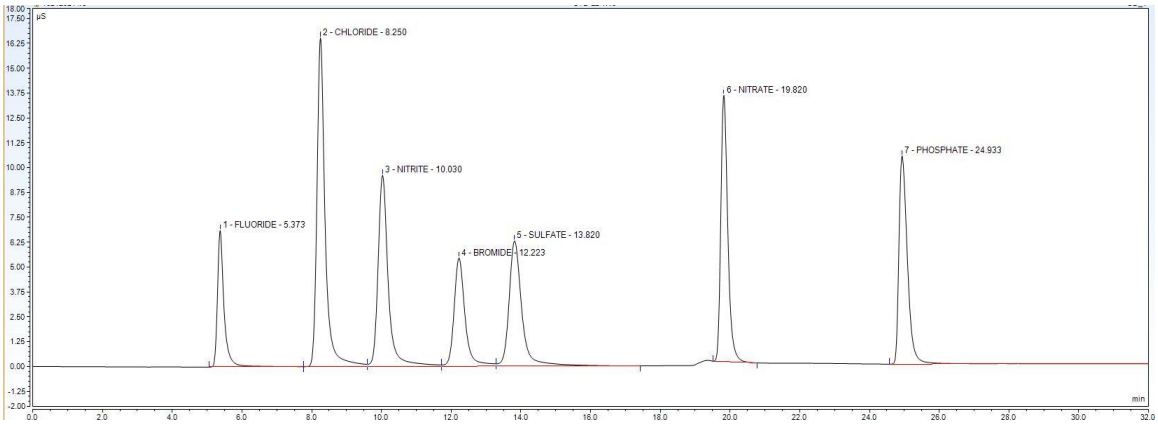



**Figure 5 Dionex Anion Chromatogram**

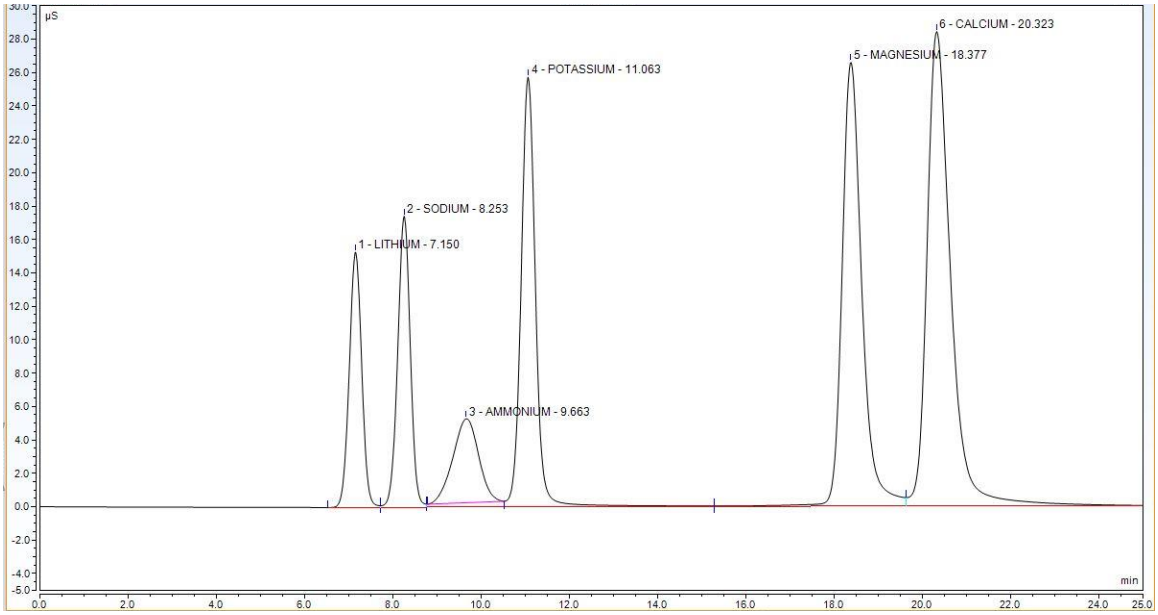



**Figure 6 Dionex Cation Chromatogram**

*2.4.2 Off site nutrient analysis*

NASL measured all nutrient samples in chapter 2. TDN, $NH_4/NH_3$, $NO_3$-$NO_2$, TDP, $PO_4$, PP, PN, and PC were measured by NASL using amended EPA methods and Standard Methods for the Examination of Water and Wastewater (American Public Health Association, Washinton, DC). The following methods were used: EPA 353.2 (Determination of Nitrate-Nitrite Nitrogen by Automated Colorimetry), EPA Method 365.1 (Determination of Phosphorus by Semi-Automated Colorimetry), Standard Methods #4500-N C, 4500-$NO_3$ F, #4500-P.B.5, and #4500 PE.

2.5 Quality Assurance

Multiple quality assurance measures were taken as part of this study. Triplicate samples were collected during every sampling event. All samples were analyzed in triplicate as well. PPCP/AS sample runs included a calibration check sample from the standard curve and an ISTD spiked blank every 20 samples. Field blanks (Milli Q water) were employed during two storm flow sampling events; each was filtered and extracted using the same procedure as all PPCP/AS samples. Chapter 4 nutrient samples were analyzed in triplicate.

# Chapter 3: Spatial and temporal distribution of PPCP and AS in headwater streams of Western, MD

## 3.1 Introduction

Pharmaceuticals, personal care products (PPCP), and artificial sweeteners (AS) are a large and growing class of human-sourced contaminants being detected increasingly in surface waters and notably in waters once thought to be pristine [Bradley et al., 2017; Bradley et al., 2019]. These compounds are essential for treating diseases, improving the quality of daily life, and some function as food additives [Boxall et al., 2012]. Despite their common use, several PPCP, including carbamazepine and diclofenac, have been identified as contaminants of emerging concern by the European Union (EU) [Ebele et al., 2017] due to growing evidence of negative impacts to the aquatic environment. The EU has proposed monitoring and regulation, but as of 2021, these compounds are still not regulated. Meanwhile, numerous studies have investigated PPCP and AS in the freshwater aquatic environment.

As discussed in Chapter 1, many PPCP and AS are not easily removed by conventional water treatment processes because of their physicochemical properties. Such contaminants are considered persistent as they accumulate in the environment. In contrast, PPCP that are more readily removed, like acetaminophen and caffeine are not considered persistent, but their continuous use and release to the environment make them what is considered "pseudo-persistent" [Ebele et al., 2017]. Pseudo-persistent pharmaceuticals can be removed from the environment by processes such as biodegradation, photodegradation and particulate sorption, but their constant release causes them to behave like persistent compounds [Brown et al., 2015; Klaminder et al., 2015; Ebele et al., 2017]. Some of the known potential negative effects of persistent and pseudo-persistent PPCP and AS on the health of humans and other organisms include endocrine disruption [Han et al., 2010], the spread of antibiotic-resistant genes [Schoenfuss et al., 2016;

Wilkinson et al., 2022], and ecological disruption [Bunch and Bernot, 2011; Underwood et al., 2011; Richmond et al., 2017].

Between 2014–2017 the United States Geological Survey (USGS) sampled 308 streams across the US and found multiple pharmaceutical compounds in 91% of the sampled streams [Bradley et al., 2020]. Both urban and rural streams were found to have PPCP contamination. Notably, 75% of the sampled streams without a wastewater treatment plant (WWTP) in the catchment had at least two types of PPCP detected. Similarly, a recent comprehensive review of the world's rivers has determined that 25% of the 1,052 sampled locations had PPCP concentrations greater than the levels considered safe for aquatic organisms based on predicted no-effect concentrations [Wilkinson et al., 2022], suggesting that the presence of PPCP and AS in aquatic ecosystems is ubiquitous and might have unintentional consequences.

Worldwide, the highest PPCP and AS concentrations in rivers and streams are found in low- to middle-income regions such as sub-Saharan Africa, southern Asia, and South America, where wastewater management is commonly deficient or inexistent [Wilkinson et al., 2022]. Therefore, high concentrations of PPCP and AS have been typically linked to poor infrastructure and point source pollution. In countries with more established waste disposal systems, PPCP and AS concentrations are lower but from more variable sources [Wilkinson et al., 2022].

Previous studies in countries with more established waste disposal systems have revealed PPCP pollution in both urban [Bradley et al., 2020] and rural [Peters et al., 2019] areas, but in both cases, concentrations have been correlated with land use [Vaicunas et al., 2013; Meng et al., 2022]. Contaminants such as herbicides and certain antibiotics are prevalent in more agricultural areas, while PPCP and AS such as Ace-K, sucralose, carbamazepine and erythromycin are more

prevalent in human dominated systems, i.e. urban/suburban [Buerge et al., 2009; Fairbairn et al., 2016].

In urbanized catchments, most pharmaceuticals enter aquatic ecosystems through human consumption, followed by excretion of un-metabolized pharmaceuticals or degradation products (e.g., nicotine to cotinine) [Halling-Sørensen et al., 1998]. Therefore, PPCP and AS contamination was initially believed to be primarily a function of population density [Bernot et al., 2016; Fairbairn et al., 2016], and presumed to come from wastewater treatment plants (WWTP) and improper disposal. However, subsequent studies have indicated that WWTP effluents were not the only source of PPCP and AS pollution; more diffuse sources were proposed, including aging sewer infrastructure and onsite wastewater treatment systems (OWTS) [Kolpin et al., 2002; Glassmeyer et al., 2005; Lissemore et al., 2006; Shala and Foster, 2010; Vaicunas et al., 2013].

In the United States, roughly 20% of households rely on OWTS for wastewater treatment [EPA, 2008]. Reliance on septic tanks is widespread in coastal communities, with the East Coast having the highest levels of septic system usage [Mallin, 2013]. Coastal communities usually rely on septic systems due to lack of sewer lines.

With a population of about 6 million people, the state of Maryland, for example, has approximately 420,000 septic systems; of these, 52,000 systems are located within 1,000 feet of tidal waters [DNR, 2021]. However, few studies have investigated the contribution of PPCP and AS contamination sourced from these systems [Arnade, 1999; EPA, 2008; Meyer et al., 2019]. Consequently, despite decentralized wastewater treatment being a common source of sewage pollution, less than 2% of papers published between 1990 and 2009 on PPCPs and ASs have focused on septic systems [Meyer et al., 2019].

In conventional, or soil-based septic systems, the effluent is slowly released directly into the soil, where it percolates and reaches groundwater. Therefore, it is not uncommon for septic systems to impact wells. For example, in a rural aquifer in Southern Ontario, Canada, >30% of groundwater wells and springs were impacted by septic system effluent [Spoelstra et al., 2017]. Within the same watershed, the contribution of septic effluent to streamflow was on average 0.52% [Spoelstra et al., 2020]. However, the contribution of septic systems to groundwater recharge varies from catchment to catchment based on a myriad of factors including water table height and soil type [Reay, 2004; Kibuye et al., 2019].

### *3.1.1 Pollution in headwater streams*

PPCP and AS have been shown to be ubiquitous in surface waters, but the majority of studies to date have focused on larger water bodies such as rivers and lakes that have point sources of contamination like a WWTP or documented sewage spills [Wilkinson et al., 2022]. Fewer studies have focused on PPCP and AS pollution in headwater streams despite the fact that they make up between 70 to 90% of the world's river network length [Downing, 2012; Wohl, 2017; Allen and Pavelsky, 2018; Ward et al., 2020] and play a crucial role in the transfer of water and materials from terrestrial to aquatic ecosystems such as rivers, lakes, estuaries, and oceans.

Little is presently known about PPCP and AS pollution in headwater streams, but there is a plethora of information about other pollutants, such as excess nutrients and sediment in streams, and how they impact the water quality and health of downstream aquatic ecosystems. The supply, transport, and fate of these common pollutants in low order streams are strongly influenced by land use in the catchment, which also affects the channel condition and its capacity to moderate loads to larger water bodies downstream [Alexander et al., 2007]. In the Chesapeake

Bay region, for instance, the degradation of headwater streams has been linked to the decline of physical and biological properties of the estuary [Goetz et al. 2004].

In the case of nitrogen, concentrations and fluxes in streams draining the Chesapeake Bay watershed vary substantially from place to place but are generally greatest in areas of concentrated agriculture, urban centers, or point sources [Ator et al. 2020]. Septic systems are responsible for 6% of the total load of nitrogen to the Bay [Lazur et al., 2020], while nitrogen concentrations have been correlated with PPCP and AS concentrations in large catchments [Humphrey et al., 2010; Underwood et al., 2011; Robertson et al., 2016]. While there is not much study on PPCP and AS contaminants in headwater streams, if trends from larger streams hold true, headwater streams draining urban catchments and receiving relatively high loads of nitrogen will also have high concentrations of contaminants such as PPCPs and ASs.

### *3.1.2 Objectives and hypotheses*

The overall objective of this chapter is to assess the presence and distribution of PPCP and AS in headwater streams draining catchments with septic systems. More specific goals are to i) investigate the dynamics of PPCP/AS concentrations according to different temporal and hydrological conditions (baseflow and stormflow), ii) identify potential easy-to-measure predictors of contaminants in headwater streams such as catchment characteristics, and iii) assess the correlation between PPCP/ASs and nutrients commonly associated with human waste pollution. These objectives were addressed by combining targeted analyses of traditional water quality parameters, quantification of PPCP and AS in streams, and land use and septic system spatial data.

*Hypotheses*

- PPCP and AS concentrations vary among streams; land use and other catchment characteristics such as the presence of septic systems influence PPCP and AS concentrations.
- PPCP and AS concentrations vary seasonally and according to hydrological conditions.
- Concentrations of PPCPs Ass are correlated to nitrogen concentrations, hence, have similar sources.

## 3.2. Materials and Methods

### *3.2.1 Study Area*

Ten headwater streams in different catchments were studied in the Western Maryland region of Anne Arundel County, MD (Figure 7). Anne Arundel County is in the Chesapeake Bay watershed region of the Mid-Atlantic, with a population of 590,336, approximately 10% of Maryland's population [Census, 2020]. The county has a total area of 1,520 $km^2$, of which 29% is covered by water. The area can be described as flat terrain with the highest point at 91 m. Anne Arundel County is majority suburban in the north and agricultural in the south. This area was chosen due to its mixed land use and relatively large suburban population.

Anne Arundel County has a humid climate with average temperatures ranging from -3 to 31°C throughout the year, and average annual precipitation of 1470 mm [Information, 2022]. Rainfall volume is greatest between March and October, with March through August having the rainiest days. Humidity during summer months ranges from 52 to 70%.

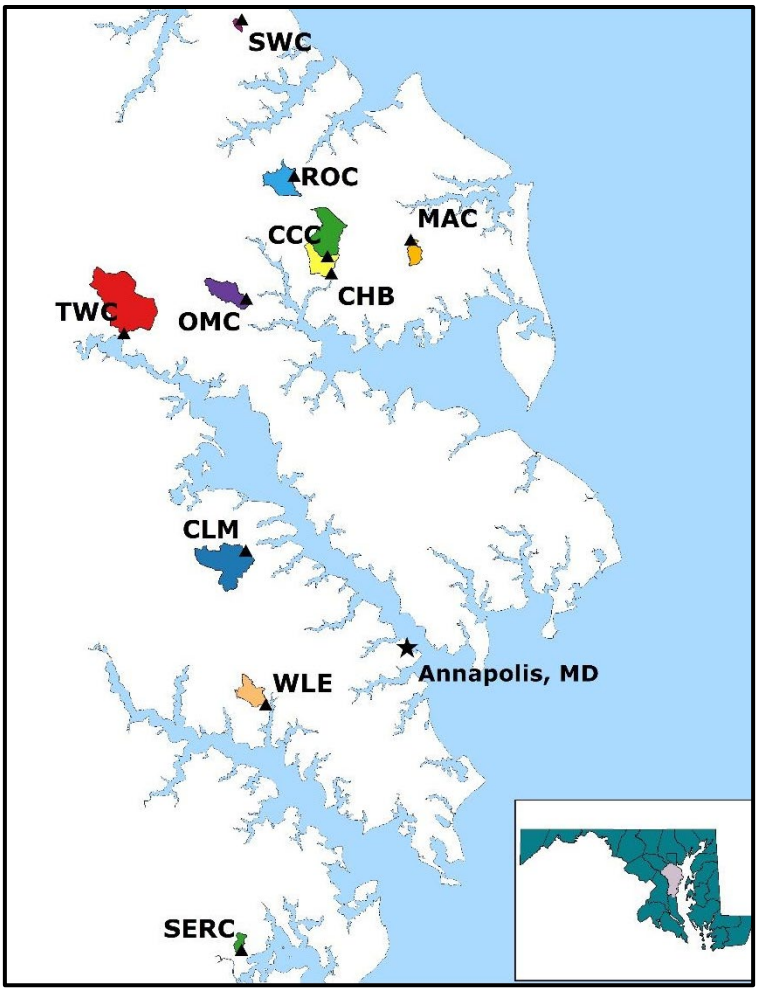



**Figure 7 Study sites and their catchments in Anne Arundel County, Maryland, USA**

*3.2.2 Site Selection*

This study focused on perennial streams because they have a continuous flow of surface water throughout the year, which allowed sampling during the entire multi-season study period. Candidate sites were first selected from Maryland Department of Natural Resources stream sampling records [County, 2019], a geospatial database was subsequently created for each site in Arc GIS. Information in the database included land ownership (i.e., parkland, private, and protected) and septic site locations in the respective catchments.

Initially, 156 sites were identified, but only the prospective with at least ten septic systems within 50 meters from a stream channel identified using ArcGIS were selected. These

sites were then visited to determine accessibility and confirm no ongoing construction. Sites with construction were excluded due to concerns about changes in water flow and sediment contamination. Ten streams that had a gradient of septic system density and land use, from highly urbanized to mostly forested land were selected. The sites with the lowest levels of septic systems acted as "septic control" sites. The septic density for these stream catchments was less than 0.1 $\frac{septics}{hectare}$, either due to sewers systems connecting to WWTP were the prevalent waste disposal method (e.g. Rock Creek) or because the stream was in a protected area (Smithsonian Environmental Research Center, SERC). SERC is an approximately 10 $km^2$ environmental research coastal area consisting of forests, wetlands, and marshes, which is open to scientists, school trips, and visitors. The center contains one legacy septic system. Rock Creek functioned as a "suburban control" as it had relatively few septic systems in a residential area.

One of the ten study streams was also selected for the collection of water samples and water level (stream stage) data during stormflow conditions. The selected site was Chartwell Creek (TWC), chosen because of its ease of access for an ISCO automatic sampler and landowner permission for long-term sampling.

*3.2.3 Characteristics of the Study Streams and their Catchments*

**Figure 8 Selected sample site images taken in October 2021**

Note: Top left Clements Creek, top right Cockey Creek, bottom left SERC, bottom right Wilelinor

Chartwell Creek is a suburban creek that along its stream reach, is culverted under roads; the creek ends with its outfall into the Severn River after flowing through residential areas with forest buffers. Chelsea Beach (CHB) is adjacent to Cockey Creek (CCC); aquatic life can often be found in this creek, one of the deepest of all the sampled creeks; this creek passes through residential neighborhoods and sports fields. The creek bed is wide-reaching and occasionally collects sediment following major storm events. Clements Creek (CLM) is one of the least densely populated catchments, passing through a sparsely populated, heavily wooded neighborhood. The sampled portion of the creek is in a valley with steep slopes and mature

forest. The creek is located behind several neighborhoods and flows through a community sports park; the creek eventually connects to the main stem of the Maggoty River. Main Creek (MAC) flows through a moderately populated residential neighborhood, and a small park, a portion of the creek is culverted under roads. Old Man Creek (OMC) is located in a residential neighborhood. A portion of the creek rests in an artificial holding pond before culverting under a highway. The creek is often contains of plant life and amphibians. Rock Creek (ROC) is located in a forested area between neighborhoods with relatively few septic systems; the creek is surrounded by artificial riprap and moderate tree cover. SERC is a protected forested area except for a handful of research facilities. Swan Creek (SWC) is in a forested area with very few homes that border an industrial park; the creek often has a sulfur smell and sheen. Wilelinor is a restored stream in a residential neighborhood; there are several pools within the stream to achieve the restoration goal of reducing nitrogen and sediment loads to the South River. All sample sites are first or second-order headwater streams that contribute to the Chesapeake Bay.

*3.2.4 Sampling Design*

Water samples and hydrological data were collected monthly from March to November 2021 in all study streams during base flow conditions. The sampling date varied from month to month as samples were only collected when there was no precipitation during the 72 hours prior to sampling. Stormflow was sampled in one study stream (Chartwell Creek). Stormflow samples were collected on an event basis at Chartwell Creek in the summer and fall of 2021, during three separate storm events in June and September.

Baseflow samples were collected manually and stormflow samples were collected with an automated sampler (Teledyne 6712 ISCO, Lincoln, NE). Baseflow grab samples were collected in 250 mL acid-washed combusted amber glass bottles with IPA-rinsed polypropylene

caps. All bottles were triple sample rinsed before water collection below the water's surface and no more than 10 mm from the surface. Water samples were also collected in triplicates for nutrient analysis using sample rinsed HDPE Nalgene bottles. Samples were stored on ice and in the dark during transport to the laboratory. In the laboratory, they were filtered within < 24 hours, processed and then stored at $0^{o}$C until they could be analyzed.

Stormflow samples at Chartwell Creek were collected with an ISCO automated sampler configured to collect up to 24 samples per event. Before each sampling event, a baseflow grab water sample was taken using the ISCO and transferred to their respective glass and HDPE bottles. Before use, all ISCO sample bottles were base washed, rinsed with IPA, and triple rinsed with MilliQ ultrapure water. The collection continued every 20 minutes, with 300 mL collected each time; these samples are composed of an hourly composite sample of 3 samples for a total of 900 mL sample. Water collection was stopped when the water level returned near baseflow. The ISCO was filled with freezer packs (Sonoco ThermoSafe PolarPacks, Arlington Heights, IL) to keep samples cool until the samples could be retrieved from the field (< 24 hours).

*3.2.4.1 Hydrological measurements*

Instantaneous discharge was measured during base flow conditions at each sample site using the cross-sectional area method [Gravelle, 2015], where a stream is divided into sections (n), the velocity of a section ($V_n$), and the cross-sectional area of the water in the stream section ($A_n$) are measured, and the product of these measurements across the stream gives discharge in volume per unit time:

$$Q = \sum_{1}^{n} V_N \times A_n$$

**Equation 1 Instantaneous discharge**

Water depth, width, and flow velocity were recorded immediately after water samples were collected at each stream site. This was accomplished by extending a meter tape across the entire width of the stream and recording the distance at regular intervals, where depths were measured with a stainless steel measuring stick. Stream flow velocity was measured at these points using a portable flow meter (Marsh-McBirney, Inc., Flo-Mate Model 2000).

In the stream selected to collect water samples during stormflow conditions (Chartwell Creek), water level was recorded continuously using a HOBO U2 Water Level pressure transducer (Onset, Cape Cod, MA) installed within the channel, a few meters from the ISCO sampler. A second pressure transducer was installed outside the channel in the riparian zone to correct the channel pressure transducer data for barometric pressure. The water level at Chartwell Creek was recorded every 5 minutes for the entire multi-month sampling period. Periodically during the study period, the stream would overflow from the stream channel and onto the flood banks; these events are noted on the corresponding hydrographs.

*3.2.4.2 Precipitation Data*

Rain depth was measured continuously during the monitoring period using an Ambient Weather WS-2902 Home Weather Station with Thermo Hygrometer (Ambient Weather, Chandler, AZ), approximately 850 m SE from the Chartwell Creek sampling point (Weather Station ID: KMDSEVER98. The station data is maintained by Weather Underground (San Francisco, CA).

*3.2.5 Sample Processing & Laboratory Analysis*

The following is a brief overview of sample processing & laboratory analysis; see Chapter 2: Methods for a detailed explanation.

Before being frozen, water samples collected for nutrient analyses were filtered using glass fiber filters (Whatman 0.45 μm, Maidstone, United Kingdom). All samples were unfrozen before

analysis via overnight defrosting in a refrigerator. All water samples were analyzed for major anions (fluoride, bromide, chloride, nitrite, nitrate, sulfate, and phosphate) and major cations (lithium, sodium, ammonium, potassium, magnesium, and calcium). Ion chromatography was performed via Dionex ICS-5000+ Reagent-Free Ion Chromatography System (Thermo Scientific, Waltham, MA) equipped with a KOH eluent generator and ion suppressor in the lab of Dr. Laura Lapham at CBL. Elution gradient for anions followed a modified version of Standard Method 4110B [Wastewater, 2012]. The elution gradian for cations was adapted from Thermo Fisher Scientific, Application Note 141 [Thomas et al., 2002; Wastewater, 2012].
The PPCP and AS quantification samples were analyzed in the lab of Dr. Michael Gonsior at CBL. To analyze these compounds, a process called solid phase extraction is required. Water is passed over a resin contained in a cartridge, which temporarily binds the chemicals, which are then released when a solvent is passed over the resin. This approach allows for low detection limits, in the ng/L range, when paired with liquid chromatography mass spectrometry (LC-MS/MS). Extracts were analyzed using an Agilent 6420 Triple Quad Mass Spectrometer.

*3.2.6 Statistical analysis*

Statistical analysis was conducted using R Studio (2022.02.0 Build 443, Boston, MA). Due to the data structure, all data was treated as nonparametric. In order to evaluate possible relationships between the target compounds and environmental factors, Spearman's rho ($r^s$) was used to compute nonparametric correlations and the associated p-values. Spearman's rho values were also calculated using all sites. The significance of this analysis was set at $\alpha = 0.05$.

To determine differences among sampling events and locations, Kruskal-Wallis was used. The significance of this analysis was set at $\alpha = 0.05$. Significant Kruskal results were followed by Dunn's multiple comparisons with a Bonferroni adjustment to correct the experiment-wise error rate.

*3.2.7 Geospatial analysis*

Each site's septic density, land use, and imperviousness was generated via ESRI ArcGIS (Version 10.5, Redlands, California). Catchment area size and shapefile, slope, and precipitation were sourced from USGS StreamStats data [Kernell, 2008].

Septic density (Table 3, Figure 10) was generated from a StreamStats generated catchment shapefile and a septic system point shapefile generated by Anne Arundel County [Services, 2018]. The catchment file was used with the *Select By Location* tool to select septic system points using the "completely contain with source" selection method to retrieve the septic count. A septic density visualization was created using the septic system point shapefile and the *Kernel Density* tool from the Spatial Analysis toolbox.

Imperviousness for each sample site was generated using a StreamStats catchment shapefile and an impervious surfaces shapefile generated by Anne Arundel county [County, 2021]. The catchment shapefile and impervious surfaces shapefile were used to create a new file using the *Intersect* tool to identify areas where the two files overlap; a intersect file was created for each catchment. The catchment shapefile and Impervious Surfaces shapefile were then used to create a new file using the *Union* tool to join the files; a union file was created for each catchment. Percent imperviousness was then calculated by dividing the sum of the area values from the intersect attributes table by the sum of the area values from the union attribute table.

Land use for each site was calculated using a StreamStats catchment shapefile and a land use shapefile generated by Anne Arundel county [County, 2021]. The land use shape file was Clipped to each catchment area. The resulting clipped file attribute table was used to determine land use for each site. The distances between the sampling site in the study streams to septic tanks within their respective catchments was calculated using ArcGIS Version 10.15.

## 3.3. Results

### *3.3.1 Stream and Catchment Characteristics*

The average depth and width of the stream sites sampled varied from 3.6 to 13.1 cm, and 59.5 to 221 cm, respectively (Table 6). The widest channel was Chelsea Beach (214.4 cm), and the deepest was Chartwell Creek (13.11 cm).

**Table 6 Summary of headwater stream site characteristics**

| Site | Stream Width (cm) | Stream Depth (cm) | Discharge (L/s) | Stream Order |
|---|---|---|---|---|
| Cockey Creek (CCC) | 97.7 | 5.77 | 12.66 | 1st |
| Chelsea Beach (CHB) | 214.4 | 12.31 | 18.13 | 1st |
| Clements Creek (CLM) | 33.6 | 3.70 | 1.23 | 2nd |
| Chartwell Creek (TWC | 97.7 | 13.11 | 17.35 | 2nd |
| Main Creek (MAC) | 100.0 | 3.59 | 5.65 | 1st |
| Old Man Creek (OMC) | 83.8 | 8.94 | 5.70 | 1st |
| Rock Creek (ROC) | 104.7 | 9.48 | 17.08 | 2nd |
| SERC | 67.3 | 3.69 | 2.35 | 1st |
| Swan Creek (SWC) | 59.5 | 3.35 | 0.62 | 1st |
| Wilelinor (WLE) | 101.7 | 11.56 | 23.48 | 1st |

Note: Width, depth, and discharge are average values of all measurements taken in the study period during base flow conditions.

Land use was mixed in all of the study catchments, ranging from mostly urban/suburban to mostly forest (Table 6), but the former type was dominant in most catchments. Urban/suburban land use was also correlated with imperviousness, with Rock Creek having the highest level (36%) (Table 7).

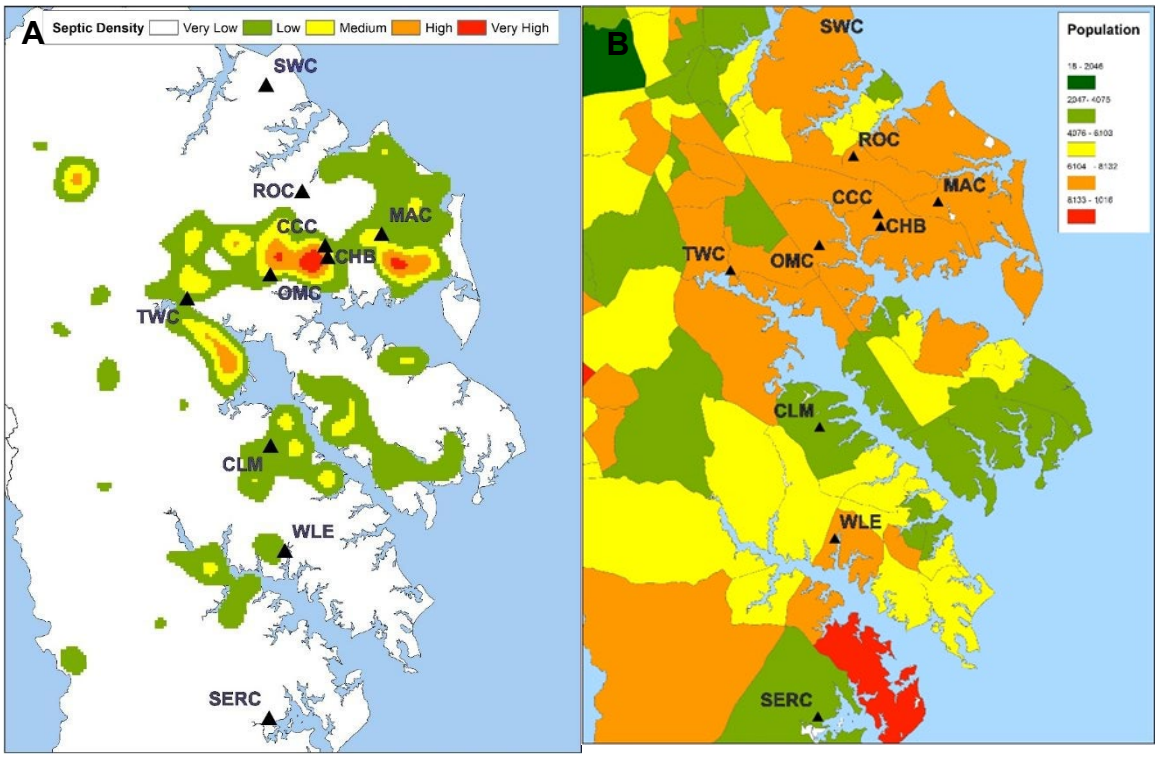



**Figure 9 Septic Density (A) and Population (B) in Anne Arundel County**

Overall, the study streams drained relatively small catchments (Table 7), which is expected for first and second-order headwater streams. Despite small catchment areas, the majority of sites had a high septic density, which correlated with the suburban population (Table 7, Figure 9 (A & B). All sites excluding the control sites of SERC and Rock Creek had a septic density of at least 0.1 $\frac{septics}{hectare}$. More site characteristics information are recorded in Appendix A.

**Table 7 Summary of land use characteristics**

| Site | Imperviousness | Land Use | | | | |
|---|---|---|---|---|---|---|
| | | Urban/ Suburban | Agri-culture | Forest | Water | Transportation |
| CCC | 22% | 66% | 2% | 30% | 0% | 2% |
| CHB | 22% | 75% | 1% | 22% | 0% | 1% |
| CLM | 12% | 72% | 0% | 28% | 0% | 0% |
| MAC | 24% | 95% | 0% | 5% | 0% | 0% |
| OMC | 18% | 83% | 0% | 17% | 0% | 0% |
| ROC* | 36% | 90% | 0% | 10% | 0% | 0% |
| SERC* | 9% | 4% | 26% | 70% | 0% | 0% |
| SWC | 32% | 72% | 1% | 27% | 0% | 0% |
| TWC | 23% | 98% | 0% | 1% | 1% | 0% |
| WLE | 35% | 72% | 0% | 22% | 0% | 7% |

| Site | Septic Count | Septic Density (septics/ha) | Drainage Area (ha) | Minimum Septic Distance (m) | Median Septic Distance (m) |
|---|---|---|---|---|---|
| CCC | 60 | 0.44 | 137 | 104 | 510 |
| CHB | 335 | 1.60 | 210 | 76 | 677 |
| CLM | 237 | 1.24 | 192 | 70 | 1018 |
| MAC | 109 | 3.24 | 34 | 32 | 429 |
| OMC | 137 | 1.76 | 78 | 39 | 698 |
| ROC* | 5 | 0.06 | 88 | 309 | 502 |
| SERC* | 1 | 0.04 | 23 | 302 | 302 |
| SWC | 7 | 0.57 | 12 | 142 | 268 |
| TWC | 675 | 2.12 | 319 | 109 | 1125 |
| WLE | 96 | 1.43 | 67 | 82 | 757 |

Note: * indicates control sites

Anne Arundel County is considered an urban/suburban area within the Washington-Baltimore metro area. Yet, despite the perceived urban nature of the county, septic systems are still a popular method of human waste treatment, especially in areas near the coast. Septic density in the catchments drained by Main Creek and Chartwell Creek are greater than 2 septics per hectare (Table 7).

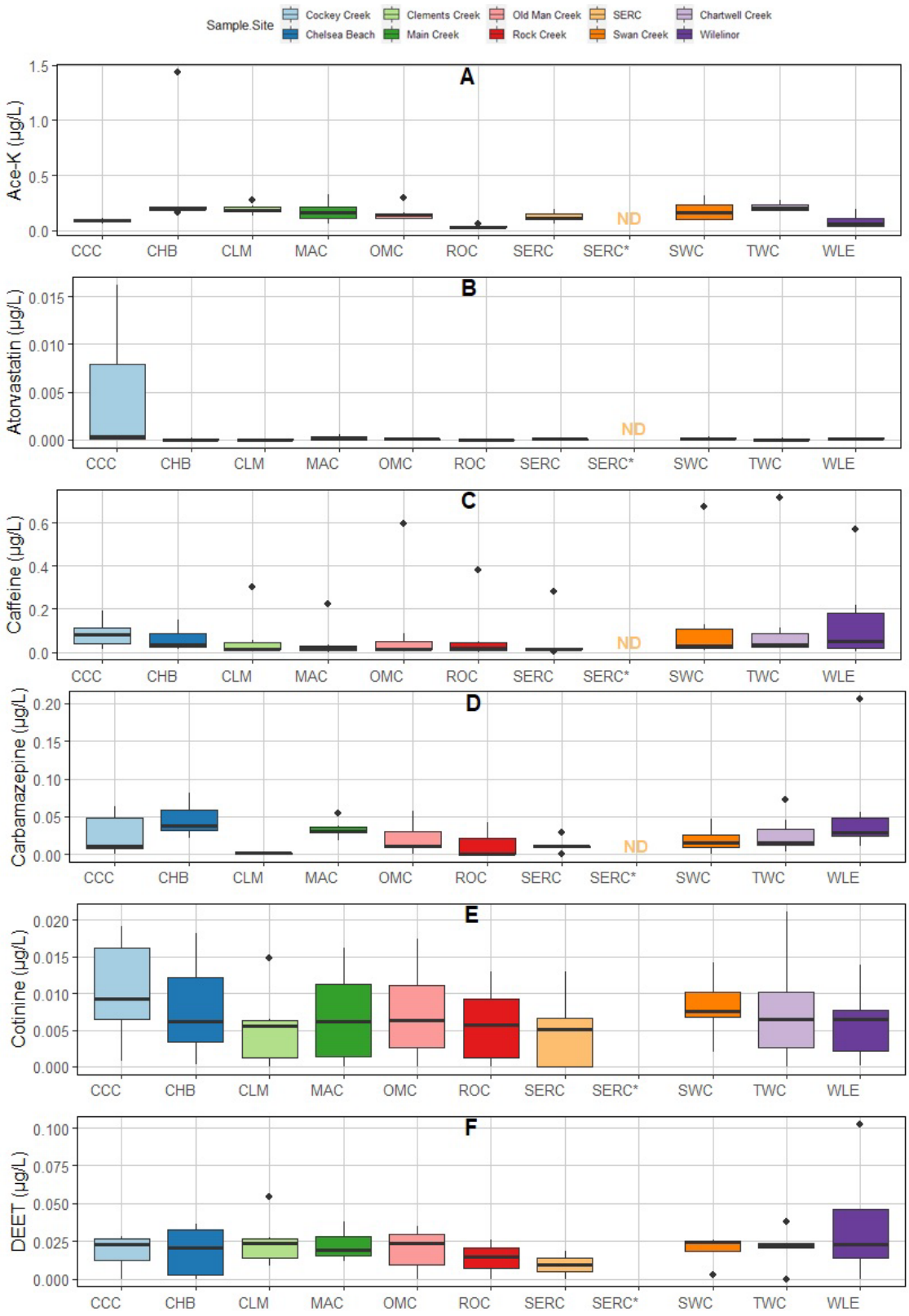
The distances between the sample site and the closest septic system varied from 32 m to 309 m. The median distance between the sample site and all septics in the catchment ranged from 302 to 1125 m. The size of the drainage area did not correlate with the minimum septic distance, though drainage area and median septic distance did correlate. Generally, larger catchments had a further median septic distance. The control sites (SERC and Rock Creek) had the largest minimum distance due to the general lack of septic systems.

The intended sampling location within the Smithsonian Environmental Research Center (SERC) was inaccessible during the spring of 2021 due to COVID-19 precautions taken by Smithsonian Institution. An alternative site within SERC was sampled for the period of the present study. Following data analysis unforeseen pollution was discovered in the alternative site sourced from agricultural runoff sourced outside of SERC. This unforeseen compilation resulted in outside contamination. In order to achieve the pristine sampling conditions (no human or agricultural waste pollution) that this study was designed to include SERC data from the intended site (SERC-110) watershed is used in all data reporting and statistical analysis in the remainder of this chapter. Data from the intended site chapter was sourced from Dr. Katie Martin during her monthly data collection between October 2016 and November 2017. Sampling and analysis methods are identical to methods outlined in chapter 2, except for some analysis optimization vis-à-vis reduction of LC-MS/MS runtime and reduction of sample amount needed for analysis. A full description of the methods used by Dr. Martin can be found in her thesis titled Characterization of Septic System Wastewater And Municipal Solid Waste Landfill Leachate, held by the University of Maryland College Park.

*3.3.2 Presence and distribution of PPCP/AS among study streams*

Ace-K, sucralose, caffeine, cotinine, and sulfamethoxazole were the most frequently detected compounds (100%, 94%, 97%, 88%, and 81%, respectively) in all the study streams

during the study period. In contrast, acetaminophen and diclofenac (3% and 2%) were the least commonly detected. The highest concentrations detected were sucralose (6.58 μg/L), Ace-K (1.433 μg/L), caffeine (0.71 μg/L) and ibuprofen (0.31 μg/L); whereas atorvastatin (0.016 μg/L) and cotinine (0.021 μg/L) were found in lower concentrations.


Sample.Site
Cockey Creek
Chelsea Beach
Clements Creek
Main Creek
Old Man Creek
Rock Creek
SERC
Swan Creek
Chartwell Creek
Wilelinor
A
Ace-K (µg/L)
B
Atorvastatin (µg/L)
C
Caffeine (µg/L)
D
Carbamazepine (µg/L)
E
Cotinine (µg/L)
F
DEET (µg/L)
ND
CCC
CHB
CLM
MAC
OMC
ROC
SERC
SERC*
SWC
TWC
WLE

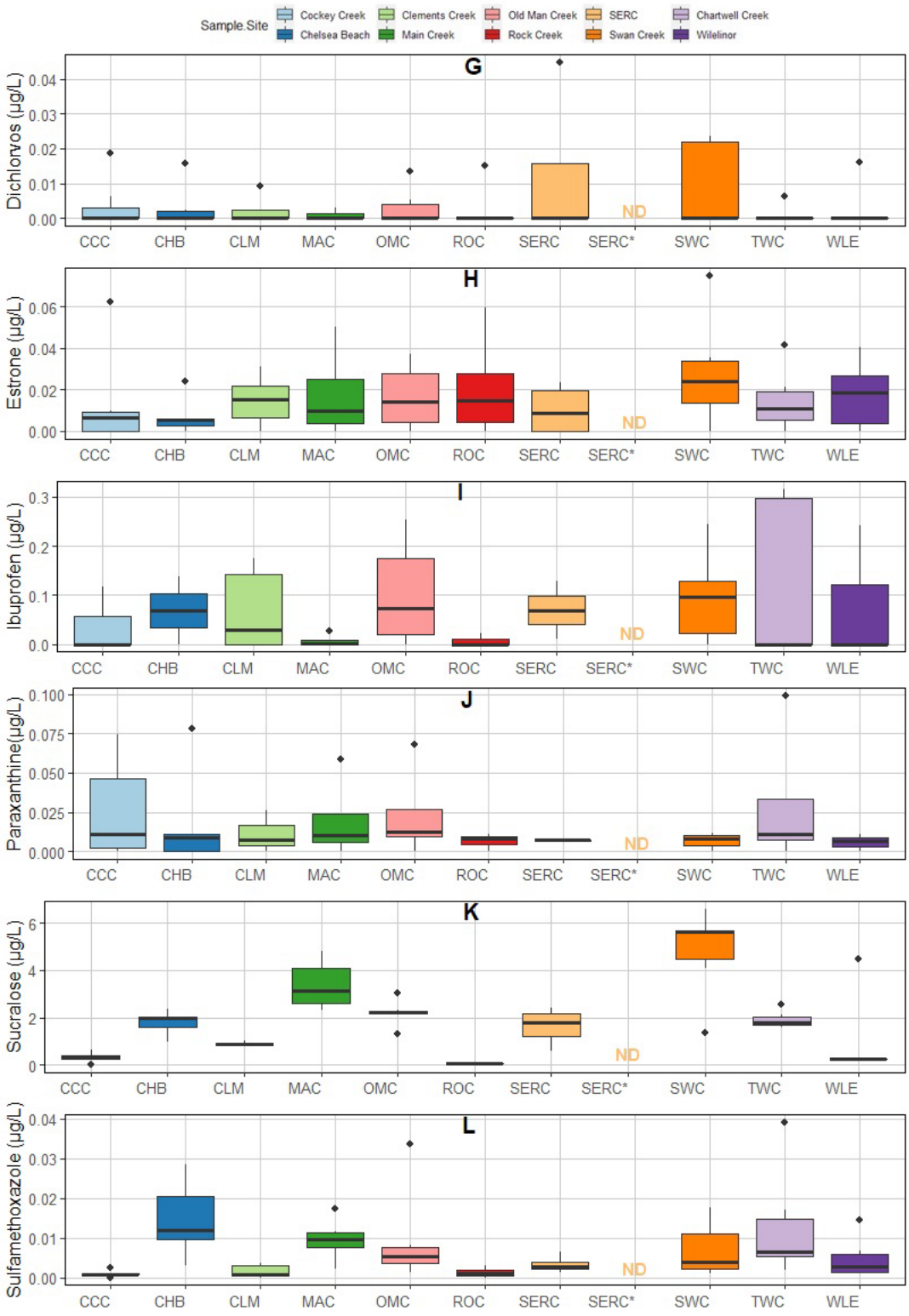



**Figure 10 PPCP & AS concentrations during monthly sampling events, (A–L) Site-specific concentrations**

Note: Boxes represent interquartile ranges (IQR) of concentrations of individual PPCPs. Lines within boxes represent median concentrations. Whiskers extend to the minimum and maximum concentrations, up to 1.5 times the IQR from each box. SERC intended site is labeled SERC*, cotinine & DEET were not sampled at the intended site.

Chelsea Beach had the highest overall Ace-K with a mean of 0.368 µg/L (Figure 10A). Rock Creek had the lowest average Ace-K concentrations (0.035 µg/L) and the lowest average sucralose concentrations (0.069 µg/L).

Swan Creek had the highest combined PPCP and AS values (32.19 µg/L, Appendix A) with the majority sourced from artificial sweeteners. While the Creek had the smallest catchment of all those studied (Table 7) and a low septic density, contaminant pollution was extremely prevalent. Swan Creek was the only site in an industrial area with a gas station, concrete supplier, and coal powered powerplant in close proximity. In addition to industrial waste, after the multi-month sampling was completed it was discovered that Swan Creek received additional contamination from dredged material from Baltimore Harbor. Maryland Port Administration maintains the Swan Creek Conservation Area and the land adjacent to it, the site of the dredge material is referred to as Cox Creek Dredged Material Containment Facility DMCF. The dredge material is highly contaminated with volatile organic compounds, petroleum constituents and heavy metals [Anna Gillmor et al., 2017; Knauff, 2020]. The contaminated dredge material is the proposed cause of the high contamination values in Swan Creek. Swan Creek data will be displayed in this chapter's figures but excluded from statistical analysis due to the contamination from the dredge material outside this study's scope.

Of the sample sites in a residential area Main Creek had the highest combined PPCP and AS values (22.37 µg/L, Appendix A). Main Creek had a relatively small catchment (Table 7) but the highest septic density. The drainage area is nearly 100% residential aside from a baseball diamond. Main Creek also has the shortest distance to its closest septic system.

Overall, Chartwell Creek has the highest total PPCP concentrations, 15% higher than the subsequent highest total PPCP concentrations found in Old Man Creek. Like Main Creek the catchment is entirely residential. The site also has the highest septic count in the largest drainage area giving it a moderately high septic density. Despite the high septic count and septic density, on average the septic tanks in this site are the furthest away. The high PPCP load correlates strongly with the septic count.

In contrast, Rock Creek and SERC (sampled site) had the lowest total PPCP concentrations (0.77 μg/L;0.71 μg/L); both of these sites were in areas with the lowest septic system density (Figure 9A, Table 7). Rock Creek drains a predominantly urban catchment, has the highest rate of imperviousness, but the catchment is almost entirely sewered. Rock Creek also had the lowest total AS concentration (0.457 μg/L). The sampled SERC site is located in a predominantly forested catchment with only one septic system, but with some agricultural activity. In the SERC* site sampled by Dr. Martin, all compounds were below detection limits for the current LC-MS/MS method. These non-detects are indicative of extremely low PPCP and as concentrations. This site had no agricultural influences.

### *3.3.3 Temporal distribution of PPCP and AS*

#### *3.3.3.1 Seasonal Distribution During Base Flow Conditions*

The concentrations of the most frequently detected compounds (Ace-K, sucralose, caffeine, and sulfamethoxazole) were highest in spring summer, summer, and spring, respectively.

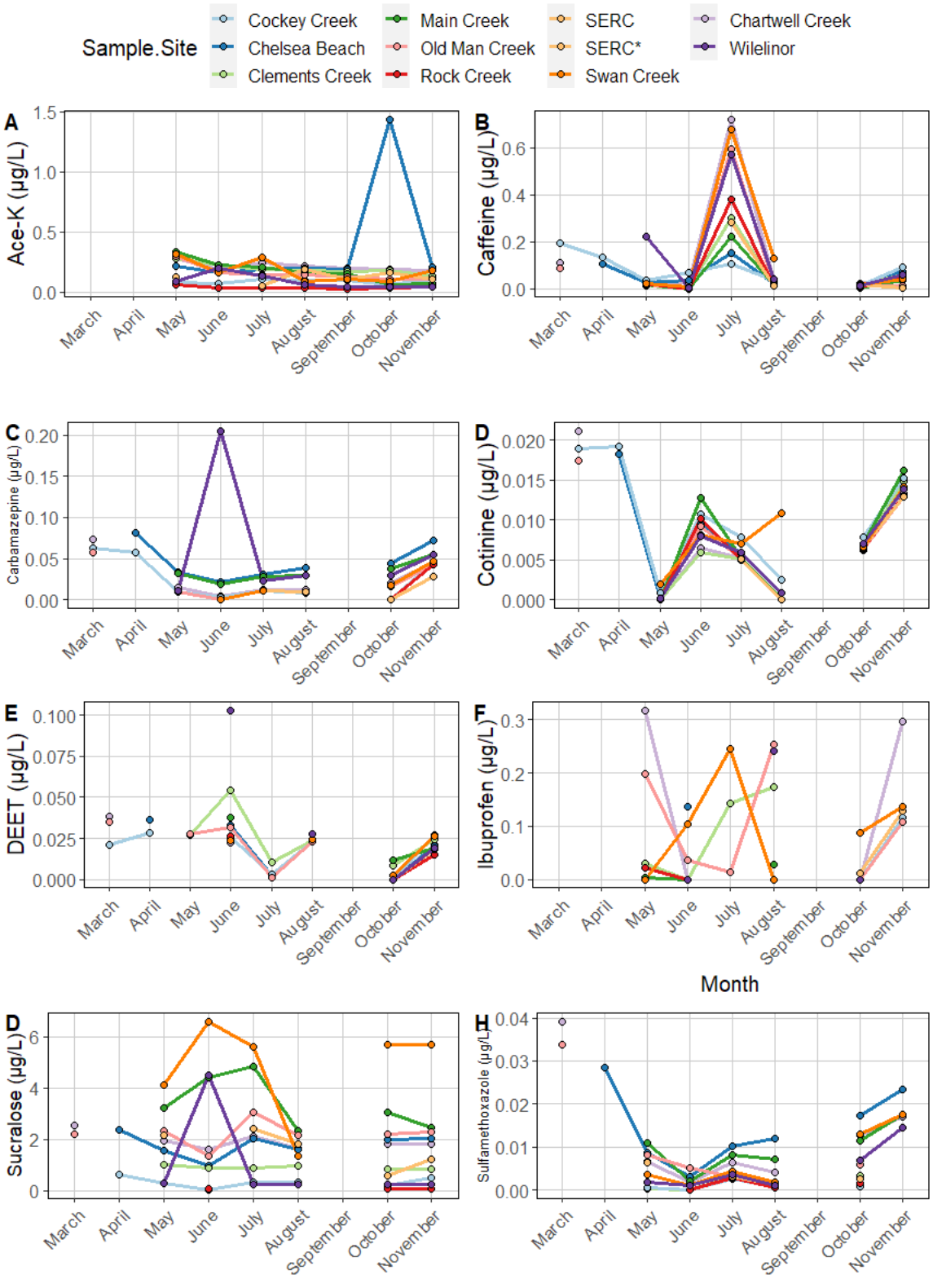



**Figure 11 Monthly concentrations of select PPCP and AS in water samples, (A-H) Site-specific concentrations**

Compounds that exhibited the least variability in concentrations throughout the seasons include atorvastatin ($2.43e^{-5}$– 0.016 µg/L), cotinine ($9.51e^{-6}$ – 0.021 µg/L), and sulfamethoxazole ($4.28e^{-4}$ – 0.039 µg/L). Both cotinine and sulfamethoxazole trended higher in the spring. Of all compounds atorvastatin varied the least. Caffeine was consistently the highest during the summer at Old Man Creek, Chartwell Creek, Old Man Creek and Clements Creek (Figure 11B). Chelsea Beach and Cocky Creek exhibited the strongest seasonal patterns with summer having the highest overall concentrations (Figure 12B). High early spring concentrations of caffeine can be observed at both Chelsea Beach, Cocky Creek and Wilelinor but overall summer caffeine concentrations are the highest. These sites also exhibited great variation in ibuprofen, but the variation does not appear to be influenced by season ($r_s \approx -0.3$). Late fall and early spring also increased most PPCP (Figure 11).

Concentrations varied over an order of magnitude across sampling events for both artificial sweeteners, Ace-K (0.025– 1.43 µg/L) and sucralose (0.026– 6.56 µg/L). Sucralose values trended higher during early summer at all sites as well as late fall at Cocky Creek, Clements Creek, Swan Creek, SERC (Figure 11D). The results of Spearman's rank correlations analysis showed that season had a statistically significant correlation with Ace-K ($r_s \approx -0.3$), cotinine ($r_s \approx 0.3$), DEET ($r_s \approx 0.6$), estrone ($r_s \approx -0.3$), and ibuprofen ($r_s \approx -0.3$), with DEET having the strongest overall correlation (p-value $\geq 6.4e^{-6}$).

*3.3.3.2 Distribution During Stormflow Conditions*

Stormflow samples were collected using an ISCO automated sampler during three storm events at Chartwell Creek. An environmental blank was also collected during the June 10th and September 22nd sampling events (Appendix A). Ace-K was not measured during these sampling events, nutrients were only measured during the June 10th storm. These samples were used to

construct a "pollutograph", visualizing PPCP and AS concentrations throughout the storm. These graphs will inform the transportation and concentration of contaminants during a stormflow event.

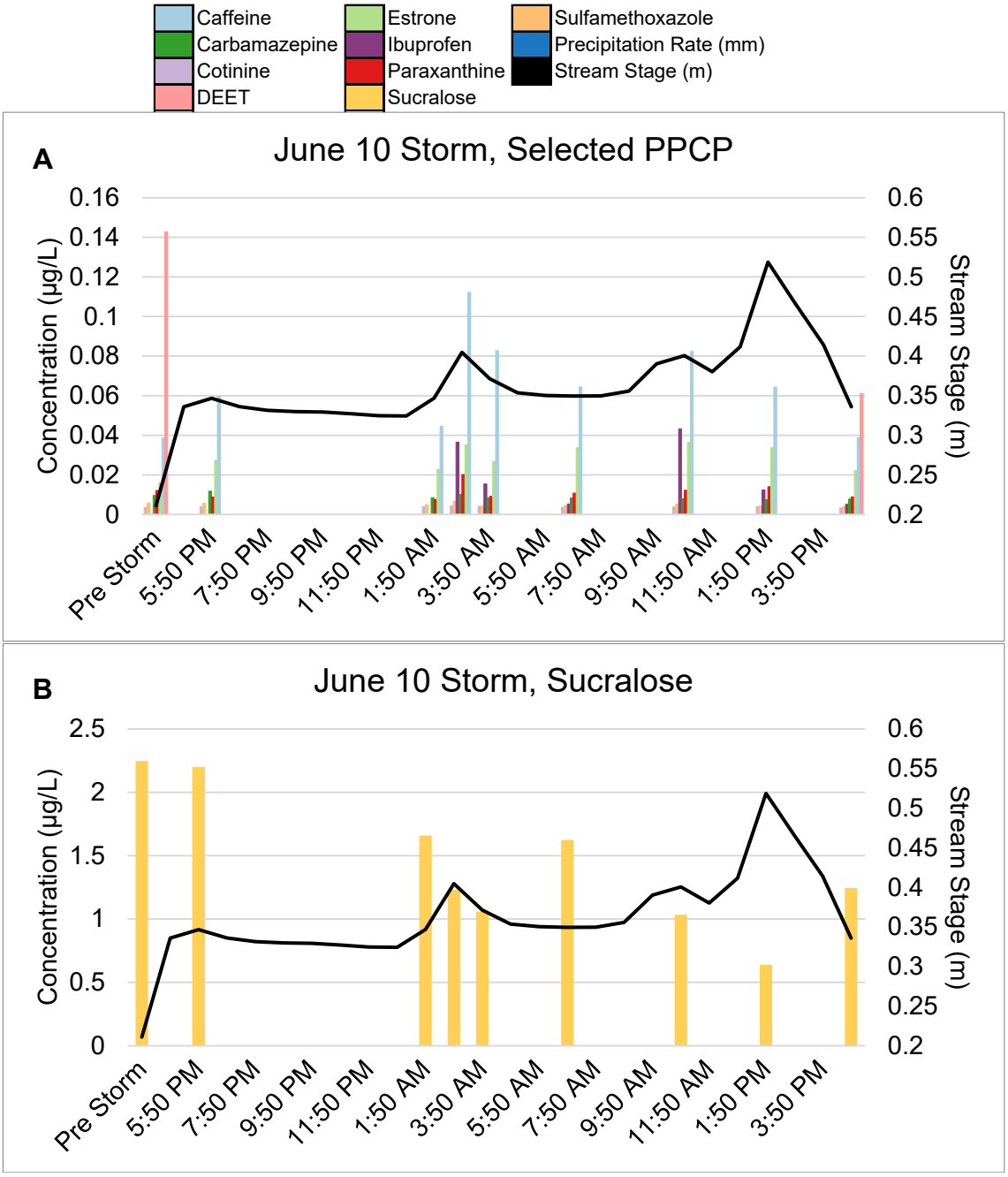



**Figure 12 June 10th storm, observed stream stage, precipitation, and concentrations of target PPCP and AS**

Note: Samples were collected for contaminants analysis before the storm, 5:50 p.m., 1:50 a.m., 2:50 a.m. (June 11th), 3:50 a.m. (June 11th), 6:50 a.m. (June 11th), 10:50 a.m. (June 11th), 1:50 pm (June 11th), and post-storm (June 11th)

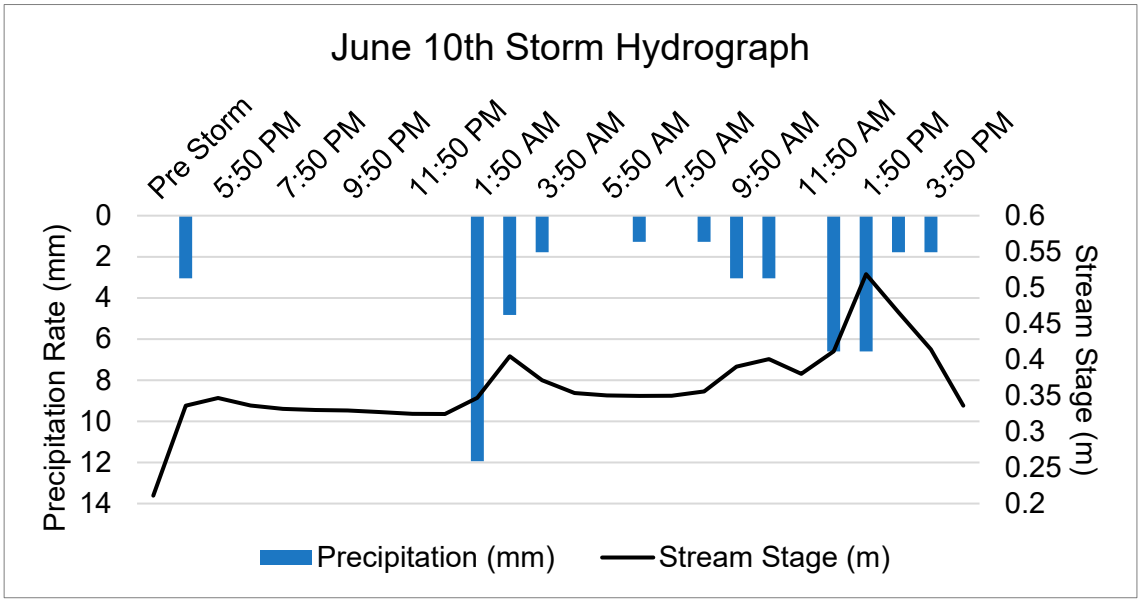



**Figure 13 June 10th storm, observed stream stage, precipitation, and concentrations of target PPCP & AS**

Note: Samples were collected for contaminants analysis before the storm, 5:50 p.m., 1:50 a.m., 2:50 a.m. (June 11th), 3:50 a.m. (June 11th), 6:50 a.m. (June 11th), 10:50 a.m. (June 11th), 1:50 pm (June 11th), and post-storm (June 11th)

The June 10th storm was the shortest rain event of the three sampled and had the smallest storm volume (Figure 12 & 13). Cotinine, atorvastatin, estrone, and sulfamethoxazole concentrations mirrored the stream stage, with concentrations peaking between 11 and 2 p.m. Sucralose concentrations were highest at the start of the storm. Caffeine, paraxanthine, and carbamazepine concentrations peaked during the first stream stage peak at 3:50 a.m. DEET was only recorded during pre and post-storm measurements. Stream stage measurements and precipitation rate closely mirrored each other.

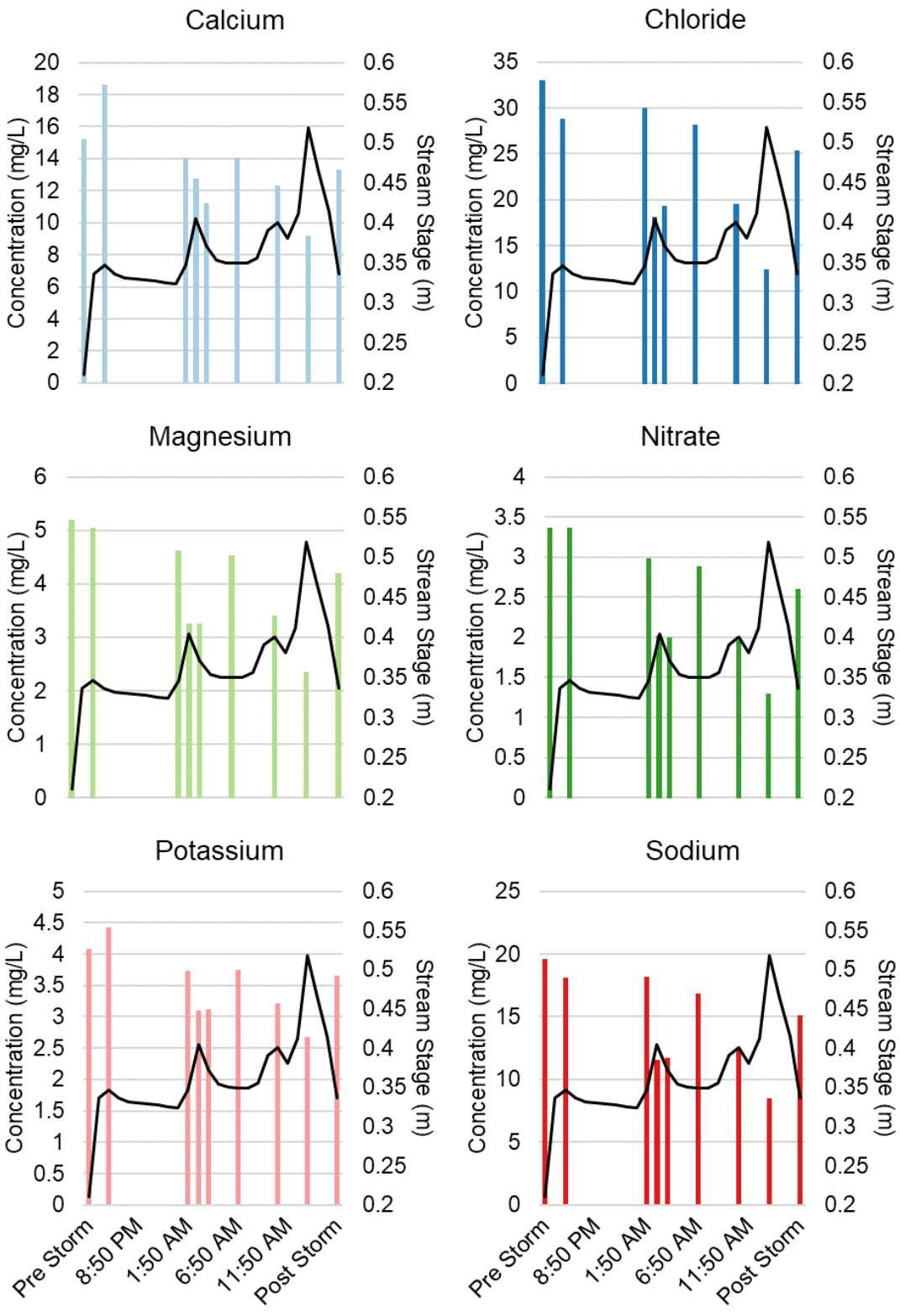



**Figure 14 June 10th storm, observed stream stage, and major ions concentration**

Note: Samples were collected for contaminants analysis before the storm, 5:50 p.m., 1:50 a.m., 2:50 a.m. (June 11th), 3:50 a.m. (June 11th), 6:50 a.m. (June 11th), 10:50 a.m. (June 11th), 1:50 pm (June 11th), and post-storm (June 11th)

Major ion concentrations remained consistent in relation to each other, but overall concentrations decreased as the storm event continued (Figure 14). Major ion concentrations did not return to their pre-storm levels during the post-storm sampling period (approximately 3 hours after the last rain). Pre-storm values are the highest overall with concentration recovering post storm. Major ion concentrations were at their lowest during periods of increased precipitation rates (Figure 13) as observed between midnight and 3 a.m. and between 10 a.m. and 2 p.m.

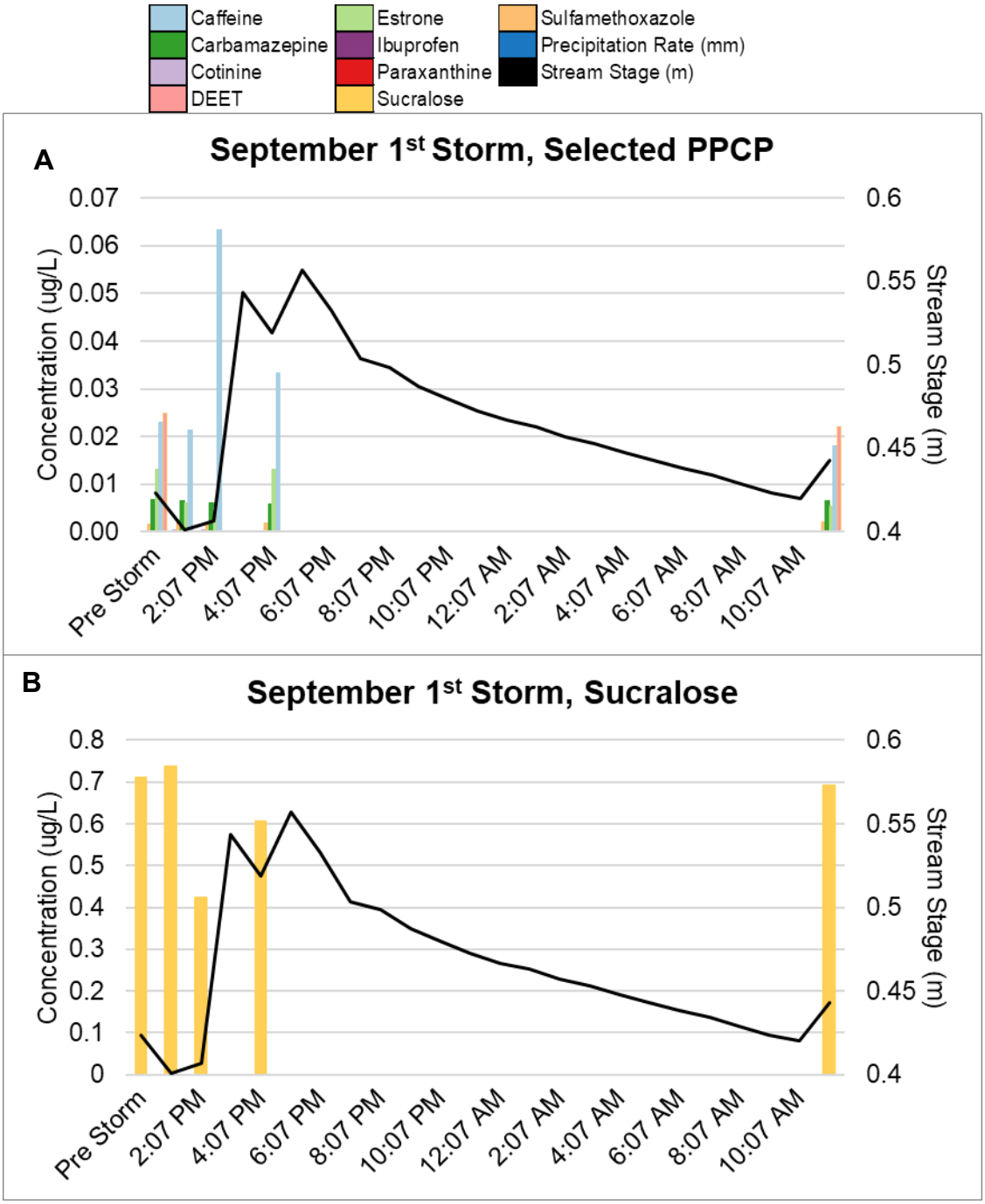



**Figure 15 September 1st storm, observed stream stage, precipitation, and concentrations of target analytes**

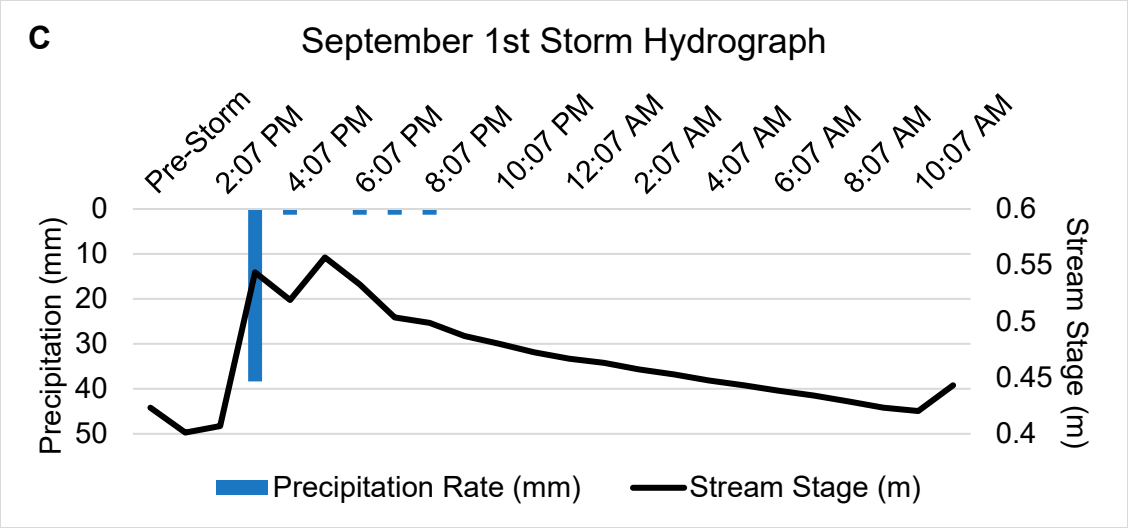
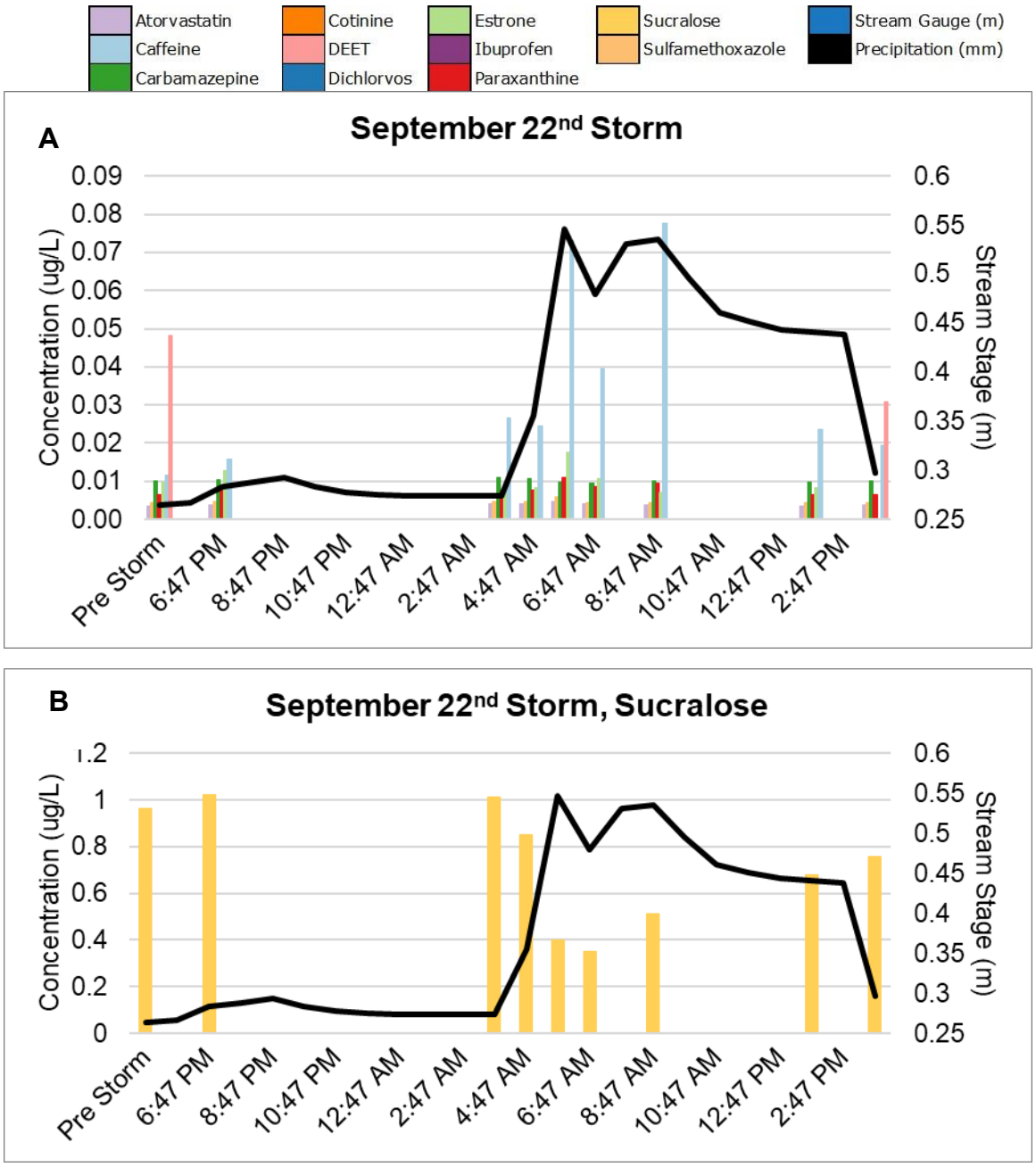



***Figure 15 September 1st storm, observed stream stage, precipitation, and concentrations of target analytes***

Note: Samples were collected for contaminants analysis before the storm, 1:07 p.m., 2:07 p.m., 4:07 p.m., and post-storm (September 2nd)

The September 1st rain event was the largest of the storms sampled. Carbamazepine, caffeine, and sulfamethoxazole all peaked in the early portions of the storm as the stream stage rose (Figure 15 A, B). These compounds also returned to their pre-storm levels following the storm. Estrone and sucralose were at their lowest concentrations during the initial peak of the storm, after which they recovered and remained elevated during the second peak. DEET concentrations are only detectable during pre and post-storm sampling events. Precipitation and stream stage mirror each other with a slight delay in the storm stage initial peak in this short intense rain event (Figure 15C).




Note: Samples were collected for contaminants analysis before the storm, 6:47 a.m., 3:47 a.m. (September 23rd), 4:47 a.m. (September 23rd), 5:47 a.m. (September 23rd), 6:47 a.m. (September 23rd), 8:47 a.m. (September 23rd), 1:47 p.m. (September 23rd), and post-storm

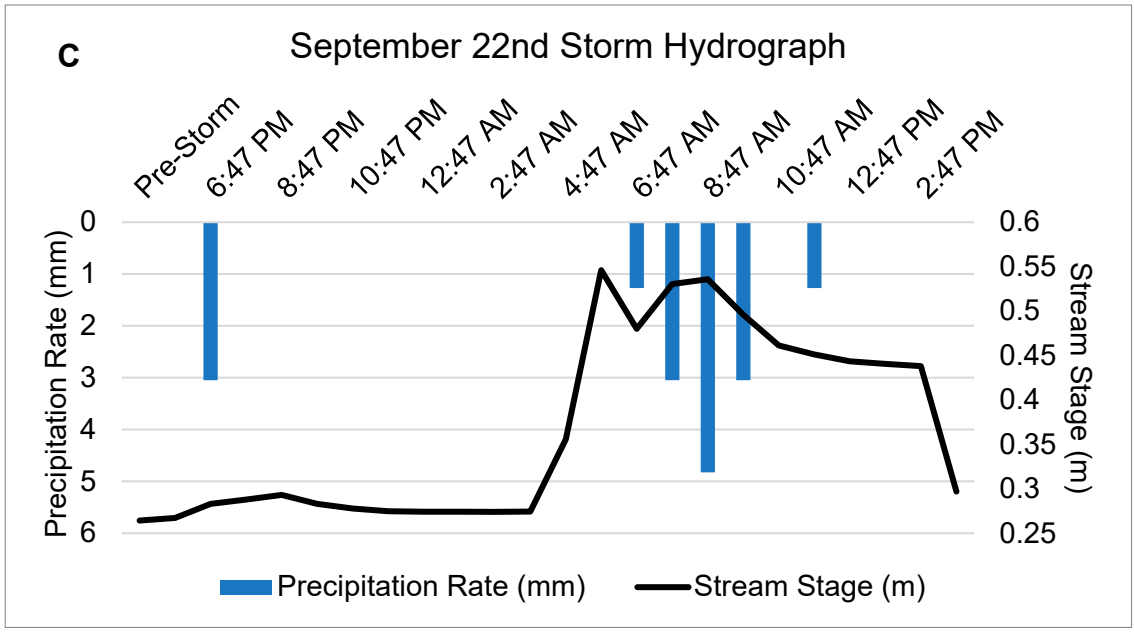



**Figure 16 September 22nd storm, observed stream stage, precipitation, and concentrations of target analytes**

The September 22nd storm was the longest studied storm (Figure 16). Caffeine and cotinine both peaked when the stream stage was at its highest. Carbamazepine, estrone, paraxanthine, sulfamethoxazole, and sucralose reached their highest concentrations, aside from pre-storm values, shortly before the stream stage increased between 2 and 5 a.m. DEET was only observed in pre and post-storm samples. The stream stage and precipitation mirrored each other during the latter half of the storm with precipitation rate proceeding any changes in stream stage by 3 hours.

The storms in this study experienced flashy hydrographs as expected in small headwater catchments with stream stage returning to pre-storm levels in 12 hours or less. Chartwell Creek has a wide flood channel that would flood when the stream stage exceeded ~0.5 m. The flow was likely higher during these events but could not be measured with the available equipment. Low rainfall during the June 10th storm resulted in several small peaks compared to subsequent storms. Across all storms, contaminant concentrations exhibited broad pollutant hydrographs

("pollutographs"). During the first peak of the June storm (midnight to 4 a.m.), 42% of in-storm pollutants were recorded. Strom peak analysis was not conducted during the September storm due to a lack of recorded sampling during the later halves of the hydrograph. During the September 22nd storm first peak (3 a.m. to 7 a.m.), 54% of in-storm pollutants were recorded.

### *3.3.4 Potential predictors of PPCP/AS contamination in urban headwater streams*

#### *3.3.4.1 PPCP/AS and Geophysical Characteristics of the Stream Catchments*

A primary goal of this study was to examine the impact human waste sourced from septic systems has on PPCP and AS contamination in headwater streams. To do this, the sum of each site's multi-month PPCP and AS concentrations were compared to several geographic parameters. Using Arc GIS, septic density, distance from the sample site to the closest septic system (minimum septic distance), the median distance from the sample site to septic systems in the catchment and land use were calculated and compared to total PPCP and AS concentrations on a site by site basis to determine overall trends.

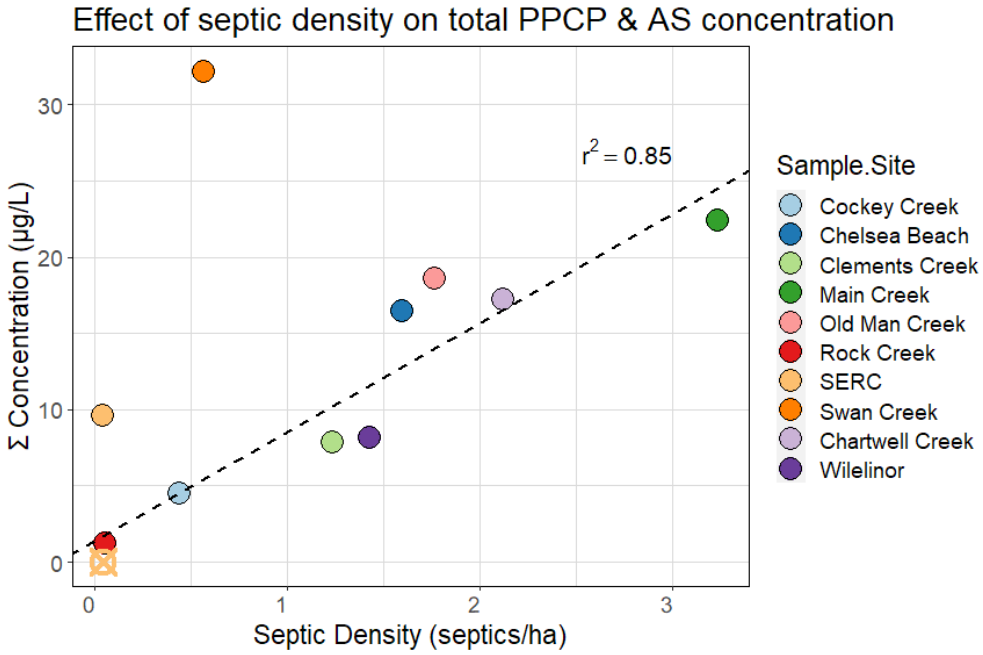



**Figure 17 Total PPCP & AS Concentration vs Septic Density**

Note: Trendline excludes outliers (SERC & Swan Creek). Data from the intended SERC* sampling site collected by Dr. Martin is represented by a ⊗ symbol with a light orange color

A positive monotonic linear relationship between total PPCP and AS concentrations and septic density can be observed (Figure 17). The only site far from the regression line was Swan Creek, probably because of contamination from dredging material. The sampled SERC site was also far from the regression line, however, the intended site SERC* sampled by Dr. Martin followed the trend, with the lowest concentration. The results of Spearman's rank correlations analysis showed septic density and total PPCP and AS concentration had a statistically significant correlation ($r_s \approx 0.9$, p-value=0).

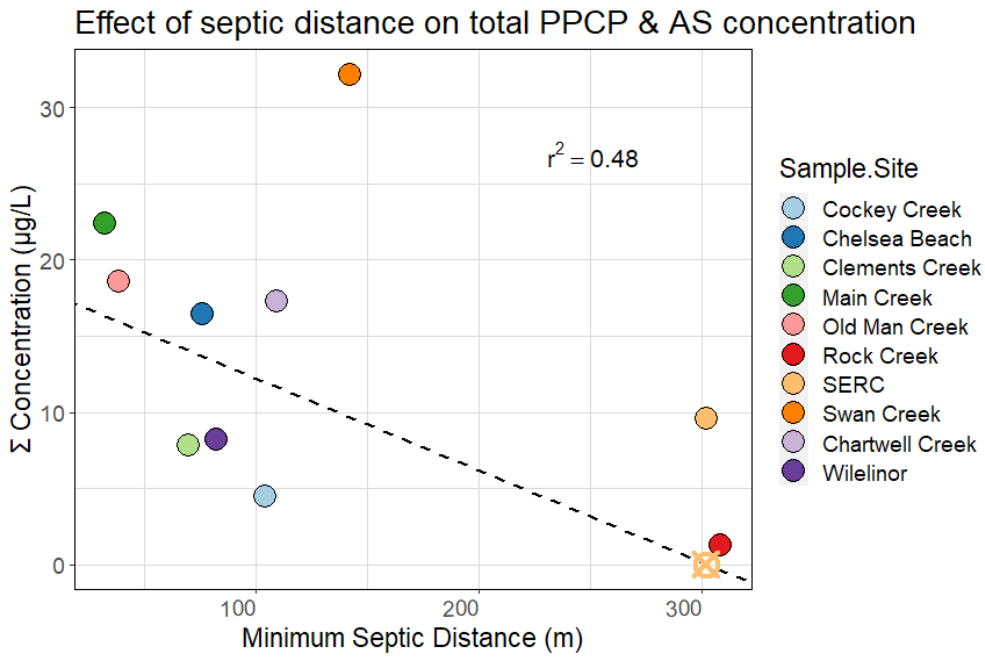



**Figure 18 Total PPCP & AS Concentration vs. Minimum Septic Distance**

Note: Trendline excludes outliers (SERC & Swan Creek). Data from the intended SERC* sampling site collected by Dr. Martin is represented by a ⊗ symbol with a light orange color

A Spearman's rank correlation coefficient was computed to assess the relationship between total PPCP and AS concentrations in baseflow and the minimum distance between the stream sampling site and septic systems in the catchment which showed a significant negative

relationship (Figure 18) ($r_s \approx -0.7$, p-value=$1.9e^{-11}$). There was a negative linear correlation between the two variables as well ($r^2= 0.48$, n=7).

The relationship between total PPCP and AS concentrations and distance between the sample site and the closest septic system is generally negative. Sites SERC* & Rock Creek, which have the largest distance to first septic system also had the lowest total PPCP & AS concentrations. The results of Spearman's rank correlations analysis showed that minimum septic distance and total PPCP and AS concentration had a statistically significant correlation ($r_s \approx -0.7$, p-value=$1.9e^{-11}$).

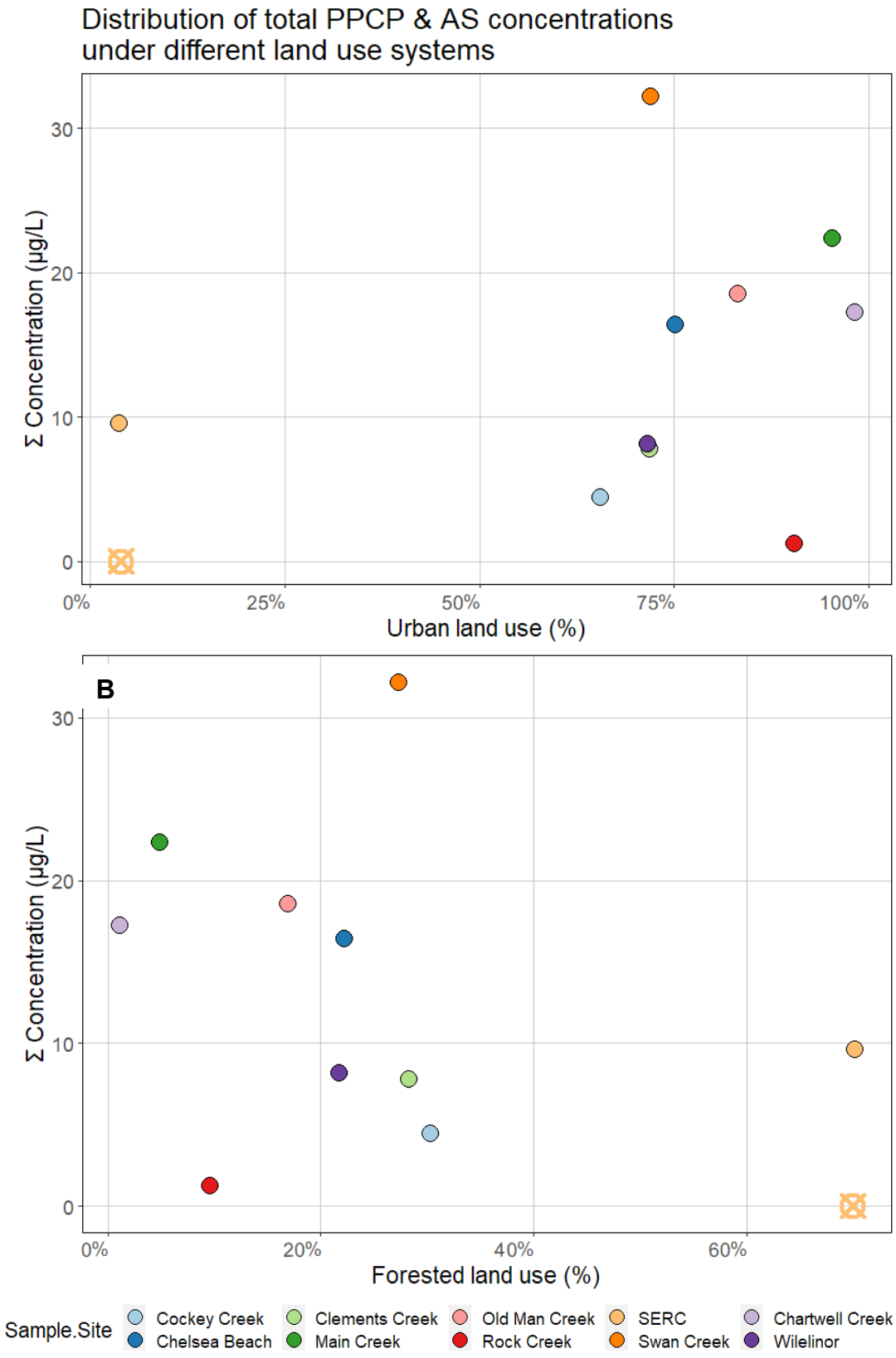


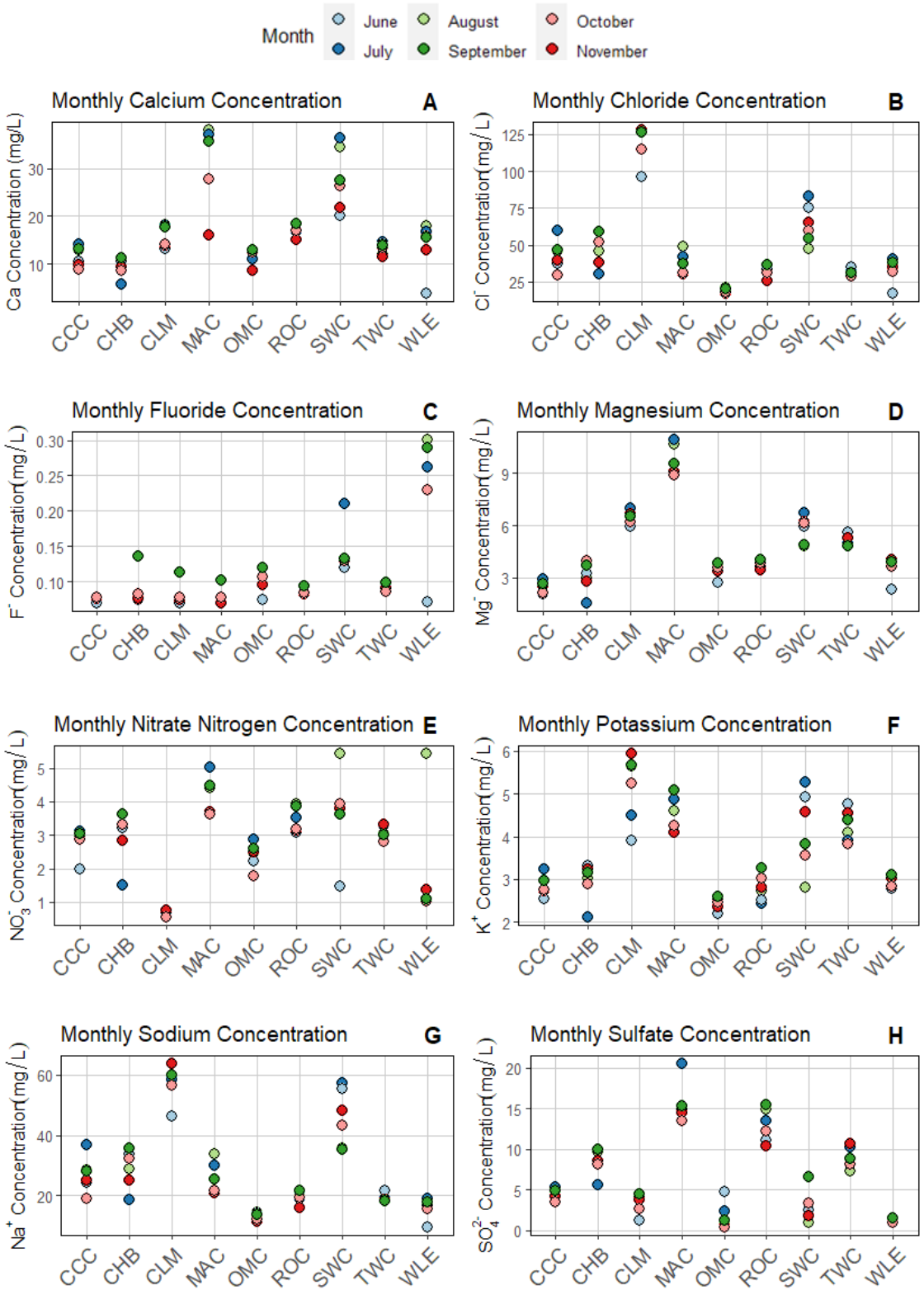

**Figure 19 Total PPCP/AS concentrations vs selected land use**

Note: Trendline excludes outliers (SERC & Swan Creek). Data from the intended SERC* sampling site collected by Dr. Martin is represented by a ⊗ symbol with a light orange color

Land use does not show any linear correlations with total PPCP/AS concentrations. This lack of correlation was also reflected in the Spearman's Rank Correlation. Generally, higher urban land use had higher total PPCP/AS concentrations with the exception of Rock Creek which has low septic density (Figure 19B).

*3.3.4.2 PPCP/AS and Chemical Characteristics of the Stream Catchments*

In this study the only traditional indicator of wastewater measured was nitrate due to analytical and fiscal limitations. In addition to nitrate, calcium, chloride, fluoride, magnesium, nitrogen, potassium, sodium and sulfate were measured as well.




**Fi**

**Figure 20 Major ion concentrations during monthly sampling events, (A–H)**

Chloride was the dominant ion during all sampling events, with concentrations ranging from 16.8 to 128.1 mg/L, with mean concentrations of 49.86 mg/L (Figure 20). SERC nutrient water samples were not analyzed due to an error in sample collection but $NO_3^-$-$NO_2^-$ values from the intended SERC* site are displayed in figure 20. During Dr. Martin's 2016 to 2017 sampling, the following average major ion concentrations were recorded for 8 mg/L for chloride, 0.15 N mg/L for nitrate, and 27 mg/L for sulfate [Martin, 2021].

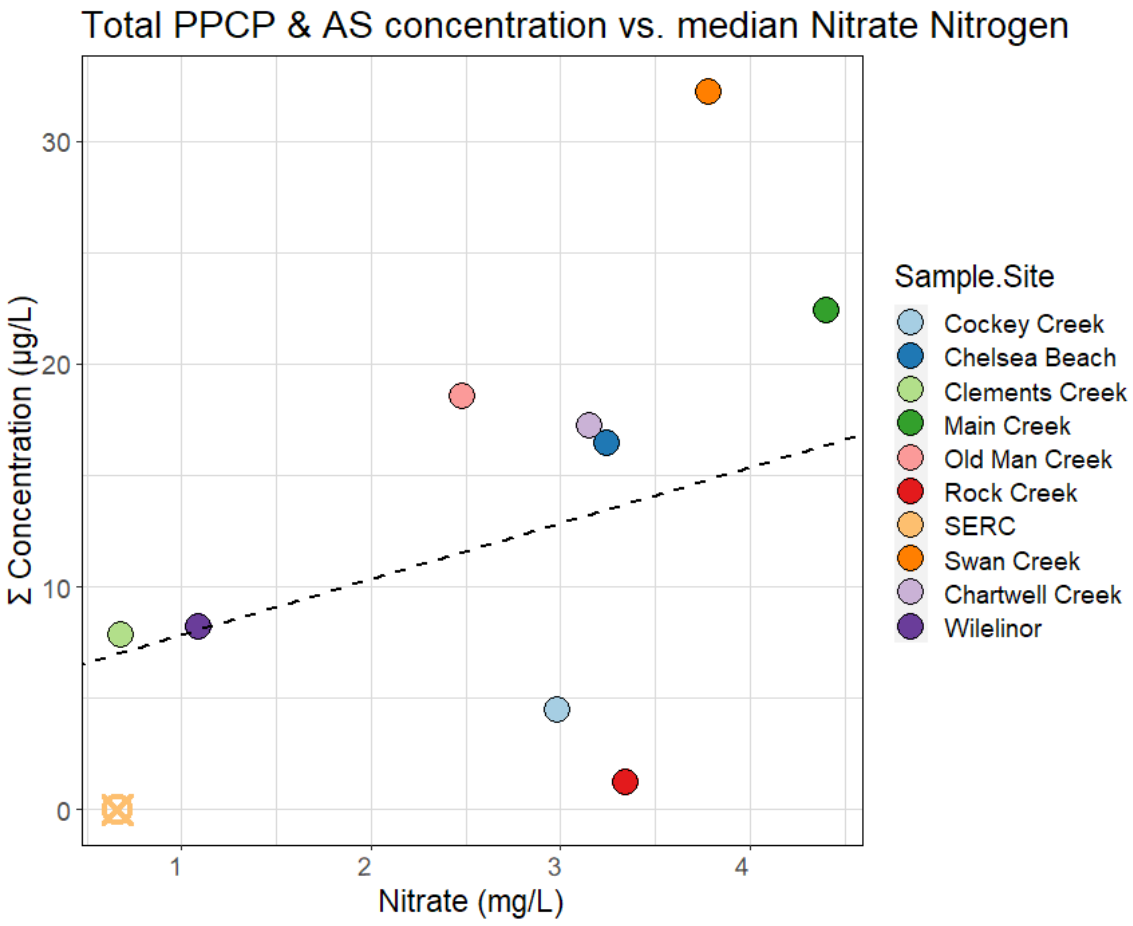



**Figure 22 Total PPCP & AS Concentration vs. Nitrate**

Note: Note: Trendline excludes outliers (SERC & Swan Creek). Data from the intended SERC* sampling site collected by Dr. Martin is represented by a ⊗ symbol with a light orange color

There was a moderate positive linear relationship between total PPCP and AS concentration and nitrate (Figure 22) ($r^2$= 0.17, n=7
). This trend was not observed at Rock Creek, which acted as a suburban control site as it was in a high population area that depended primarily on a sewer system. The Spearman's rank correlation between total contaminant concentration and nitrate concentrations was not significant (p-value= 0.38).

## 3.4 Discussion

Results from the PPCP and AS measured at each site indicate that contamination is commonplace in the studied Maryland headwater streams. Contaminants with a high detection frequency did not necessarily correlate with a high observed concentration; for example, ibuprofen has one of the highest detected concentrations but a low detection frequency (33%). However, artificial sweeteners (Ace-K 100%, sucralose 94%) had high detection levels and high concentrations. This study showed a low detection frequency of acetaminophen (3%), which is not consistent with previous studies [Veach and Bernot, 2011; Cantwell et al., 2018]. This lack of detection may be due to different sample processing methods as well as varied sources/treatments of waste [Sun et al., 2016]. Variation in detection frequency and concentration measured in previous studies may also indicate differences in stream discharge, human waste input, PPCP and AS usage, and degradation pathways in varied environments [Wilkinson et al., 2022].

**Table 8 Select PPCP and AS concentrations reported in previous studies**

| Site | Catchment Size (ha) | Population Density (persons per km$^2$) | Sulfamethoxazole (µg/L) |
|---|---|---|---|
| Northeast Anacostia River, Washington, DC | 44000 | ~2000 | NA |
| Confluence of Mohawk River & Upper Hudson River, NY | Unreported | NA | 0.012 |
| Swift Creek near Apex, NC | 5439 | 830 | 0.047 |
| Obed River at Potter Ford near Crossville, TN | 27820 | 27 | 0.047 |
| This study (site averages) | 12-319 | 680 | 0.007 |

| Site | Caffeine (µg/L) | Sucralose (µg/L) | Carbamazepine (µg/L) | Citation |
|---|---|---|---|---|
| Northeast Anacostia River, Washington, DC | ~0.04 | NA | ~0.03 | Shala & Foster [2010] |
| Confluence of Mohawk River & Upper Hudson River, NY | 0.070 | 0.870 | 0.0039 | Cantwell et al., [2018] |
| Swift Creek near Apex, NC | 0.084 | NA | <0.011 | Bradly et al., [2016] |
| Obed River at Potter Ford near Crossville, TN | 0.110 | NA | 0.0182 | Bradly et al., [2019] |
| This study (site averages) | 0.096 | 1.881 | 0.0288 | This study |

Pharmaceutical concentrations in this study were comparable to concentration ranges previously measured in US streams (Table 8). Caffeine concentrations were lower than those found in Cantwell et al., [2018] which may be attributed to larger inputs in the larger watersheds studied (Hudson River Estuary and New York Harbor) or to differences in ratio of treated to untreated waste. Previously, pharmaceutical concentrations in streams were thought to be

connected with areas of higher population densities [Ellis, 2006]; the present study supports Bunch and Bernot's [2010] conclusion that non-point pollution originating from septic tanks and aging infrastructure is a more significant driver of PPCP pollution. The Obed River in Crossville, TN has the lowest population density of all sites in Table 8, however their PPCP and AS pollution is comparable, indicating that population is not a major driver of PPCP and AS pollution. The Anne Arundel County sample sites were significantly smaller, less urban and less populous, with the exception of Oben River, TN, catchments than those found in Table 8 but had comparable concentrations. The present study focused on headwater streams catchments; headwaters streams are more sensitive to natural and anthropogenic disturbances such as changes in riparian buffer and chemical inputs [MacDonald and Coe, 2007]. Understanding the impact of human waste on headwater stream contamination is an important factor to understand overall water quality downstream as headwater streams make up the majority share of world's stream length [Wohl, 2017].

*3.4.1 Hydrological influences on headwater stream contamination*

PPCP and AS contamination in headwater streams is driven by several factors, including wastewater treatment type and microbial activity in groundwater [Underwood et al., 2011; Withers et al., 2011; Schenck et al., 2015]. In surface waters in general, the hydrological conditions are also important, e.g. Reckhow et al., [2014]; Yuan et al., [2020]; Zhao et al., [2021]. In the present study, the slight negative correlation between total PPCP and AS concentrations and drainage area ($r_s$= -0.24, p-value= 0.044) suggests that streams draining small catchments may be more susceptible to PPCP and AS contamination than larger catchments. With a small drainage area, the actions of a small community can have large impacts on the watershed. For example a catchment saturated with antimicrobials sourced from wastewater may be unable to degrade PPCP, AS and nutrients such as nitrogen and phosphorus due to a soil

microbial community, which assists in degradation and transformation, that has been destroyed. Likewise, the impact of sewer leaks or aging septic systems can be disproportionally large in small catchments. Future studies should consider the age and maintenance of septic systems in the study catchments to determine the cause of this relationship.

Burns et al. [2011] suggested the incorporation of stream depth and flow velocity in discussions about temporal variations in PPCP concentrations in stream water. Stream depth and flow velocity were intermittently measured at all sample sites as a proxy for discharge. The summer months had significantly higher PPCP and AS concentrations (Figure 11), which coincided with a 13% decline in freshwater depth and width during summer months compared to both fall and spring (Appendix A). This correlation between discharge and PPCP and AS concentrations is confirmed by Burns et al., [2011] and Cantwell et al., [ 2018], who found that periods of low discharge had higher PPCP and AS concentrations.

Hydrological dynamics did not follow baseflow actions of low flow, higher contamination load. During stormflow changes in stream depth, PPCP and AS concentrations could be observed to change with changes in stream stage (Figures 12, 13, 14). During the June and September storms, total PPCP and AS concentrations were highest during the first storm peak. This effect could be observed particularly well during the June storm, the smallest of the three storms. Thus, relatively small precipitation events can cause a first storm peak with substantial contaminant transport and rapid water quality degradation.

*3.4.2 Chemical influences on headwater stream contamination*

PPCP and AS concentrations were not significantly correlated with major ions in the studied streams. Moderate correlations were only observed between sucralose and magnesium, with $NO_3$-N. Ace-K exhibited a mild correlation with potassium which is in part linked to the

potassium in Ace-K. Total PPCP and AS concentrations showed a moderate correlation with nitrate. This trend has been shown previously by Yang et al., [2013], Gonçalves et al., [2016], and Schaider et al., [2016]. The correlation may indicate that some PPCP and AS have the same source of human waste and may be transported and degraded at similar rates. In a drain field of the septic system, pharmaceuticals such as cotinine, caffeine, DEET and ibuprofen are all removed well by sorption and the same aerobic microbial process that transforms ammonium from wastewater into nitrate [Roberts et al., 2014; Schaider et al., 2017]. Therefore, a correlation between these compounds and nitrate is expected, and it is difficult to find it in stream water because degradation has probably occurred by the time the septic effluent reaches the stream channel as surface water. Additionally, the degradation rate of contaminates and the effectiveness of nitrification are likely to vary greatly according to catchment characteristics such as soil type and stream physio-chemical variables oxygenation rate [Wherry et al., 2021].

Other compounds such as sulfamethoxazole work against a septic system's drain field's microbial process and degradation ability. Sulfamethoxazole is an antibiotic that has been shown to have a negative effect on the microbial community found in a drain field that assists in PPCP and nutrient transformation and degradation. [Underwood et al., 2011]. The presence of sulfamethoxazole in soils (i.e., septic leach fields) leads to negative impacts on microbial growth, nitrate reduction activity, and abundance of nitrate-reducing bacteria *Pseudomonas sp.* and *Variovorax sp* [Underwood et al., 2011]. Stream ecosystems rely on bacterial populations to degrade excess nutrients such as nitrate.

*3.4.3 Spatial variation of PPCP and AS among sites*

A Kruskal Test and a post hoc Dunn test with Bonferroni correction were used to investigate contaminant concentrations between sites. This was explored on a compound-by-compound basis, with compounds with detection frequency less than 50% excluded. Of these

compounds, Ace-K, sucralose, and sulfamethoxazole showed significant differences across sites. When comparing Ace-K values across sites, significant differences were observed only when comparing sites to Rock Creek after the Bonferroni correction (Figure 11, p-value < 0.001). Rock Creek was significantly different regarding Ace-K probably because its catchment had the lowest septic density among all urban and suburban catchments (Figure 17). The sites that deviated from Rock Creek (Chartwell Creek, Chelsea Beach, Cockey Creek, Main Creek) did not have similar catchment characteristics, suggesting that no one catchment characteristic studied was a predicting factor for Ace-K concentration. Site-to-site sucralose concentrations in all study sites varied when compared to sites Rock Creek and Main Creek ($p < 0.001$). The deviation from Rock Creek was expected due to previously discussed factors. Sites that varied with Main Creek's (Clements Creek, Cockey Creek, Wilelinor) sucralose values all had similar imperviousness (22 to 25%), urban/suburban land use (66 to 72%), and median septic distance (540 to 757 m). The variation between sites' sulfamethoxazole values were slight and only occurred in two instances. The correlations between land use/imperviousness were not universal. These findings correlate with Bunch and Bernot, [2010] and Veach et al., [2011], which concluded that land use is not an essential factor controlling PPCP and AS concentrations. Land use cannot be used as a solitary predictor of PPCP and AS contamination sourced from human waste as it does not consider the wastewater treatment used in an area. It would be flawed to assume that urban/suburban areas only have WWTPs, and rural areas have septic systems, particularly on the East Coast, which has both a high population density and septic count.

The location of septic systems played a key role in PPCP and AS concentrations in this study. This study is one of a handful that addresses septic systems' influence on PPCP and AS concentration [Robertson et al., 2013] though this idea has been suggested by others before

[Shala and Foster, 2010; Burns et al., 2018; Wilkinson et al., 2022]. The results of this study showed a strong positive correlation ($r^2$=0.85) between total PPCP and AS concentrations and septic density (Figure 17). Ace-K, sucralose, and sulfamethoxazole concentrations increased with septic density. Sucralose and Ace-K have been suggested as indicators of domestic wastewater pollution in surface water [Van Stempvoort et al., 2013; Cantwell et al., 2018], but the present study showed that Ace-K, sucralose, and sulfamethoxazole are indicators of septic system effluent in headwaters. Both sucralose and sulfamethoxazole are hydrophilic and unlikely to be removed effectively by sorption during septic treatment. Ace-K's presence in treated waste can be attributed to its poor removal in wastewater treatment [Van Stempvoort et al., 2020] and its ubiquitous use [Buerge et al., 2009]. Ace-K concentrations have been previously reported to correlate with carbamazepine and sulfamethoxazole concentrations [Van Stempvoort et al., 2013]. Sulfamethoxazole is highly water soluble and not likely to be removed by adsorption during septic system treatment [Underwood et al., 2011; Larcher and Yargeau, 2012]. Removal is possible under aerobic conditions found in a non-saturated well-functioning leach field. Additionally, total PPCP and AS concentration showed an inverse relationship with the distance of the closest septic, indicating that streams with close proximity to a septic system have an increased risk of human waste pollution ($r_s \approx -0.6$, p-value=$1.9e^{-11}$).

The data from Rock Creek and SERC (as well as the intended SERC* site) further confirmed this conclusion, that septic count is an important factor controlling total PPCP pollution in headwater streams; Rock Creek had the lowest septic count and the lowest total AS concentration among the streams studied. Total PPCP and AS concentrations showed a strong trend with septic system density, with sites with higher total concentrations correlating with higher septic density. The strong connection between total PPCP and AS concentration and

septic's has been shown previously in urban river systems [Burns et al., 2018], but the present study is likely the first to show the correlation in headwater streams.

Land use was not as a strong of a predictor of PPCP and AS presence in the study as septic systems. Previous studies had varied correlations with land use [Vaicunas et al., 2013; Bradley et al., 2020; Meng et al., 2022] with some suggesting land use in agricultural areas have higher PPCP and AS concentrations while others make the connection between suburban/urban land use and high PPCP and AS concentrations. However, these studies did not investigate wastewater treatment's role on PPCP and AS contamination in streams. For example, an urban area with poor/aging WWTP infrastructure may skew data in favor of urban areas, while an agricultural area with poorly maintained septic systems or animal water lagoons may skew PPCP and AS contamination data in favor of urban areas. Incorporating wastewater treatment techniques that are found in a catchment would strengthen future studies, as there is not a consensus in the literature on land use's role in predicting PPCP and AS pollution.

*3.4.4 Temporal influences on PPCP and AS*

A Kruskal Test and a post hoc Dunn test with Bonferroni correction was conducted to investigate the seasonal variation within all sites. Monthly samples were grouped into seasons as defined by NOAA, meteorological spring in the Northern Hemisphere includes March, April, and May; meteorological summer includes June, July, and August; meteorological fall includes September, October, and November.

The 11 PPCP and AS with at least 50% detection frequency were selected and analyzed for statistical analysis (Appendix A). Ace-K, carbamazepine, cotinine, DEET, estrone, paraxanthine, and sulfamethoxazole were all shown to have seasonal variation. A significantly higher concentration of Ace-K was found in fall compared to spring. Significantly lower concentrations of carbamazepine were found in spring compared to summer. The lower

carbamazepine concentration in spring and the early summer are consistent with previous studies of mixed land use watersheds [Fairbairn et al., 2016]. Summer had significantly higher concentrations of DEET than fall and spring, which was expected due to higher usage during the summer months [Fairbairn et al., 2016]. In general PPCPs and AS concentrations were highest in late spring and summer, which is a period of low flow in North America. The reasons for temporal variations in pharmaceutical concentrations have varied between studies, with several reporting flow as the major driver. Higher contaminant concentrations were observed during times of low flow in large catchments in urban areas [Kolpin et al., 2004; Kasprzyk-Hordern et al., 2008].

Consistently when comparing labile caffeine to less easily degradable Ace-K, sucralose, and carbamazepine, caffeine was proportionally higher during the summer months, particularly at Cockey Creek and Wilelinor. (Appendix A). Busse and Nagoda, [2015], found that caffeine is more likely to be detected in summer months and at higher concentrations, consistent with the findings of this study. It can be assumed that caffeine and carbamazepine (an anti-seizure medication) have similar usage rates year-round, which is not the cause of the trend. In stream processing of these compounds may be a potential cause of the changes in concentrations during the summer months.

*3.4.5 PPCP and AS distribution during stormflow conditions*

Urban stormwater runoff degrades water quality in headwater streams by transporting complex mixtures of contaminants to receiving waters [Alexander et al., 2007; Meyer et al., 2007; Bricker et al., 2014]. In small streams with a low baseflow, the response to storms can be described as "flashy" with high peak discharges shortly after rain and high rates of transportation of pollutants [Peter et al., 2020]. Contaminants derived from the landscape typically have

decreasing concentrations during elevated flows (i.e. stormflow) with a return to normality post-storm [Kolpin et al., 2004; Fairbairn et al., 2016; Peter et al., 2020].

In the present study's stormflow sampling at Chatwell Creek, the majority of PPCP and AS pollution was observed during the first peak of the storm (>50%), with PPCP and AS concentrations returning to their pre-storm values following the storm. Notably, the total detected contaminant concentrations during the first peak of the June 10$^{th}$ storm were nearly equivalent to baseflow concentrations found in Chartwell Creek in June (first storm peak (1.47 µg/L, baseflow total =1.70 µg/L) (Figure 13). This trend was weaker during September sampling events (fall average baseflow total=2.07, September 1$^{st}$ single storm peak=0.68 µg/L, September 22$^{nd}$ single storm peak=0.54 µg/L), however the first storm peak held the majority of contaminant load in the September storms as well (Figure 14, 15). The September storms were longer and had more intense rainfall, which may contribute to the lesser first peak concentration.

Pre and post-storm contaminant profiles were similar to the monthly baseflow. DEET, caffeine, and estrone dominated baseflow, pre and post-flow pollutant profiles. DEET is noticeably absent during storms when the stream stage is above 0.2 m (Figueres 12, 13,14). The trend of distinct storm peak and baseflow profiles was also reflected by Peter et al., [2020], who found that pesticides were more common in baseflow and pre-storm profiles and PPCPs were the majority of stormflow profiles. In a 2002 to 2004 multiyear water quality survey of Johnson County, Kansas, the trend of pesticides (DEET) present pre-storm but below detection limits during stormflow was also observed [Lee et al., 2005]. In surface waters, DEET degrades at a moderate to rapid rate (half-life: days to weeks), but DEET is not rapidly degrading enough to become undetectable during the course of a 12-hour storm [Calza et al., 2011; Santos et al., 2019]. Combining half-life information with the findings of Lee et al., [2005] lead to the

conclusion that DEET is not being removed by stormflow but is rapidly diluted below detection limits only to return to pre-storm levels.

The first peak of the hydrograph in the sampled Chartwell Creek appears to have the largest contribution of PPCP and AS contaminants. Secondary peaks during the June 10$^{th}$ storm and September 22$^{nd}$ storm also contributed a notable amount of contaminants, approximately 7% less than in the first peak. This trend aligns with Bertrand-Krajewski et al., [1998], who first noted that the first flush (peak) of a storm accounted for the majority of pollutant mass in a storm. Stormflow appears to cause a temporary high output of PPCP and AS during the first storm peak followed by a gradual decline with concentrations returning to normal following, indicating that stormflow only temporalty exacerbates contamination as sources are probably finite.

### 3.5. Conclusions

In this study, ten suburban headwater streams in Anne Arundel County, Maryland, were studied for eight months to determine the presence of twelve PPCP and two AS. The most frequently detected compounds included Ace-K, caffeine, carbamazepine, sucralose, and sulfamethoxazole. In general, higher concentrations of PPCP and AS were found during the summers, which were attributed to lower stream depth/stream width, used as a proxy for stream flow. While PPCP and AS concentrations varied seasonally, this study showed that contamination persisted year-round in the studied perennial headwater catchments. Contaminants concentrations had no to moderate correlation with major ions, incongruent with previous studies with the exception of nitrate. Therefore, more work is needed to identify connections between degradation pathways shared by PPCP/AS and major ions. No one factor could accurately

predict PPCP and AS presence; however, the presence and location of septic systems, season and water level were the strongest predictors in this study.

Stormflow data showed that PPCP and AS are flushed from the catchment during rain events, with the majority of PPCP and AS contamination being found in the first storm peak. Following storms, wastewater contamination levels tend to return to their pre-storm values, indicating continuous contamination.

Previous studies have primarily focused on the occurrence of PPCP and AS sourced from WWTP effluent. Fewer studies have analyzed the fate of PPCP and AS sourced from septic systems; this study is among the few to review PPCP and AS connected to septic systems and in small headwater catchments. Headwater streams make up most of the world's drainage networks and are severely understudied in the search for PPCP and AS contamination. This study examined the presence and behavior of PPCP and AS in headwater streams that contribute to one of the most influential water bodies in the United States, the Chesapeake Bay. Future studies would benefit from increasing the number of catchments sampled, determining the age and type of septic infrastructure, and monitoring larger storms to better predict PPCP and AS contamination drivers.

# Chapter 4: Occurrence and trends in short-term sampling in Benedict, MD and Anne Arundel County, MD

## 4.1 Introduction

From 2006 to 2019, there has been a 94% increase in publications about pharmaceuticals and personal care products (PPCP) globally [Meyer et al., 2019]. This increase in attention can be attributed to recognizing these compounds usefulness for detecting the presence of human wastewater pollution and improved analytical methods [Deo and Halden, 2013; Nash Jett et al., 2021].

Human waste contamination of surface water originates from various sources, with wastewater treatment plants (WWTP) effluent being among the most studied [Nash Jett et al., 2021]. PPCP and artificial sweeteners (AS) have been shown to pass through WWTP either largely unaltered or partially degraded, hence, they are constantly introduced into the aquatic environment through WWTP effluent [Blair et al., 2015; Yang et al., 2017]. Furthermore, PPCP and AS sourced from WWTP effluent are not regulated in the US and their frequency of detection is increasing together with their overall concentrations in freshwater [Wang and Wang, 2016; Nash Jett et al., 2021; Wilkinson et al., 2022].

In addition to wastewater from centralized WWTP, onsite wastewater treatment systems (OWTS) are significant sources of PPCP and AS [Meyer et al., 2019]. While a less studied field (2% of papers published between 1990 and 2019), there has been increasing documentation of PPCP and AS sourced OWTS (e.g., Septic systems) [Meyer et al., 2019].

Over a decade ago, it was estimated that decentralized OWTS processed and discharged about 15 billion liters/day of wastewater into the environment in the US [Conn et al., 2006]. This value is relatively small compared to estimates for WWTP daily processing (128 billion liters/day) [Michielssen et al., 2016], but the output from OWTS is less closely monitored. Septic tanks and

leach fields are ideally installed 30 m downgradient of household wells but even then, wastewater can degrade groundwater quality, especially if a septic tank is not maintained [HUD, 2012; Lapworth et al., 2012; Kibuye et al., 2019; Meyer et al., 2019]. Septic systems also pose an increased risk to coastal communities due to shallow water tables and rising sea water levels [Reay, 2004; Humphrey et al., 2010; Conn et al., 2012; Vogelsong, 2019]. Lack of septic system monitoring and potential for groundwater and tidal water interaction make septic systems a potential source of pollution, particularly in coastal communities [Van Stempvoort et al., 2013].

Within Maryland, the last 20 years of wastewater management has been shaped by Senate Bill 320 (Bay Restoration Fund), which was enacted to repair the health of the Chesapeake Bay via upgrading Maryland's wastewater treatment plants and reducing excess nutrients coming from WWTP [Haines et al., 2004]. Following the law's implementation, OWTS were identified by the state as a source of excess nutrients, consequently the state established additional funding to provide pathways for their upgrades. As mentioned in chapter 1, failing and outdated OWTS pose a risk to ground and surface waters in coastal areas. Maryland has approximately 420,000 septic systems; of these, 52,000 systems are located within 1,000 feet of tidal waters [DNR, 2021]. Maryland septic systems may be contributing excess PPCP and AS in addition to nutrients to the Chesapeake Bay.

The overall goal of this chapter was to determine the abundance and spatial distribution of PPCP and AS in Chesapeake Bay coastal watersheds with OWTS. The PPCP/AS measured are discussed in detail in Chapter 1. More specific goals were to i) assess how PPCP/AS concentrations correlate to commonly used water quality variables such as nutrients, water turbidity, conductivity, and dissolved oxygen; ii) examine the correlation between PPCP/AS concentrations and other tracers used for source and fate identification of N pollution (nitrate and

oxygen isotopes), and ii) determine the correlations between different contaminants, especially conservative versus labile PPCP to explore the relative importance of pollution from septic systems versus WWTP in ground and surface waters.

*4.1.1 Hypotheses*

- Septic dominated catchments have higher PPCP concentrations than sewered catchments.
- Concentrations of PPCP and AS are correlated with nitrogen pollution and other commonly used water quality variables.
- Concentrations of PPCP and AS are correlated with nitrate and oxygen isotopes.
- Surface waters adjacent to catchments dominated by septic systems have higher ratios of labile versus conservative contaminants.

*4.1.2 Background information about the impetus of the present study*

The study described in this chapter is the culmination of two studies implemented in Maryland to evaluate the impacts of wastewater, specifically septic waste, on coastal waters draining into the Chesapeake Bay. The studies were requested by the Anne Arundel County Department of Public Works and Charles County Planning Division and were similar enough to allow the comparison of contrasting catchments regarding land use; suburban in Anne Arundel County, and rural in Benedict, Charles County.. The sites chosen in both studies were at the suggestion of their respective county representatives. Each Anne Arundel site was adjacent to an urban/suburban population, and each Benedict site was close to or within the township of Benedict, MD, population 261 [Census, 2020].

PPCP and AS have variable degradability in WWTP; comparing conservative and labile compounds allows for the waste in freshwater to be "aged" from fresh untreated sewage to treated sewage (Table 2, Chapter 1) [Cantwell et al., 2018]. Caffeine and sucralose are

particularly useful in this estimation due to their high use in US populations and common detection in wastewater [Buerge et al., 2009; Yang et al., 2017]. In addition to PPCP and AS, stable isotopic nitrogen and oxygen ratios of nitrate were utilized in the Anne Arundel county samples. Stable isotopic nitrogen and oxygen ratios of nitrate is commonly used to source excess nitrogen from agricultural, atmospheric and wastewater sources [Kendall et al., 2007; Kaushal et al., 2011]. All of the factors mentioned above, and spatial distribution were used to access potential waste sources and find correlations between them.

## 4.2. Materials and methods

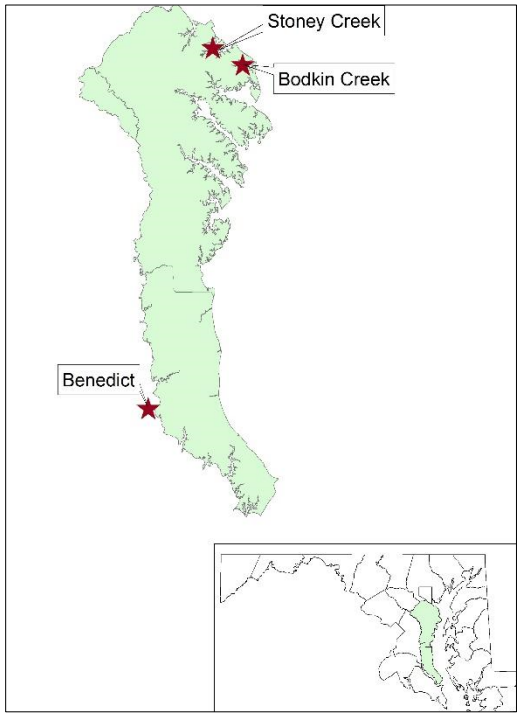



**Figure 23 Map of the study region showing Stoney and Bodkin Creek and Benedict, MD**


**Figure 24 (A) Map of the Stoney Creek, Bodkin, Creek and Patapsco River sample sites in Anne Arundel County, MD; (B) Map of surface and groundwater sample sites in Benedict, MD**

Note: Anne Arundel County Septic systems are identified as black dots and sewer lines are pink lines

*4.2.1 Study Area*

This study focused on four watersheds in Maryland's Coastal Plains physio-geographic region, with watersheds draining into the largest estuary in the USA, the Chesapeake Bay (Figure 23). Bodkin and Stoney Creek are sub-estuaries in the Patapsco River estuary, located just south of Baltimore in Anne Arundel County, MD (Figure 24A). Both can be classified as suburban estuaries, with the Stoney Creek watershed dominated by sewer for human waste disposal while septic systems dominate Bodkin Creek. The tidal Patapsco River estuary was sampled in order to associate conditions in Stoney and Bodkin Creek with conditions at their downstream boundary in the vicinity of the outflows of the Patapsco and Cox Creek WWTP.

**Table 9 Population & Septic Density in Anne Arundel Sample Sites**

| Catchment | Population | Septic system count | Area (km²) | Population density (pop/km²) | Septic density (septic/km²) |
|---|---|---|---|---|---|
| Bodkin Creek | 33507 | 3053 | 2.65 | 12644 | 0.24 |
| Stoney Creek | 60165 | 1102 | 3.13 | 19222 | 0.06 |
| Patapsco River | 549588 | N/A | 4.77 | 115218 | NA |

Note: Septic system GIS data was not publicly available for all of the Patapsco watershed.

Stoney and Bodkin Creek are comparable in catchment area (Table 9), but Stoney Creek has a larger discharge ($6.55 \times 10^6$ $m^3$) than Bodkin Creek ($4.40 \times 10^6$ $m^3$) (calculated via ArcGIS). Stoney Creek also has a larger watershed area (107 $km^2$) than Bodkin Creek (44.3 $km^2$) but far fewer septic systems (Table 9) [Kernell, 2008].

The fourth study area in this study was located in Benedict, MD, approximately 70 km southwest of Stoney Creek and Bodkin Creek. Benedict is located within the Patuxent River estuary in Charles County, MD. The area surrounding the small township of Benedict can be described as rural and only contains homes served by septic systems. The watershed of Benedict being entirely served by septic's provided a "septic control" unlike Bodkin Creek which contains some homes served by a WWTP. Benedict is a peninsula on the Patuxent River with a rural population, surrounded by agriculture and parkland, adjoining with the Patuxent River and an unnamed tributary (Figure 23).

*4.2.2 Sample Collection*

To evaluate the impact of wastewater, nutrients and PPCP/AS were measured in surface water, water at the bottom of the water column (Anne Arundel only), and groundwater (Benedict only). In Anne Arundel County, twenty-eight sampling sites were sampled. Twelve sites were located in Stoney Creek, eight in Bodkin Creek, and eight in the Patapsco River that runs along the outflows of Stoney and Bodkin (Figure 23A). Each creek had two main branches that were

sampled as well as in the coalescences of the two branches (SC #7, BC #4, BC #5 & BC #10). Each stream was sampled first from a boat-accessible starting point (BC #1, BC #8, SC #1 & SC #5), then in stream channel confluences (SC #3, SC #4, SC #7, BC #2, BC# 5, BC #7, BC #8, BC #9), and at the mouth of the stream (SC #8 & BC #12). Stoney Creek and Bodkin Creek are both tidal creeks with high tides at 1.25 ft & 1.1 ft and low tides at 0.25 ft & 0.22 ft, respectively, during the week of sampling [tides4fishing, 2021b]. The tidal Patapsco River estuary was also sampled in order to associate conditions in Stoney and Bodkin Creek with conditions near vicinity of the outflows of the Patapsco and Cox Creek WWTP. The Patapsco River was sampled along the channel with upriver sites (PT #1, PT #2 & PT #3), sites near the coalescence of Stoney Creek (PT #4 & PT #5), sites near the coalescence of Bodkin Creek (PT #7 & PT #8), and a site west of the Bodkin and Stoney coalescence point (PT #8). At each site, water temperature, salinity, dissolved oxygen, specific conductivity, and pH were measured at approximately 0.5 m intervals throughout the water column using a calibrated YSI EXO$^2$ multiparameter sonde (Xylem Inc., Yellow Springs, OH). Water clarity was measured using a Secchi disk. Grab samples were collected using a submersible pump at each station near-bottom (~0.5 m above the sediment) and surface water (~0.5 m below the surface). Samples were collected in April 2021. Sample bottles were rinsed three times with site water prior to final collection and then stored on ice until samples could be processed at the lab at the end of each field day. Samples used for PPCP and AS analysis were stored in a purposely random mix of combusted clear and amber bottles with no headspace. Samples used for nutrient analysis were collected in HDPE Nalgene bottles.

In rural Benedict, five surface water sites and six groundwater sites were sampled on two occasions in 2021, on June 24 and August 4. Surface water samples for PPCP/AS and nutrients

analyses were collected manually in the Patuxent River main stem via kayak. Surface water samples were taken from approximately fifty meters NW offshore in the Patuxent River, above (Site 10) and below Benedict, Md (Site 11), the mouth of the small bay (Site 12), right adjacent to the "mainland" where agricultural runoff might be found (Site 13), and to the left of the mainland in a small vegetation dominated creek (Site 14). The upper portion of the creek was very shallow (water <20 cm deep) with soft organic sediment. During the days of surface water sampling events, high tides were 2.5 ft & 2.15 ft, and low tides were 0.5 ft & 1.05 ft, respectively, in the Patuxent River [tides4fishing, 2021a].

Groundwater sites were accessed through 8-foot deep wells made of 1.25 in diameter PVC pipes with a mesh screen. The wells were pumped before the second sampling event. Groundwater samples were collected from four upland well sites and two water's edge sites. Site 1 was located in a moderately dense housing area. Site 3 was located central to the island in an area among houses. Sites 4 and 5 were installed to create a two-point transect on the east side of the peninsula wand and were close to businesses. Site 4 was located just east of Mill Creek Rd, and Site 5 was located between Benedict Avenue and the Patuxent River (Figure8A). Sites 6 and 7 formed a second transect further south and were located on a property undergoing renovations, including installing a septic system. The inland Site 6 was located just east of Mill Creek Road, and Site 7 was adjacent to the Patuxent River. These wells provided a gradient between the land and the receiving water of the Patuxent River. Groundwater flow direction is unknown.

Observations of the soil and sediment made while coring to install the wells indicated that sediment underlying Benedict range from sandy to gravel, with some pockets of more organic-rich soils, especially at site 7. Rainwater drains rapidly in these types of soils, with the release possibly controlled by river stage, at least at the lower elevation sites. From west to east, the

town slopes from a significant bluff (approx. 10 m high) along the western side bordering Back Creek to a soft entry into the Patuxent River. Water levels in the wells were low during every visit. Samples used for PPCP and AS analysis were stored in sample rinsed combusted 200 mL amber glass bottles with no headspace. Samples used for nutrient analysis were collected in sample rinsed 60 mL HDPE Nalgene bottles. All samples were kept on ice until reaching the lab the same day.

*4.2.3 Statistical analysis*

Statistical analysis was conducted using R studio (2022.02.0 Build 443, Boston, MA). All data were nonparametric. In order to evaluate possible relationships between the target compounds and environmental factors, Spearman's rho ($r^s$) was used to compute correlations and the associated p-values. When computing Spearman's rho, all non-detects were treated as ties to avoid substituting values for non-detects. Spearman's rho values were calculated for each site, surface, and bottom (or surface and groundwater). Extended Spearman's correlation results can be found in Appendix B. The significance of this analysis was set at $\alpha = 0.05$.

To determine differences among sampling events and sampling location a Wilcoxon signed-rank test was used as a post hoc test. The significance of this analysis was set at $\alpha = 0.05$.

Anne Arundel Sample sites were sampled once, and Benedict was sampled twice. Stanfourd et al., [2014] found that monthly and bimonthly sampling frequencies had little effect on PPCP trends observed over a five-year period, as did quarterly sampling; however, there was additional variability; the differences were not statistically significant. These results allowed the results from few sampling events to be reported confidently.

*4.2.4 Geospatial analysis*

Area, septic density and population density data for each site were generated via ArcGIS (Version 10.5). Catchment area was determined via a *Analysis Tool Spatial Join* of Maryland

MDE 12-digit watershed polygon shapefiles and Maryland Stream and river polyline shapefiles by 8-digit watershed HUC code [Administration, 2018; Resources, 2018]. The resulting files were then *Clipped* by their corresponding MDE 12-digit watershed polygon shapefile. The catchment area polygon was used to Clip 2020 census tract data to calculate area and population [Census, 2020].

Septic density was generated from the *Clipped* MDE 12-digit watershed polygon shape file and a septic system point shapefile generated by Anne Arundel County [Services, 2018]. The *Clipped* MDE 12-digit watershed polygon shape file was used with the *Select By Location* tool to select septic system points using the "completely contain with source" selection method to retrieve appropriate data.

*4.2.5 Sample Processing & Laboratory Analysis*

The following is a brief overview of sample processing and laboratory analyses; see Chapter 2: Methods for a more detailed description.

Grab samples collected for analysis of nutrients and stable isotopes were filtered using glass fiber filters and a pressure-adjusted vacuum before being frozen. The Chesapeake Biological Laboratory Nutrient Analytical Services Laboratory measured all nutrient concentrations (CBL NASL, Solomons, MD). Central Appalachians Stable Isotope Facility processed isotope samples, Appalachian Laboratory of the University of Maryland Center for Environmental Science (CASIF, Frostburg, MD).

The samples collected for PPCP and AS quantification were analyzed in the Gonsior Lab at CBL. To analyze these compounds, a process called solid phase extraction is required. Water is passed over a resin contained in a cartridge, which temporarily binds the chemicals, which are then released when a solvent is passed over the resin. This approach allows for low detection

limits, in the ng/L range, if paired with liquid chromatography mass spectrometry (LC-MS/MS). Extracts were analyzed using an Agilent 6420 Triple Quad Mass Spectrometer.

*4.2.6 Stable Isotope Analyses*

Nitrate-specific isotopic analysis, ($\delta^{15}N_{NO3}$, and $\delta^{18}O_{NO3}$) was conducted by CASIF. Surface and bottom water samples collected in Anne Arundel County were filtered (0.45 μm), frozen, and shipped to CASIF for analysis. Benedict, MD samples were not analyzed for nitrate-specific isotopes. The isotope composition of nitrate was measured following the denitrifier method outlined in Casciotti et al., [2002], and Sigman et al., [2001]. In this method, denitrifying bacteria are used to convert nitrate in samples to $N_2O$ gas, which is then collected and sent through a mass spectrometer to determine the stable isotopic ratios for N and O of nitrate ($^{15}N$ /$^{14}N$ and $^{18}O$ /$^{16}O$). Values for $\delta^{15}N\text{-}NO^-_3$ and $\delta^{18}O\text{-}NO^-_3$ are reported as per mL (‰) relative to atmospheric $N_2$ ($\delta^{15}N$). Measurements were made on a ThermoFisher Delta V+ Isotope Ratio Mass Spectrometer. For data correction and normalization, CASIF uses calibration nitrate standards USGS34 and USGS35 for O and USGS32 and USGS34 for N isotopes (National Institute of Standards and Technology, Gaithersburg, MD).

## 4.3 Results and Discussion

*4.3.1 Concentrations of and spatial distribution of major-use PPCP and AS among sites*

This study sought to assess human waste pollution in coastal waters based on the presence of PPCP and AS commonly associated with wastewater in the US. The central hypothesis was that coastal waters adjacent to septic dominated watersheds (Bodkin Creek and

Benedict) would have elevated concentrations of PPCP/AS compared to coastal waters adjacent to communities who' mostly use WWTPs to treat waste (Patapsco River and Stoney Creek).

The results from the analysis of 82 water samples collected from Bodkin Creek, Stoney Creek, Patapsco River and Benedict during the summer of 2021 show that all contaminants analyzed were detected in the sites sampled with varying detection frequencies (Appendix B). Concentrations varied among contaminants and sites but stayed reasonably consistent between surface and bottom water samples. Figure 24 shows a log scale's five-number summary (minimum, first quartile, median, third quartile, and maximum) and outliers for each sample site. Concentrations for each sample site can be found in Appendix B.

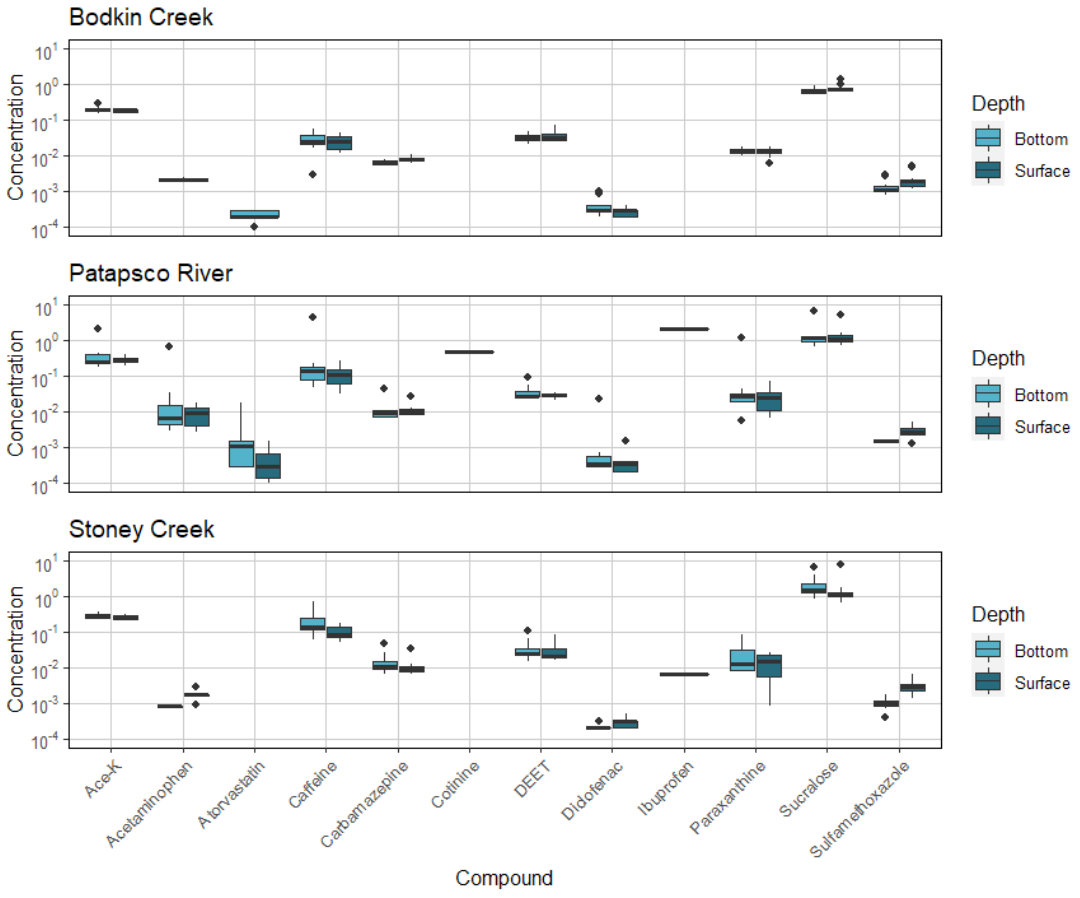



**Figure 25 Boxplots of PPCP and AS in all Anne Arundel County Sample Sites in Log Scale**

In the Patapsco greater watershed and its two sub estuaries, Ace-K, caffeine, carbamazepine, DEET, paraxanthine, and sucralose, and had the highest rate of detection ( 98%, 100%, 100%, 100%, 98%, 100%) in surface and lower water column samples. Figure 24 shows whole stream data summarized in quartiles and their outliers on a uniform log scale; individual site data can be found in Appendix B These compounds were all expected to be found due to their high use in the US. Caffeine and carbamazepine concentrations in these sites were consistent with concentrations previously found in urban areas (Anacostia River, DC) and in rural areas (Congaree National Park, SC); comparable DEET concentrations were also found in SC but were not detected in a similar study in DC [Shala and Foster, 2010; Bradley et al., 2017]. Sucralose concentrations were consistent with concentrations found in the Upper North East Passage of Narragansett Bay, RI [Cantwell et al., 2019]. All three of these studies cited human waste connected to an upstream WWTP as the likely source of PPCP and AS.

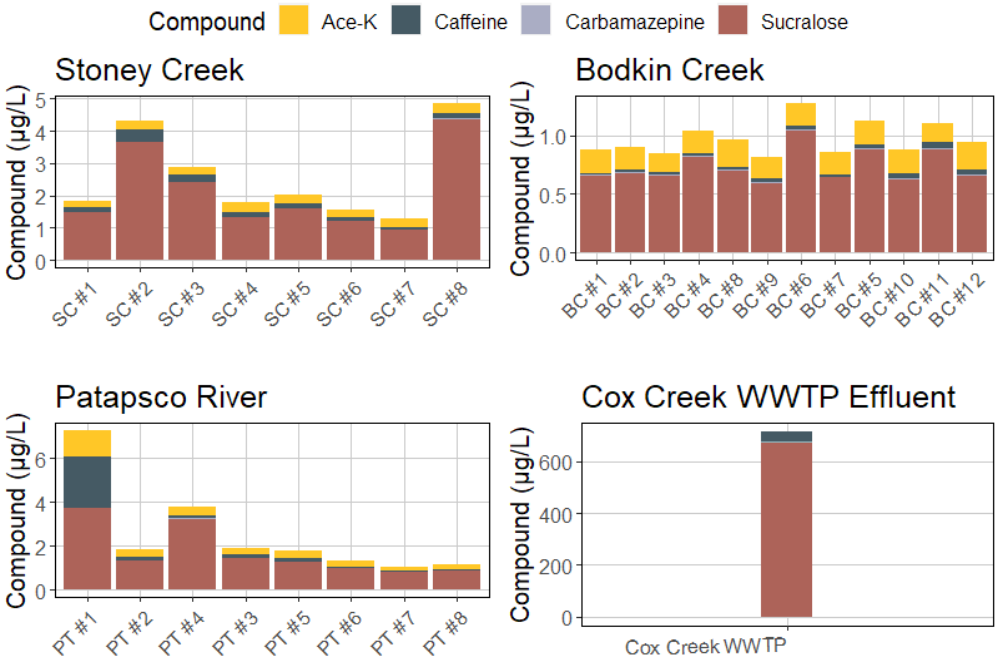



**Figure 26 Top 4 Commonly Detected PPCP/AS in Anne Arundel County Sample Sites**

Figure 26 shows the concentrations of 4 of the most frequently detected PPCP & AS, graphed from upstream to downstream. The concentrations for Cox Creek WWTP effluent are also shown, Ace-K was not measured at this site (Figure 26D). Sucralose concentrations generally decrease from headwaters to the mouth of the stream in Stoney Creek (Figure 25A), with the exception of SC #8, which was at the confluence of the Patapsco River and Stoney Creek. The decreasing sucralose concentrations may be attributed to a dilution effect in this well-mixed creek. The WWTP's low ratio of labile caffeine to conservative sucralose indicates the dominance of treated wastewater inputs. Bodkin Creek and the Patapsco River had generally consistent levels of PPCP and AS, which may indicate additional inputs to these streams given that concentrations did not decrease further downstream. These inputs may have been from septic systems or ageing sewer systems.

Every suburban Anne Arundel county sample site had detectable levels of at least seven target PPCP & AS (Figure 25). This is to be expected in densely populated suburban areas as more people result in a diverse spectrum of PPCP use (Table 9) [Meyer et al., 2019]. Site PT #1 consistently had elevated levels of Ace-K, DEET, acetaminophen, atorvastatin, caffeine, carbamazepine, cotinine, diclofenac, ibuprofen, paraxanthine, and sucralose (Figure 26). This sample site was close to the Cox Creek WWTP effluent which had elevated concentrations of all the previously mentioned compounds (Figure25D). The Bodkin Creek sites that had two or greater target compounds with concentrations higher than 75% of all other samples in that catchment were BC S#6, BC S#8, BC S#10, and BC B#12. These sites were the most contaminated of all of the sites in their catchments. Sample site BC #12 was located at the confluence of Bodkin Creek and the Patapsco River. While BC#12 was interacting with more polluted water from Stony Creek, which likely caused the increase in PPCP and AS pollution,

the other elevated sites may have received other wastewater sources. Bodkin Creek was in a septic system dominated area but had the lowest overall PPCP and AS concentrations among the sites sampled in Anne Arundel County.

Within the Stoney Creek samples, SC B#2 SC S#5, SC S#8, and had two or greater target compounds with concentrations above 75% of all other sample sites in that catchment. Stoney Creek was located in a sewer dominated catchment, with Cox Creek WWTP located in a cove near the confluence of Stoney Creek and the Patapsco River. When comparing all of the Anne Arundel catchments, caffeine and sucralose were found in the highest concentrations; 115% and 263% higher than the concentration of any other PPCP or AS.

There was no significant difference in PPCP and AS concentrations between surface and bottom samples in Bodkin, Stoney and Patapsco sites ($p>0.05$), presumably because the water column was well-mixed . There was a significant difference between septic-dominated Bodkin Creek and Patapsco River surface water samples ($p<0.05$), which had a mix of septic systems and homes connected to WWTP. These differences may be explained by the larger catchment area in Patapsco given the positive correlation between PPCP detection and sewage volume [Wilkinson et al., 2022]. There was no significant difference in PPCP/AS concentrations between septic-dominated Bodkin Creek and Stoney Creek, which had a mix of septic and sewered homes ($p >0.05$). Contrary to the initial hypothesis, septic-dominated watersheds had comparable levels of wastewater tracers as sewered watersheds. This may be due to additional waste inputs from aging sewer infrastructure, combined sewer overflows, or the contribution from the main stem of the Patapsco River, which also had relatively high levels of contamination.

A paired Wilcoxon signed rank test was used to investigate contaminant concentrations within sites. This was explored on a site to site basis, with compounds with detection frequency less than 50% excluded. When comparing adjacent sites within the same stream BC #7 & #11, BC #8 & #9, PT #5 & #6, PT #5 & #7, SC #4 & #7, SC #5 & #6, SC #6 & #7, and SC #7 & #8 had PPCP and AS concentrations were significantly different among them (p-values $\leq 0.013$) (Appendix B). Significant differences among sites within Bodkin and Stoney Creek may have been caused by the fact that sites SC #6, SC #7, SC #8, BC #9 & BC #11 were located at confluence points, closer to the stream's mouth. A significant difference was observed between PT #5, #6 & #7, which were located near the confluence of the Patapsco River and Rock Creek, an unsampled catchment located between Stoney Creek and Bodkin Creek. Rock Creeks has an even distribution of homes reliant on septic systems and sewered homes. PPCP and AS concentrations differences between SC #5 and #6 can be attributed to SC #5 being at the start of the cove and SC #6 being located at a confluence point with a larger drainage area that could have more waste sources. Location appears to be a larger factor in PPCP and AS concentrations than water depth; a reasonable assumption in well-mixed streams. This finding is consistent with the Ferguson et al., [2013] conclusion that location rather than water depth influenced PPCP

concentrations when comparing surface and bottom sample

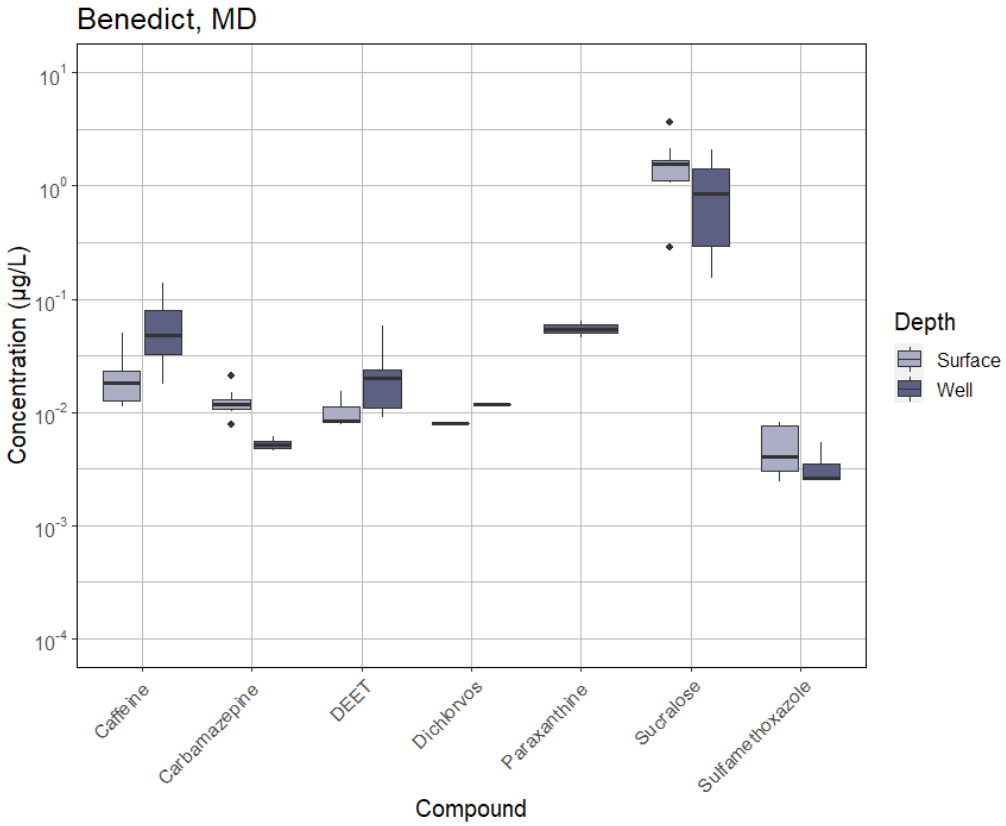



**Figure 27 Plots showing concentration range, median and outliers of PPCP & AS in all Benedict, MD Sample Sites in Log Scale** Note: Cotinine, Diclofenac, Estrone and Ibuprofen were not detected

Within Benedict, sucralose, DEET, and caffeine had the highest detection rates among all surface and groundwater samples (100%, 96%, 100%) (Figure 27). Concentrations were generally similar to those observed in the Patapsco watersheds but Benedict had lower overall detection frequency, likely due to a lower population density and wastewater load in this small catchment with fewer septic systems. The only sites in Benedict where two or greater target compounds had concentrations above 75% of other samples for both sampling events were well 5 and surface sample site 8. Differences among sites were significant between the June and August sampling events in surface water samples ($p \leq 0.05$) but not in groundwater samples ($p \geq 0.05$). In general, concentrations were higher in June in all sites but one; the higher June

concentrations may be partly due to more human activity and higher population in the summer as Benidict is home to several seasonal homes. However, this trend does not reflect the results of Quadra et al., [2021] and Burns et al., [2018], who found lower PPCP & AS concentrations during the more rainy months such as June. In the 30-day period leading up to the June sampling event in Benedict, the total rain depth was 11.85 inches, compared to 3.89 inches preceding the August sampling event[6].

There was also a significant difference between surface and groundwater samples in Benedict ($p \leq 0.05$) according to paired Wilcoxon signed rank tests, as well as a significant difference when comparing surface vs. groundwater labile tracers ($p \leq 0.05$) and surface vs. ground conservative tracers ($p < 0.05$), with groundwater having more labile tracers. This result was expected as wastewater is generally fresher in wells directly adjacent to septic system drain fields like found in this small isolated catchment than in surface waters [Arnade, 1999; Schaider et al., 2013]. However, groundwater concentrations were overall lower than those in surface water.

[6] Precipitation data sourced from National Weather Service station in Mechanicsville, MD. Approximately 14 km SW from the sample site

*4.3.2 Correlations between PPCP/AS and other variables used to predict human waste contamination*

*4.3.2.1 Isotopic tracers in suburban Anne Arundel County samples*

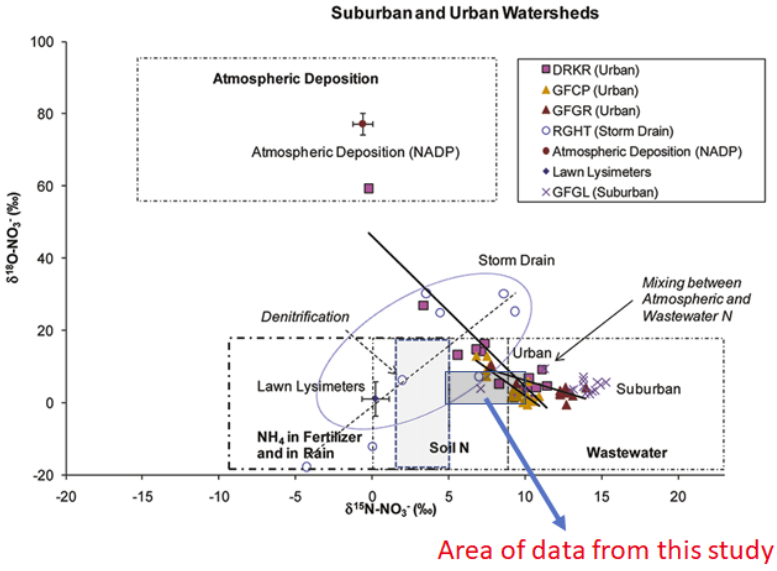



**Figure 28 Dual $\delta^{15}N\text{-}NO_3$– and $\delta^{18}O\text{-}NO_3$– source plots for suburban and urban watersheds Adapted from: Kaushal et al., [2011]**

Isotopic nitrogen tracers have been used in estuarine settings to investigate the role of wastewater for decades. Isotopic fractionation discards proportionally heavier isotopes of nitrogen into waste, making wastewater effluent frequently higher in $N^{15}$ isotopes e.g., Oczkowski et al., [2008]. Natural denitrification rates in sediments or groundwater can similarly create heavier inorganic nitrogen. In Figure 28, from Kaushal et al., [2011], the culmination of a meta-analysis of previous isotopic nitrate studies was used to associate isotopic nitrate ratios with nitrogen sources in urban and suburban areas.

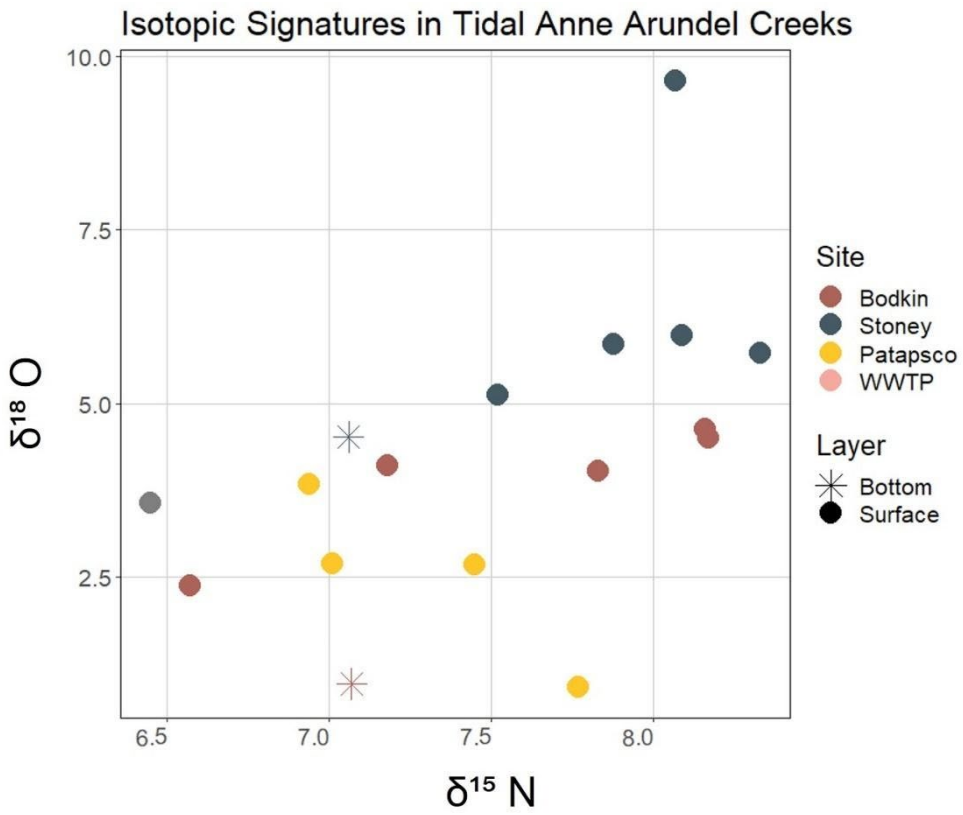



**Figure 29 Scatterplot of $\delta^{18}O$ vs. $\delta^{15}N$ from Anne Arundel County samples**

The Patapsco bottom samples showed the highest $NO_{3-}$ concentrations, but no $\delta^{15}N$ or $\delta^{18}O$ values were recorded and were excluded from Figure 29. Stoney Creek generally had the highest concentrations of $\delta^{15}N$/ $\delta^{18}O$ ratios, and the Patapsco surface trended lower. The overall grouping of $\delta^{15}N$ and $\delta^{18}O$ is consistent with isotopic signatures of N and O from atmospheric and wastewater sources, as reported in Kaushal et al., [2011]. Isotopic tracers were not analyzed for Benedict samples.

*4.3.2.2 Water Quality Parameters*

The environmental parameters measured at each Anne Arundel sample site during each sampling event are shown in Table 10.

**Table 10 Summary of average values and standard deviations for each environmental parameter in each watershed**

| All Sites Combined | Depth (m) | Secchi Disk Depth (m) | Temp. (°C) | Conductivity (mS/cm) | pH | Dissolved Oxygen (%) |
|---|---|---|---|---|---|---|
| Surface | 3.89 ± 1.42 | 0.90 ± 0.19 | 16.08 ± 1.14 | 7.13 ± 0.61 | 7.73 ± 0.19 | 97.24 ± 5.21 |
| Bottom | 3.96 ± 1.41 | 0.92 ± 0.17 | 14.79 ± 1.74 | 8.94 ± 2.24 | 7.39 ± 0.16 | 72.49 ± 18.87 |
| **Patapsco River** | **Depth (m)** | **Secchi Disk Depth (m)** | **Temp. (°C)** | **Conductivity (mS/cm)** | **pH** | **Dissolved Oxygen (%)** |
| Surface | 5.56 ± 0.84 | 1.04 ± 0.13 | 14.76 ± 0.37 | 7.04 ± 0.82 | 7.84 ± 0.15 | 96.85 ± 5.14 |
| Bottom | 5.56 ± 0.84 | 1.04 ± 0.13 | 12.59 ± 0.62 | 11.95 ± 1.59 | 7.23 ± 0.06 | 58.90 ± 7.27 |
| **Bodkin Creek** | **Depth (m)** | **Secchi Disk Depth (m)** | **Temp. (°C)** | **Conductivity (mS/cm)** | **pH** | **Dissolved Oxygen (%)** |
| Surface | 2.93 ± 0.58 | 0.85 ± 0.16 | 16.88 ± 0.78 | 6.82 ± 0.18 | 7.71 ± 0.15 | 98.75 ± 3.48 |
| Bottom | 2.93 ± 0.58 | 0.85 ± 0.16 | 15.69 ± 1.24 | 7.16 ± 0.19 | 7.42 ± 0.08 | 81.98 ± 6.78 |
| **Stoney Creek** | **Depth (m)** | **Secchi Disk Depth (m)** | **Temp. (°C)** | **Conductivity (mS/cm)** | **pH** | **Dissolved Oxygen (%)** |
| Surface | 3.66 ± 1.32 | 0.84 ± 0.24 | 16.21 ± 0.91 | 7.67 ± 0.45 | 7.67 ± 0.26 | 95.36 ± 7.14 |
| Bottom | 3.89 ± 1.25 | 0.90 ± 0.17 | 15.76 ± 0.78 | 8.55 ± 0.26 | 7.54 ± 0.19 | 71.74 ± 31.14 |

Note: ± values are standard error

The average depth was 3.7 m, with Bodkin having the shallowest water (2.9 m) and Patapsco having the deepest (5.6 m). The average Secchi disk depth was 0.9 m, a value consistent across all streams. Typically, the average temperature was highest near the stream headwaters streams (16.83 ºC) and lowest near the confluence (13.72 ºC). The Patapsco river bottom had the highest average specific conductivity (11.9 $\frac{mS}{cm}$), with 8.02 $\frac{mS}{cm}$ being the overall average. pH remained constant across all sites (7.57), while dissolved oxygen concentrations were typically 24% lower in the bottom than in the surface of the water column.

**Table 11 Summary of average values and standard deviations for NH4, $NO_{23}$-, TDN, TDP, and DOC in each Anne Arundel County watershed**

| All Sites Combined | $NH_4$ (mg/L) | $NO_{23}^-$ (mg/L) | TDN (mg/L) | TDP (mg/L) | DOC (mg/L) |
|---|---|---|---|---|---|
| Surface | 0.06 ± 0.03 | 0.75 ± 0.11 | 1.15 ± 0.09 | 0.01 ± 0.00 | 2.71 ± 0.49 |
| Bottom | 0.18 ± 0.25 | 0.69 ± 0.08 | 1.19 ± 0.27 | 0.02 ± 0.02 | 2.62 ± 0.47 |
| **Patapsco River** | **$NH_4$ (mg/L)** | **$NO_{23}^-$ (mg/L)** | **TDN (mg/L)** | **TDP (mg/L)** | **DOC (mg/L)** |
| Surface | 0.08 ± 0.03 | 0.85 ± 0.06 | 1.27 ± 0.04 | 0.01 ± 0.01 | 2.34 ± 0.17 |
| Bottom | 0.37 ± 0.43 | 0.67 ± 0.08 | 1.34 ± 0.46 | 0.03 ± 0.03 | 2.65 ± 0.81 |
| **Bodkin Creek** | **$NH_4$ (mg/L)** | **$NO_{23}^-$ (mg/L)** | **TDN (mg/L)** | **TDP (mg/L)** | **DOC (mg/L)** |
| Surface | 0.04 ± 0.01 | 0.71 ± 0.09 | 1.10 ± 0.04 | 0.01 ± 0.00 | 2.75 ± 0.35 |
| Bottom | 0.12 ± 0.03 | 0.72 ± 0.10 | 1.15 ± 0.07 | 0.01 ± 0.00 | 2.54 ± 0.22 |
| **Stoney Creek** | **$NH_4$ (mg/L)** | **$NO_{23}^-$ (mg/L)** | **TDN (mg/L)** | **TDP (mg/L)** | **DOC (mg/L)** |
| Surface | 0.07 ± 0.03 | 0.70 ± 0.10 | 1.11 ± 0.05 | 0.01 ± 0.00 | 3.03 ± 0.67 |
| Bottom | 0.08 ± 0.02 | 0.66 ± 0.04 | 1.08 ± 0.01 | 0.01 ± 0.00 | 2.72 ± 0.22 |

Note: ± values are standard error

**Table 12 Table 15 Summary of average values and standard deviations for $NH_4$, $NO_2$, $NO_3$-, ON, $PO_4$, TDN, and TDP in Benedict, MD**

| Surface & Well Combined | $NH_4$ (mg/L) | $NO_2$ (mg/L) | $NO_3$- (N mg/L) | ON (mg/L) | PO4 (mg/L) | TDN (mg/L) | TDP (mg/L) |
|---|---|---|---|---|---|---|---|
| | 0.07 ± 0.16 | 0.02 ± 0.03 | 0.64 ± 0.86 | 0.36 ± 0.43 | 0.05 ± 0.05 | 0.99 ± 0.78 | 0.08 ± 0.07 |
| **Surface Sites** | **$NH_4$ (mg/L)** | **$NO_2$ (mg/L)** | **$NO_3$- (N mg/L)** | **ON (mg/L)** | **PO4 (mg/L)** | **TDN (mg/L)** | **TDP (mg/L)** |
| | 0.04 ± 0.10 | 0.01 ± 0.02 | 0.05 ± 0.10 | 0.30 ± 0.04 | 0.06 ± 0.05 | 0.40 ± 0.22 | 0.09 ± 0.07 |
| **Well Sites** | **$NH_4$ (mg/L)** | **$NO_2$ (mg/L)** | **$NO_3$- (N mg/L)** | **ON (mg/L)** | **PO4 (mg/L)** | **TDN (mg/L)** | **TDP (mg/L)** |
| | 0.10 ± 0.20 | 0.02 ± 0.05 | 1.32 ± 0.85 | 0.43 ± 0.66 | 0.03 ± 0.05 | 1.75 ± 0.53 | 0.07 ± 0.07 |

Note: ± values are standard error

The average $NH_4$ concentration across Anne Arundel sites was 0.12 mg/L, with bottom samples having twice the concentration values. Concentrations of $NO_3$-, TDN, TDP, and DOC were also consistent across the Anne Arundel sites, averaging 0.71, 1.17, 0.02, and 2.71 mg/L, respectively (Table 11). PT B #1 had consistently elevated concentrations (above 75% of all other Anne Arundel Samples) of $NH_4$, TDN, TDP, and DOC (Table 4). Except for TDP, all nutrient concentrations in Benedict groundwater samples were lower than in surface water (Table 12).

*4.3.2.2.1 Nitrogen and PPCP & AS*

Excess nitrogen has been identified as a leading cause of the Chesapeake Bay's water quality problem; and 16% of that nitrogen has been estimated to originate from wastewater [Liner et al., 2017]. Therefore, nitrogen is a common cost-effective indicator of waste impacted water [National Research Council . Committee on Wastewater Management for Coastal Urban, 1993; Reynolds, 2021]. However, nitrogen detection is not enough to confirm human waste sources. More sophisticated methods such as $\delta^{15}N/\ \delta^{18}O$ ratio have helped, but it cannot definitely indicate human waste either. Therefore, human waste sources have been estimated based on land use and human population (i.e. human dominated catchments vs agricultural/animal husbandry dominated catchments), or by pairing nitrogen concentrations with a biological marker like human-associated *bacteroidales* and *escherichia coli* [Tanvir Pasha et al., 2019].

More recently, PPCP and AS detection has become a helpful tool for identifying human wastewater pollution in water. When paired with nitrate, PPCP and AS detection can also help determine the predominance of human waste as a nitrogen source. Nitrate is commonly found in human waste but is also sourced from fertilizers and atmospheric deposition. Therefore, identifying sources is extremely important to guide efforts by the Chesapeake Bay Program and the Bay Restoration to reduce nitrogen inputs to the Bay [Haines et al., 2004; DNR, 2021].

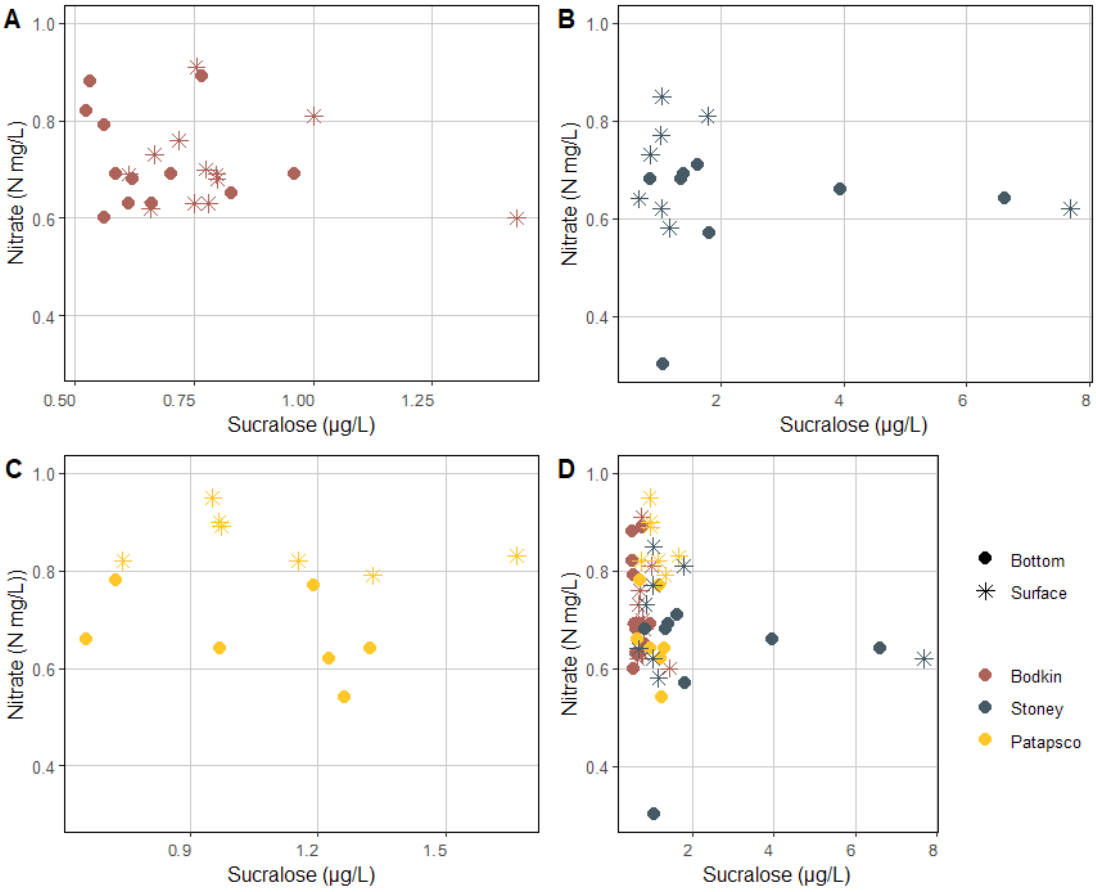



**Figure 30 Sucralose versus Nitrate across Anne Arundel County sampling sites**

Nitrate and sucralose concentrations were compared in surface water and water near the bottom of the water column. Figure 30D shows all site values, no overarching trends were observed. Septic dominated Bodkin Creek (Figure 30A) showed no observable trends with the majority of sucralose values clustered between 0.5-1.00 µg/L and nitrate clustered between 0.6-0.1 N mg/L. Results of Spearman's rank correlation agreed with these findings of no significance (p-value= 0.75).

Sewer dominated Stoney Creek and Patapsco River (Figure 30 B, C) both showed no observable trends, with Stoney Creek nitrate values primarily between 0.5-0.9 N mg/L, with sucralose mainly between 0-2.00 µg/L. The Patapsco River showed no groping of nitrate or

sucralose values. Results of Spearman's rank correlation agreed with these findings of no significance (p-value ≥ 0.13).

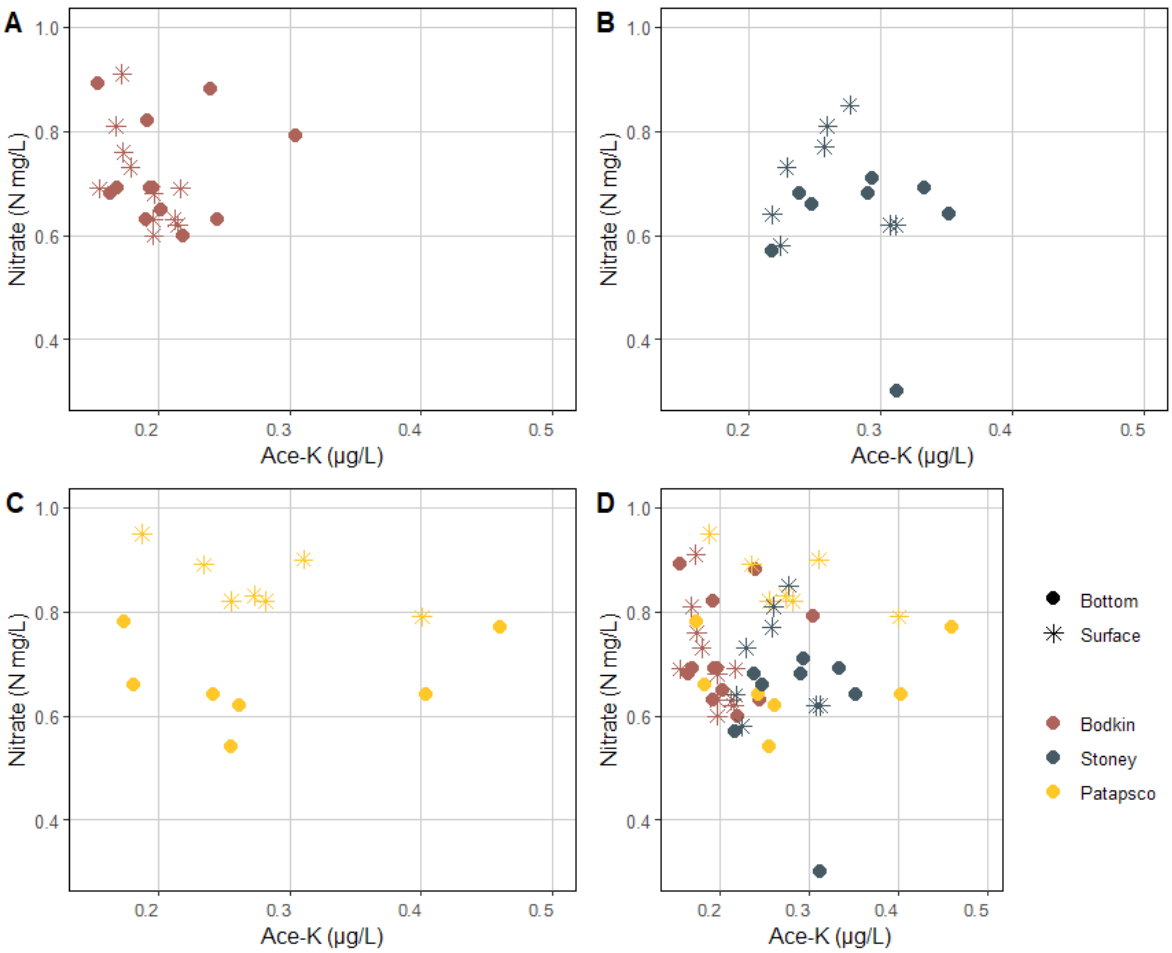



**Figure 31 Ace-K versus Nitrate across Anne Arundel County sampling sites**

Nitrate and Ace-K concentrations were compared in surface water and water near the bottom of the water column. Figure 31D shows all site values, no overarching trends were observed. Septic dominated Bodkin Creek (Figure 31A) showed no observable trends with Ace-K values clustered between 0.0-0.3 µg/L and nitrate clustered between 0.6-0.1 N mg/L. Surface water values appear to have a moderate negative linear relationship. Results of Spearman's rank

correlation agreed with these findings of a negative significant correlation ($r_s$= -0.63, p-value= 0.04).

Sewer dominated Stoney Creek (Figure 31 B) showed no observable trends, with Stoney Creek nitrate values majority between 0.5-0.9 N mg/L, with Ace-K concentrations between 0.2-0.35 µg/L. Spearman's rank correlation agreed with these findings of no significance (p-value ≥ 0.85). The Patapsco River showed a moderate negative linear correlation in surface water values, with Patapsco River nitrate values majority between 0.5-0.9 N mg/L, with Ace-K concentrations between 0.0-0.45 µg/L. Results of Spearman's rank correlation agreed with these findings of a negative significant correlation ($r_s$= -0.71, p-value= 0.05).

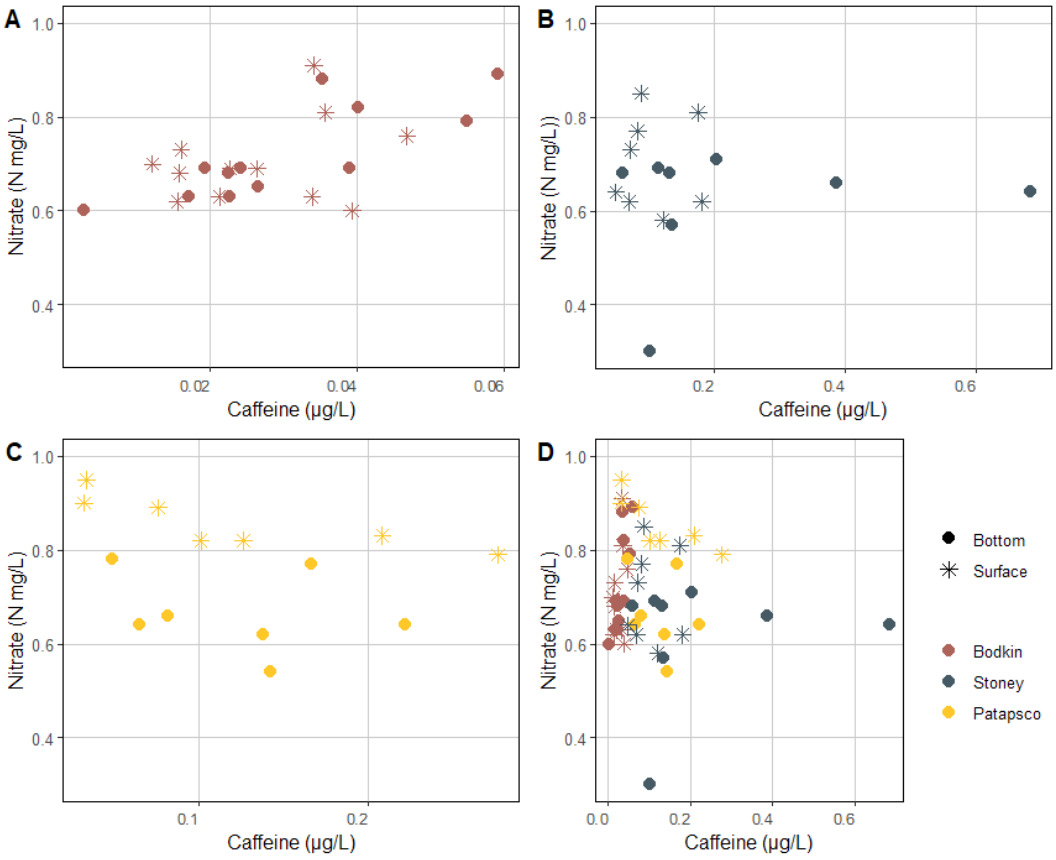



**Figure 32 Caffeine versus Nitrate across Anne Arundel County sampling sites**

Nitrate and caffeine concentrations were compared in surface water and water near the bottom of the water column. Figure 32D shows all site values, no overarching trends were observed. Septic dominated Bodkin Creek (Figure 32A) a moderate positive trend can be observed, with caffeine values clustered between 0.02-0.4 μg/L and nitrate clustered between 0.6-0.1 N mg/L. Results of Spearman's rank correlation did not agreed with these findings of a positive significant correlation (p-value= 0.44).

Sewer dominated Stoney Creek (Figure 32 B) showed no observable trends, with Stoney Creek nitrate values majority between 0.5-0.9 N mg/L, with caffeine concentrations between 0.0-0.2 μg/L. Spearman's rank correlation agreed with these findings of no significance (p-value = 0.95). The Patapsco River showed no correlation, with Patapsco River nitrate values majority between 0.5-0.9 N mg/L, with caffeine concentrations between 0.0-0.3 μg/L. Results of Spearman's rank correlation disagreed with these findings of no significant correlation and observed a significant negative correlation ($r_s$ value= -0.81, p-value= 0.02).

Within the Anne Arundel sites correlation varied greatly with compound and location. Generally septic dominated Bodkin Creek showed strong correlation between nitrate and Ace-K. Stoney Creek showed no correlation between nitrate with caffeine, sucralose or Ace-K. Within the Patapsco River significant negative correlations between nitrate with Ace-K and caffeine. No site showed a strong correlation between nitrate and sucralose.

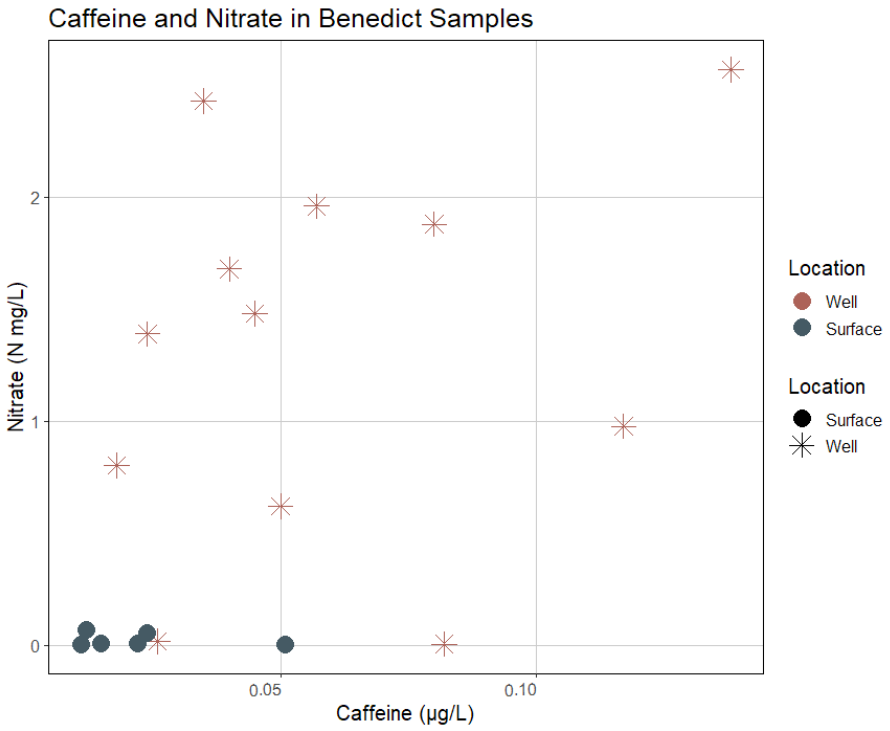



**Figure 33 Relationship between caffeine and NO3- concentrations in well and surface water samples from Benedict sites.**

Note: Well samples are red * and surface water samples are grey circles.

Where there was no correlation between sucralose and nitrate concentrations in surface water samples from rural Benedict, there was a strong moderate positive in groundwater samples (Figure 33). This correlation is inverse of that reported in Whitall et al., [2021], but among the first relationships demonstrated for groundwater. The close correlation in groundwater samples indicates that both caffeine and nitrate come from similar sources, probably septic systems as there is little agriculture in the area. Yet, further study is still needed to confirm such suggestions (e.g. $\delta^{18}O$ vs. $\delta^{15}N$ ratios and microbial indicator). Green et al., [2005] estimated that in this part of the Mid-Atlantic region, there is a low risk of nitrogen pollution in shallow groundwater. However, across the bay, in the agricultural dominated Eastern Shore of Maryland, nitrate in groundwater commonly exceeds 3 mg/L [Greene et al., 2005]. Additionally, low nitrate

values accompanied by elevated caffeine to sucralose ratios suggests a well-functioning septic system that is not designed to remove PPCP/AS but efficiently removes nitrate. In groundwater, N sources seem to be more homogeneous sources, as observed in this study by the relatively strong correlation between N and contaminants such as caffeine. This correlation also encourages further studies about nitrogen and PPCP sources and sinks in groundwater.

In earlier studies, significant negative relationships between total nitrogen and sucralose and caffeine have been observed [Oppenheimer et al., 2011; Whitall et al., 2021] and theoretically attributed to biological processing (e.g., conversion of urea to ammonium to nitrate or uptake by algae) [Pajares and Ramos, 2019; Whitall et al., 2021]. According to Whitall et al., [2021] this trend was more substantial in freshwater streams than in marine waters. Further study is needed to fully understand the relationship between nitrogen and PPCP and AS in estuarine environments.

*4.3.3 Relationships among contaminants*

Varied sources and degradation types of PPCP and AS complicate contaminants correlation assessments [Hedgespeth et al., 2012; Du et al., 2014]. Chemical transformation during downstream transport contributes to variability as well as multiple sources of PPCP & AS contamination (e.g. septic systems, land-applied biosolids, and combined sewer overflows [Fairbairn David, 2016; Zhang et al., 2022].

Confounding factors such as septic systems, land-applied biosolids, and combined sewer overflows have all been used to explain weak or non-existent trends between PPCP, nutrients, and environmental parameters [Shala and Foster, 2010; Bernot et al., 2016]. Likewise, associations of PPCP concentrations with seasonal factors such as temperature, or precipitation are often insignificant or inconsistent within or between study areas [Shala and Foster, 2010; Veach and Bernot, 2011].

#### *4.3.3.1 Correlations between PPCP/AS and water quality parameters commonly associated with human waste contamination*

The relationships between PPCP and AS concentrations and water quality parameters were examined using a Spearman's rho correlation matrix (Table 13).

Within Stoney Creek surface water samples there were no significant correlations between any PPCP or AS and nutrients and other water quality parameters (e.g. temperature, salinity, dissolved oxygen or pH), with the exception of a strong positive correlation between DEET and particulate carbon ($r_s$=0.73, p-value=0.03) (Table 13). When comparing PPCP and AS detected in Stoney Creek to each other, several positive correlations are observed. Strong positive correlations were found between caffeine and carbamazepine, caffeine and sucralose, carbamazepine and sucralose, DEET and sucralose, and diclofenac and sulfamethoxazole ($r_s \geq 0.71$, p-value$\leq$0.05) (Table 13). Strong positive correlations between liable compounds (e.g. caffeine) and conservative compounds (e.g. sucralose) may indicate that there is continual release of PPCP and AS to water bodies associated with wastewater.

**Table 13 Relationships between PPCP and AS concentrations and water quality parameters for Stoney Creek surface samples**

| | Ace-K | | Acetaminophen | | Caffeine | | Carbamazepine | | DEET | |
|---|---|---|---|---|---|---|---|---|---|---|
| | r | p-value | r | p-value | r | p-value | r | p-value | r | p-value |
| Acetaminophen | 0 | 1 | 1 | NA | 0.2 | 0.74706 | -0.1 | 0.87289 | 0.6 | 0.28476 |
| Sulfamethoxazole | 0.54762 | 0.16003 | -0.6 | 0.28476 | -0.04762 | 0.91085 | 0.14286 | 0.73576 | -0.2381 | 0.57016 |
| Atorvastatin | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| Caffeine | 0.45238 | 0.2604 | 0.2 | 0.74706 | 1 | NA | **0.95238** | **0.00026** | 0.66667 | 0.07099 |
| Carbamazepine | 0.5 | 0.20703 | -0.1 | 0.87289 | **0.95238** | **0.00026** | 1 | NA | 0.59524 | 0.11953 |
| DEET | 0.16667 | 0.69324 | 0.6 | 0.28476 | 0.66667 | 0.07099 | 0.59524 | 0.11953 | 1 | NA |
| Didofenac | 0.45644 | 0.25562 | -0.44721 | 0.45018 | 0.18257 | 0.6652 | 0.36515 | 0.37377 | -0.03912 | 0.92672 |
| Paraxanthine | 0.2381 | 0.57016 | 0.7 | 0.18812 | -0.2619 | 0.53092 | -0.16667 | 0.69324 | -0.02381 | 0.95537 |
| Sucralose | 0.61905 | 0.10173 | 0.4 | 0.50463 | **0.92857** | **0.00086** | **0.92857** | **0.00086** | **0.71429** | **0.04653** |
| Ace-K | 1 | NA | 0 | 1 | 0.45238 | 0.2604 | 0.5 | 0.20703 | 0.16667 | 0.69324 |
| Temperature °C | -0.14286 | 0.73576 | 0.2 | 0.74706 | -0.07143 | 0.86653 | 0 | 1 | 0.42857 | 0.2894 |
| salinity ppt | 0.30952 | 0.45564 | -0.2 | 0.74706 | 0.42857 | 0.2894 | 0.5 | 0.20703 | 0.61905 | 0.10173 |
| DO (mg/L) | 0.09524 | 0.82251 | 0.7 | 0.18812 | -0.04762 | 0.91085 | -0.14286 | 0.73576 | 0.02381 | 0.95537 |
| pH | 0.07143 | 0.86653 | 0.1 | 0.87289 | 0.02381 | 0.95537 | 0.09524 | 0.82251 | 0.2381 | 0.57016 |
| $NH_4$ (mg/L) | 0.03683 | 0.93101 | -0.56429 | 0.32172 | -0.20869 | 0.61992 | -0.01228 | 0.97699 | -0.02455 | 0.95398 |
| $NO_{23}$ (mg/L) | 0.08383 | 0.84355 | 0.56429 | 0.32172 | 0.02395 | 0.95511 | -0.08383 | 0.84355 | -0.26348 | 0.52837 |
| TDN (mg/L) | 0.0482 | 0.90977 | -0.2 | 0.74706 | 0.13254 | 0.75438 | 0.07229 | 0.86492 | -0.37352 | 0.36206 |
| $PO_4$ (mg/L) | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| TDP (mg/L) | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| DOC (mg/L) | -0.35714 | 0.38512 | 0.2 | 0.74706 | -0.30952 | 0.45564 | -0.28571 | 0.49273 | 0.19048 | 0.6514 |
| TOC (mg/L) | -0.33333 | 0.41975 | 0.1 | 0.87289 | -0.35714 | 0.38512 | -0.35714 | 0.38512 | 0.07143 | 0.86653 |
| PN (mg/L) | -0.11905 | 0.77889 | 0.6 | 0.28476 | -0.33333 | 0.41975 | -0.30952 | 0.45564 | 0.38095 | 0.35181 |
| PC (mg/L) | 0.28571 | 0.49273 | 0.5 | 0.391 | 0.16667 | 0.69324 | 0.19048 | 0.6514 | **0.7381** | **0.03655** |
| PP (mg/L) | 0.65465 | 0.07814 | 0 | 1 | 0.10911 | 0.79704 | 0.21822 | 0.60365 | 0.21822 | 0.60365 |

| | Diclofenac | | Paraxanthine | | Sucralose | | Sulfamethoxazole | |
|---|---|---|---|---|---|---|---|---|
| | r | p-value | r | p-value | r | p-value | r | p-value |
| Acetaminophen | -0.44721 | 0.45018 | 0.7 | 0.18812 | 0.4 | 0.50463 | -0.6 | 0.28476 |
| Sulfamethoxazole | **0.91287** | **0.00155** | 0.30952 | 0.45564 | 0.07143 | 0.86653 | 1 | NA |
| Atorvastatin | NA | NA | NA | NA | NA | NA | NA | NA |
| Caffeine | 0.18257 | 0.6652 | -0.2619 | 0.53092 | **0.92857** | **0.00086** | -0.04762 | 0.91085 |
| Carbamazepine | 0.36515 | 0.37377 | -0.16667 | 0.69324 | **0.92857** | **0.00086** | 0.14286 | 0.73576 |
| DEET | -0.03912 | 0.92672 | -0.02381 | 0.95537 | **0.71429** | **0.04653** | -0.2381 | 0.57016 |
| Didofenac | 1 | NA | 0.37819 | 0.35561 | 0.27386 | 0.51161 | **0.91287** | **0.00155** |
| Paraxanthine | 0.37819 | 0.35561 | 1 | NA | 0.04762 | 0.91085 | 0.30952 | 0.45564 |
| Sucralose | 0.27386 | 0.51161 | 0.04762 | 0.91085 | 1 | NA | 0.07143 | 0.86653 |
| Ace-K | 0.45644 | 0.25562 | 0.2381 | 0.57016 | 0.61905 | 0.10173 | 0.54762 | 0.16003 |
| Temperature °C | 0.07825 | 0.85389 | 0.45238 | 0.2604 | 0.16667 | 0.69324 | 0 | 1 |
| salinity ppt | 0.27386 | 0.51161 | -0.16667 | 0.69324 | 0.52381 | 0.18272 | 0.28571 | 0.49273 |
| DO (mg/L) | -0.20866 | 0.61998 | -0.07143 | 0.86653 | -0.14286 | 0.73576 | -0.16667 | 0.69324 |
| pH | 0.2869 | 0.49085 | -0.16667 | 0.69324 | -0.04762 | 0.91085 | 0.30952 | 0.45564 |
| $NH_4$ (mg/L) | 0.30257 | 0.46636 | 0.38055 | 0.35237 | 0.03683 | 0.93101 | 0.356 | 0.38676 |
| $NO_{23}$ (mg/L) | -0.17711 | 0.6748 | -0.04791 | 0.91032 | -0.11976 | 0.77758 | -0.2036 | 0.62867 |
| TDN (mg/L) | -0.066 | 0.87662 | -0.36147 | 0.37896 | -0.10844 | 0.79826 | -0.08434 | 0.8426 |
| $PO_4$ (mg/L) | NA | NA | NA | NA | NA | NA | NA | NA |
| TDP (mg/L) | NA | NA | NA | NA | NA | NA | NA | NA |
| DOC (mg/L) | 0.07825 | 0.85389 | 0.40476 | 0.31989 | -0.14286 | 0.73576 | 0.02381 | 0.95537 |
| TOC (mg/L) | -0.01304 | 0.97555 | 0.38095 | 0.35181 | -0.19048 | 0.6514 | -0.02381 | 0.95537 |
| PN (mg/L) | -0.27386 | 0.51161 | 0.38095 | 0.35181 | -0.14286 | 0.73576 | -0.21429 | 0.61034 |
| PC (mg/L) | -0.07825 | 0.85389 | 0.33333 | 0.41975 | 0.40476 | 0.31989 | -0.07143 | 0.86653 |
| PP (mg/L) | 0 | 1 | 0.10911 | 0.79704 | 0.32733 | 0.42869 | 0.21822 | 0.60365 |

Note: Spearman's correlation matrix. R values greater than 0.60 are significant at $p < 0.05$ (shown in bold). Atorvastatin, cotinine, and ibuprofen were omitted to the lack of data necessary to perform the Spearman's correlation.

In surface water samples from the Patapsco River, a strong relationship between PPCP/AS and nutrients and other water quality parameters was observed (Table 14). A strong negative relationship was observed between Ace-K and nitrate, caffeine and total dissolved phosphorus, caffeine and phosphate, diclofenac and nitrate, and paraxanthine and nitrate ($r_s \geq 0.76$, $r_s \geq -0.7$, p-value$\leq 0.05$) (Table 14). This negative relationship may indicate that PPCP/AS and nutrients have different sources. It is noteworthy that liable compounds only correlated with nitrate and conservative compounds with phosphorus; further study is needed to understand this dynamic.

Several PPCP and AS correlated with water quality parameters other than nutrients. A significant positive relationship was observed between acetaminophen and salinity, atorvastatin and salinity, caffeine and salinity, caffeine and dissolved oxygen, diclofenac and salinity, paraxanthine and salinity, and paraxanthine and dissolved oxygen ($r_s \geq 0.7$, p-value$\leq 0.05$) (Table 14), which may be explained by different water sources along the Patapsco River. Water sources in the river range from freshwater at the upper reach to tidal water in the lower reach, by the Chesapeake Bay. Several positive correlations were observed among the PPCP and AS detected in the Patapsco River (Table 14). Strong positive correlations were found between Ace-K and paraxanthine, atorvastatin and caffeine, caffeine and diclofenac, caffeine and paraxanthine, and carbamazepine and sulfamethoxazole ($r_s \geq 0.71$, p-value$\leq 0.05$) (Table 14).

**Table 14 Relationships between PPCP and AS concentrations and water quality parameters for Patapsco River surface samples**

| | Ace-K | | Acetaminophen | | Atorvastatin | | Caffeine | | Carbamazepine | |
|---|---|---|---|---|---|---|---|---|---|---|
| | r | p-value | r | p-value | r | p-value | r | p-value | r | p-value |
| Acetaminophen | 0.10 | 0.87 | 1.00 | NA | 1.00 | 0.00 | 0.70 | 0.19 | -0.20 | 0.75 |
| Sulfamethoxazole | 0.30 | 0.62 | 0.10 | 0.87 | 0.10 | 0.87 | 0.60 | 0.28 | **0.90** | **0.04** |
| Atorvastatin | 0.67 | 0.10 | 1.00 | 0.00 | 1.00 | NA | **0.88** | **0.01** | 0.23 | 0.61 |
| Caffeine | 0.50 | 0.21 | 0.70 | 0.19 | **0.88** | **0.01** | 1.00 | NA | 0.64 | 0.09 |
| Carbamazepine | 0.62 | 0.10 | -0.20 | 0.75 | 0.23 | 0.61 | 0.64 | 0.09 | 1.00 | NA |
| DEET | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| Diclofenac | 0.55 | 0.16 | 0.22 | 0.72 | 0.74 | 0.06 | **0.85** | **0.01** | 0.60 | 0.12 |
| Paraxanthine | **0.71** | **0.05** | 0.70 | 0.19 | **0.88** | **0.01** | **0.93** | **0.00** | 0.64 | 0.09 |
| Sucralose | 0.62 | 0.10 | -0.20 | 0.75 | 0.23 | 0.61 | 0.64 | 0.09 | 1.00 | 0.00 |
| Ace-K | 1.00 | NA | 0.10 | 0.87 | 0.67 | 0.10 | 0.50 | 0.21 | 0.62 | 0.10 |
| Temperature °C | 0.20 | 0.63 | -0.82 | 0.09 | 0.35 | 0.45 | 0.66 | 0.08 | 0.57 | 0.14 |
| salinity ppt | 0.40 | 0.32 | **0.90** | **0.04** | **0.95** | **0.00** | **0.98** | **0.00** | 0.48 | 0.23 |
| DO (mg/L) | 0.45 | 0.26 | -0.30 | 0.62 | 0.52 | 0.23 | **0.79** | **0.02** | 0.69 | 0.06 |
| pH | 0.24 | 0.57 | -0.20 | 0.75 | 0.56 | 0.19 | 0.69 | 0.06 | 0.40 | 0.32 |
| $NH_4$ (mg/L) | 0.04 | 0.93 | **0.97** | **0.00** | 0.61 | 0.14 | 0.41 | 0.32 | -0.17 | 0.68 |
| $NO_{23}$ (mg/L) | **-0.71** | **0.05** | -0.21 | 0.73 | -0.72 | 0.07 | -0.81 | 0.02 | -0.58 | 0.13 |
| TDN (mg/L) | -0.04 | 0.93 | 0.87 | 0.05 | 0.47 | 0.29 | -0.05 | 0.91 | -0.59 | 0.12 |
| $PO_4$ (mg/L) | -0.33 | 0.43 | NA | NA | -0.51 | 0.24 | **-0.73** | **0.04** | -0.51 | 0.19 |
| TDP (mg/L) | -0.25 | 0.55 | NA | NA | -0.51 | 0.24 | **-0.76** | **0.03** | -0.50 | 0.20 |
| DOC (mg/L) | 0.26 | 0.53 | 0.40 | 0.50 | **0.77** | **0.04** | **0.76** | **0.03** | 0.31 | 0.46 |
| TOC (mg/L) | 0.52 | 0.19 | 0.82 | 0.09 | **0.93** | **0.00** | **0.99** | **0.00** | 0.58 | 0.13 |
| PN (mg/L) | 0.60 | 0.12 | 0.87 | 0.05 | **0.95** | **0.00** | **0.89** | **0.00** | 0.44 | 0.27 |
| PC (mg/L) | 0.53 | 0.18 | 0.80 | 0.10 | **0.92** | **0.00** | **0.89** | **0.00** | 0.42 | 0.30 |
| PP (mg/L) | 0.27 | 0.51 | **0.95** | **0.01** | **0.93** | **0.00** | **0.84** | **0.01** | 0.20 | 0.64 |

| | DEET | | Diclofenac | | Paraxanthine | | Sucralose | | Sulfamethoxazole | |
|---|---|---|---|---|---|---|---|---|---|---|
| | r | p-value | r | p-value | r | p-value | r | p-value | r | p-value |
| Acetaminophen | -0.50 | 0.39 | 0.22 | 0.72 | 0.70 | 0.19 | -0.20 | 0.75 | 0.10 | 0.87 |
| Sulfamethoxazole | 0.60 | 0.28 | **0.89** | **0.04** | 0.60 | 0.28 | **0.90** | **0.04** | 1.00 | NA |
| Atorvastatin | -0.34 | 0.45 | 0.74 | 0.06 | **0.88** | **0.01** | 0.23 | 0.61 | 0.10 | 0.87 |
| Caffeine | -0.29 | 0.49 | **0.85** | **0.01** | **0.93** | **0.00** | 0.64 | 0.09 | 0.60 | 0.28 |
| Carbamazepine | 0.36 | 0.39 | 0.60 | 0.12 | 0.64 | 0.09 | 1.00 | 0.00 | **0.90** | **0.04** |
| DEET | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| Diclofenac | -0.30 | 0.47 | 1.00 | NA | **0.85** | **0.01** | 0.60 | 0.12 | **0.89** | **0.04** |
| Paraxanthine | -0.12 | 0.78 | **0.85** | **0.01** | 1.00 | NA | 0.64 | 0.09 | 0.60 | 0.28 |
| Sucralose | 0.36 | 0.39 | 0.60 | 0.12 | 0.64 | 0.09 | 1.00 | NA | **0.90** | **0.04** |
| Ace-K | 0.19 | 0.65 | 0.55 | 0.16 | **0.71** | **0.05** | 0.62 | 0.10 | 0.30 | 0.62 |
| Temperature °C | -0.17 | 0.69 | 0.68 | 0.06 | 0.59 | 0.13 | 0.57 | 0.14 | -0.05 | 0.93 |
| salinity ppt | -0.38 | 0.35 | **0.80** | **0.02** | **0.90** | **0.00** | 0.48 | 0.23 | 0.30 | 0.62 |
| DO (mg/L) | 0.00 | 1.00 | 0.65 | 0.08 | **0.79** | **0.02** | 0.69 | 0.06 | 0.00 | 1.00 |
| pH | -0.14 | 0.74 | 0.60 | 0.12 | 0.69 | 0.06 | 0.40 | 0.32 | -0.40 | 0.50 |
| $NH_4$ (mg/L) | -0.44 | 0.27 | 0.18 | 0.67 | 0.39 | 0.34 | -0.17 | 0.68 | 0.21 | 0.74 |
| $NO_{23}$ (mg/L) | 0.28 | 0.51 | **-0.86** | **0.01** | **-0.81** | **0.02** | -0.58 | 0.13 | -0.26 | 0.67 |
| TDN (mg/L) | -0.15 | 0.73 | -0.15 | 0.72 | 0.06 | 0.89 | -0.59 | 0.12 | -0.21 | 0.74 |
| $PO_4$ (mg/L) | 0.03 | 0.94 | -0.66 | 0.08 | -0.65 | 0.08 | -0.51 | 0.19 | NA | NA |
| TDP (mg/L) | 0.13 | 0.77 | -0.66 | 0.07 | -0.63 | 0.09 | -0.50 | 0.20 | NA | NA |
| DOC (mg/L) | -0.29 | 0.49 | **0.85** | **0.01** | **0.76** | **0.03** | 0.31 | 0.46 | 0.30 | 0.62 |
| TOC (mg/L) | -0.27 | 0.53 | **0.84** | **0.01** | **0.95** | **0.00** | 0.58 | 0.13 | 0.46 | 0.43 |
| PN (mg/L) | -0.23 | 0.59 | **0.76** | **0.03** | **0.96** | **0.00** | 0.44 | 0.27 | 0.10 | 0.87 |
| PC (mg/L) | -0.25 | 0.55 | 0.71 | 0.05 | **0.92** | **0.00** | 0.42 | 0.30 | -0.10 | 0.87 |
| PP (mg/L) | -0.42 | 0.30 | 0.68 | 0.07 | **0.78** | **0.02** | 0.20 | 0.64 | -0.16 | 0.80 |

Note: Spearman's correlation matrix. R values greater than 0.60 are significant at $p < 0.05$ (shown in bold). Ibuprofen was omitted to the lack of data necessary to perform the Spearman's correlation

Within Bodkin Creek, few correlations were observed between PPCP/AS, nutrients and other water quality parameters (Table 15). The only correlations between a PPCP/AS and nutrients or other water quality parameters were observed between sulfamethoxazole and pH ($r_s$=-0.85, p-value<0.001) (Table 15) and sulfamethoxazole and ammonium ($r_s$=0.61, p-value<0.05) (Table 18). Of all the sites sampled, Bodkin Creek was the only one where contaminants were associated with pH or ammonium.

When assessing relationships among PPCP and AS detected in Bodkin Creek, several positive correlations were observed. Strong positive correlations were found between caffeine and paraxanthine, carbamazepine and sucralose, and carbamazepine and DEET ($r_s \geq 0.62$, p-value$\leq$0.05) (Table 15). Varied correlations in Patapsco and Bodkin Creek, Stoney Creek reflect varied stream mixing and wastewater sources; a similar conclusion is reflected in Fairbairn et al., [2016].

**Table 15 Relationships between PPCP and AS concentrations and water quality parameters for Bodkin Creek surface samples**

| | Ace-K | | Caffeine | | Carbamazepine | | DEET | |
|---|---|---|---|---|---|---|---|---|
| | r | p-value | r | p-value | r | p-value | r | p-value |
| Acetaminophen | NA | NA | NA | NA | NA | NA | NA | NA |
| Sulfamethoxazole | -0.21 | 0.53 | -0.02 | 0.96 | 0.13 | 0.68 | 0.24 | 0.45 |
| Atorvastatin | NA | NA | NA | NA | NA | NA | NA | NA |
| Caffeine | -0.37 | 0.26 | 1 | NA | 0.32 | 0.31 | 0.01 | 0.97 |
| Carbamazepine | 0.07 | 0.83 | 0.32 | 0.31 | 1 | NA | **0.62** | **0.03** |
| DEET | 0.29 | 0.39 | 0.01 | 0.97 | **0.62** | **0.03** | 1 | NA |
| Diclofenac | 0.19 | 0.59 | 0.00 | 0.99 | 0.00 | 0.99 | 0.32 | 0.33 |
| Paraxanthine | 0.10 | 0.77 | **0.75** | **0.01** | 0.31 | 0.32 | 0.07 | 0.83 |
| Sucralose | 0.22 | 0.52 | 0.34 | 0.29 | **0.91** | **0.00** | 0.50 | 0.10 |
| Ace-K | 1 | NA | -0.37 | 0.26 | 0.07 | 0.83 | 0.29 | 0.39 |
| Temperature °C | 0.25 | 0.46 | -0.38 | 0.23 | 0.24 | 0.46 | 0.27 | 0.40 |
| salinity ppt | 0.29 | 0.38 | -0.29 | 0.36 | -0.09 | 0.77 | -0.04 | 0.90 |
| DO (mg/L) | 0.28 | 0.40 | -0.03 | 0.91 | -0.04 | 0.90 | -0.32 | 0.31 |
| pH | 0.34 | 0.31 | 0.03 | 0.93 | -0.20 | 0.53 | -0.38 | 0.22 |
| $NH_4$ (mg/L) | -0.26 | 0.43 | 0.29 | 0.36 | 0.47 | 0.13 | 0.32 | 0.31 |
| $NO_{23}$ (mg/L) | **-0.63** | **0.04** | 0.25 | 0.44 | -0.19 | 0.55 | -0.40 | 0.20 |
| TDN (mg/L) | -0.48 | 0.14 | 0.39 | 0.22 | -0.37 | 0.23 | -0.47 | 0.12 |
| $PO_4$ (mg/L) | NA | NA | NA | NA | NA | NA | NA | NA |
| TDP (mg/L) | 0.40 | 0.22 | -0.39 | 0.21 | -0.48 | 0.11 | -0.22 | 0.50 |
| DOC (mg/L) | 0.29 | 0.39 | -0.30 | 0.34 | 0.28 | 0.38 | 0.19 | 0.56 |
| TOC (mg/L) | 0.30 | 0.37 | -0.26 | 0.42 | 0.17 | 0.60 | 0.15 | 0.63 |
| PN (mg/L) | 0.41 | 0.21 | -0.26 | 0.42 | 0.22 | 0.50 | 0.39 | 0.22 |
| PC (mg/L) | 0.29 | 0.39 | -0.20 | 0.53 | 0.10 | 0.76 | 0.04 | 0.90 |
| PP (mg/L) | 0.43 | 0.19 | 0.20 | 0.54 | -0.05 | 0.87 | 0.34 | 0.28 |

| | Diclofenac | | Paraxanthine | | Sucralose | | Sulfamethoxazole | |
|---|---|---|---|---|---|---|---|---|
| | r | p-value | r | p-value | r | p-value | r | p-value |
| Acetaminophen | NA | NA | NA | NA | NA | NA | NA | NA |
| Sulfamethoxazole | -0.27 | 0.43 | -0.27 | 0.39 | -0.15 | 0.65 | 1.00 | NA |
| Atorvastatin | NA | NA | NA | NA | NA | NA | NA | NA |
| Caffeine | 0.00 | 0.99 | **0.75** | **0.01** | **0.34** | **0.29** | -0.02 | 0.96 |
| Carbamazepine | 0.00 | 0.99 | 0.31 | 0.32 | **0.91** | **0.00** | 0.13 | 0.68 |
| DEET | 0.32 | 0.33 | 0.07 | 0.83 | 0.50 | 0.10 | 0.24 | 0.45 |
| Diclofenac | 1.00 | NA | 0.22 | 0.52 | 0.07 | 0.83 | -0.27 | 0.43 |
| Paraxanthine | 0.22 | 0.52 | 1.00 | NA | 0.48 | 0.11 | -0.27 | 0.39 |
| Sucralose | 0.07 | 0.83 | 0.48 | 0.11 | 1.00 | NA | -0.15 | 0.65 |
| Ace-K | 0.19 | 0.59 | 0.10 | 0.77 | 0.22 | 0.52 | -0.21 | 0.53 |
| Temperature °C | -0.21 | 0.53 | -0.55 | 0.07 | 0.08 | 0.81 | 0.39 | 0.21 |
| salinity ppt | 0.06 | 0.86 | 0.09 | 0.78 | -0.02 | 0.94 | -0.12 | 0.71 |
| DO (mg/L) | 0.00 | 0.99 | 0.14 | 0.66 | 0.17 | 0.60 | -0.57 | 0.05 |
| pH | 0.25 | 0.46 | 0.35 | 0.27 | 0.11 | 0.73 | **-0.85** | **0.00** |
| $NH_4$ (mg/L) | -0.15 | 0.66 | -0.04 | 0.91 | 0.20 | 0.54 | **0.61** | **0.04** |
| $NO_{23}$ (mg/L) | 0.23 | 0.49 | 0.17 | 0.59 | -0.10 | 0.75 | -0.30 | 0.34 |
| TDN (mg/L) | 0.30 | 0.37 | 0.32 | 0.31 | -0.21 | 0.51 | -0.47 | 0.12 |
| $PO_4$ (mg/L) | NA | NA | NA | NA | NA | NA | NA | NA |
| TDP (mg/L) | 0.11 | 0.75 | -0.22 | 0.50 | -0.39 | 0.21 | -0.48 | 0.11 |
| DOC (mg/L) | -0.23 | 0.50 | -0.31 | 0.33 | 0.06 | 0.86 | 0.57 | 0.05 |
| TOC (mg/L) | -0.32 | 0.33 | -0.02 | 0.95 | 0.14 | 0.66 | 0.08 | 0.79 |
| PN (mg/L) | -0.22 | 0.52 | -0.36 | 0.24 | -0.01 | 0.98 | 0.32 | 0.31 |
| PC (mg/L) | -0.32 | 0.33 | -0.42 | 0.17 | -0.01 | 0.97 | 0.45 | 0.14 |
| PP (mg/L) | **0.76** | **0.01** | 0.55 | 0.06 | 0.08 | 0.80 | -0.46 | 0.13 |

Note: Spearman's correlation matrix. R values greater than 0.60 are significant at $p < 0.05$ (shown in bold). Acetaminophen, atorvastatin, ibuprofen, and cotinine were omitted to the lack of data necessary to perform the Spearman's correlation

Within Benedict, strong relationships between PPCP/AS, nutrients and other water quality parameters were observed for surface water samples (Table 16). A strong negative relationship was observed between carbamazepine and organic nitrogen, carbamazepine and phosphate, carbamazepine and total dissolved phosphate, sucralose and organic nitrogen, sucralose and phosphate, sucralose and total dissolved phosphate, sulfamethoxazole and organic nitrogen, sulfamethoxazole and phosphate, and sulfamethoxazole and total dissolved phosphate ($r_s \geq -0.64$, p-value$\leq 0.04$) (Table 16).

Among all the PPCP and AS detected in Benedict, strong positive correlations were found between carbamazepine and sucralose, carbamazepine and sulfamethoxazole, sulfamethoxazole and sucralose, and sulfamethoxazole and DEET ($r_s \geq 0.82$, p-value$\leq 0.00$) (Table 16)

**Table 16 Relationships between PPCP and AS concentrations and water quality parameters for Benedict surface samples**

| | Caffeine | | Carbamazepine | | DEET | |
|---|---|---|---|---|---|---|
| | r | p-value | r | p-value | r | p-value |
| Sucralose | 0.49 | 0.33 | **0.96** | **0.00** | 0.50 | 0.67 |
| Sulfamethoxazole | 0.03 | 0.96 | **0.82** | **0.00** | -1.00 | 0.00 |
| Paraxanthine | NA | NA | NA | NA | NA | NA |
| Dichlorvos | NA | NA | NA | NA | NA | NA |
| DEET | NA | NA | 0.50 | 0.67 | 1.00 | NA |
| Carbamazepine | 0.43 | 0.40 | 1.00 | NA | 0.50 | 0.67 |
| Caffeine | 1.00 | NA | 0.43 | 0.40 | NA | NA |
| $NH_4$ | -0.39 | 0.44 | -0.19 | 0.51 | 0.87 | 0.33 |
| $NO_2$ | 0.03 | 0.95 | -0.11 | 0.70 | 0.50 | 0.67 |
| $NO_{23}$- | -0.23 | 0.66 | -0.11 | 0.70 | 1.00 | 0.00 |
| TDN | -0.55 | 0.26 | -0.39 | 0.17 | 1.00 | 0.00 |
| ON | -0.66 | 0.16 | **-0.74** | **0.00** | -0.50 | 0.67 |
| $PO_4$ | -0.66 | 0.16 | **-0.64** | **0.01** | 0.50 | 0.67 |
| TDP | -0.60 | 0.21 | **-0.63** | **0.02** | 0.50 | 0.67 |

| | Sucralose | | Sulfamethoxazole | |
|---|---|---|---|---|
| | r | p-value | r | p-value |
| Sucralose | 1.00 | NA | **0.80** | **0.00** |
| Sulfamethoxazole | **0.80** | **0.00** | 1.00 | NA |
| Paraxanthine | NA | NA | NA | NA |
| Dichlorvos | NA | NA | NA | NA |
| DEET | 0.50 | 0.67 | **-1.00** | **0.00** |
| Carbamazepine | **0.96** | **0.00** | **0.82** | **0.00** |
| Caffeine | 0.49 | 0.33 | 0.03 | 0.96 |
| $NH_4$ | -0.15 | 0.61 | -0.06 | 0.87 |
| $NO_2$ | 0.00 | 0.99 | -0.30 | 0.37 |
| $NO_{23}$- | -0.03 | 0.92 | -0.08 | 0.82 |
| TDN | -0.36 | 0.21 | -0.56 | 0.07 |
| ON | **-0.74** | **0.00** | **-0.71** | **0.01** |
| $PO_4$ | **-0.67** | **0.01** | **-0.77** | **0.01** |
| TDP | **-0.65** | **0.01** | **-0.75** | **0.01** |

Note: Spearman's correlation matrix. R values greater than 0.60 are significant at $p < 0.05$ (shown in bold). Paraxanthine and dichlorvos were omitted to the lack of data necessary to perform the Spearman's correlation. Acetaminophen, atorvastatin, ibuprofen, and cotinine were omitted due to numerous non-detects.

In bottom/groundwater samples, strong positive correlations were found between PPCP & AS and TDN in the Patapsco and Benedict samples. The Spearman's correlation matrix values for these samples can be found in Appendix B.

*4.3.3.2 Wastewater freshness indicators*

Caffeine to sucralose ratios have been considered a promising tool to differentiate between sources of treated and untreated wastewater (ex., properly functioning wastewater treatment vs. untreated/poorly treated wastewater) in coastal watersheds [Cantwell et al., 2018] as both caffeine and sucralose are widely used, but only caffeine is readily degradable in wastewater treatment systems. In the US, 30% of adults use sucralose, also known by its brand name Splenda, daily [Sylvetsky and Rother, 2016]. In WWTP, sucralose has been shown to have a low to negative removal efficiency ranging from -41.3–19% [Van Stempvoort et al., 2020]. The poor removal combined with high use makes sucralose a commonly found artificial sweetener in treated wastewater.

While naturally occurring in some plants, untreated sewage is the primary source of caffeine found in rivers and lakes [Sankararamakrishnan and Guo, 2005; Froehner et al., 2010; Froehner et al., 2011]. In natural environments, caffeine has a half-life of 30 days, but with human intervention during activated sludge treatment in an WWTP, that time is reduced to 24 hours at concentrations as high as 6.4 g/L [Edwards et al., 2015; Silva-Filho, 2016]. In WWTP, caffeine has been shown to have a removal efficiency of >99% [Padhye and Huang, 2012; Cantwell et al., 2018]. This high removal efficiency is also reflected in OWTS [Schaider et al., 2017]. Given caffeine's high removal efficiency in wastewater treatment, its persistence in freshwater is a strong indicator of less treated sewage. A high ratio of caffeine to sucralose is potentially indicative of fresh untreated sewage. Sucralose is a common conservative wastewater tracer that is not well removed in WWTP.

The effectiveness of using Ace-K, another conservative sweetener, as a conservative treated waste indicator was examined in this study. Ace-K is a calorie-free artificial sweetener found in drinks (ex., Sugar-free Red Bull and many diet-soft drinks) and foods (ex., Sugar-free

yogurt, and low sugar ice cream). Depending on the WWTP process Ace K is removed at rates between 19 and 99% [Van Stempvoort et al., 2020]  In the most prevalent type of secondary WWT for residential waste (activated sludge and ultraviolet disinfection), the removal efficiency of Ace-K is 20% [Van Stempvoort et al., 2020] . As Ace-K is a conservative human waste indicator, pairing it with caffeine for a freshness indicator may be an option in populations where sucralose is not the prevalent artificial sweetener.

This study also included caffeine to carbamazepine ratios as a wastewater freshness indicator. While carbamazepine is not as ubiquitous as artificial sweeteners, it is frequently detected in WWTP effluents at rates of 50 to 100% [Huerta-Fontela et al., 2010; Rosal et al., 2010; Evgenidou et al., 2015]. Carbamazepine is poorly degraded in WWTP due to its low water-sludge distribution coefficient (1.2 l/kg), which is much lower than the 500 l/kg necessary for significant sorption onto the sludge [Ternes et al., 2004; Dwivedi et al., 2017]. Roberts et al., [2016] described a negative removal efficiency for carbamazepine in WWTP due to a lack of removal capacity and subsequent buildup as this compound is widely used by people. Therefore, carbamazepine is an ideal non-AS conservative tracer candidate to detect human waste pollution.

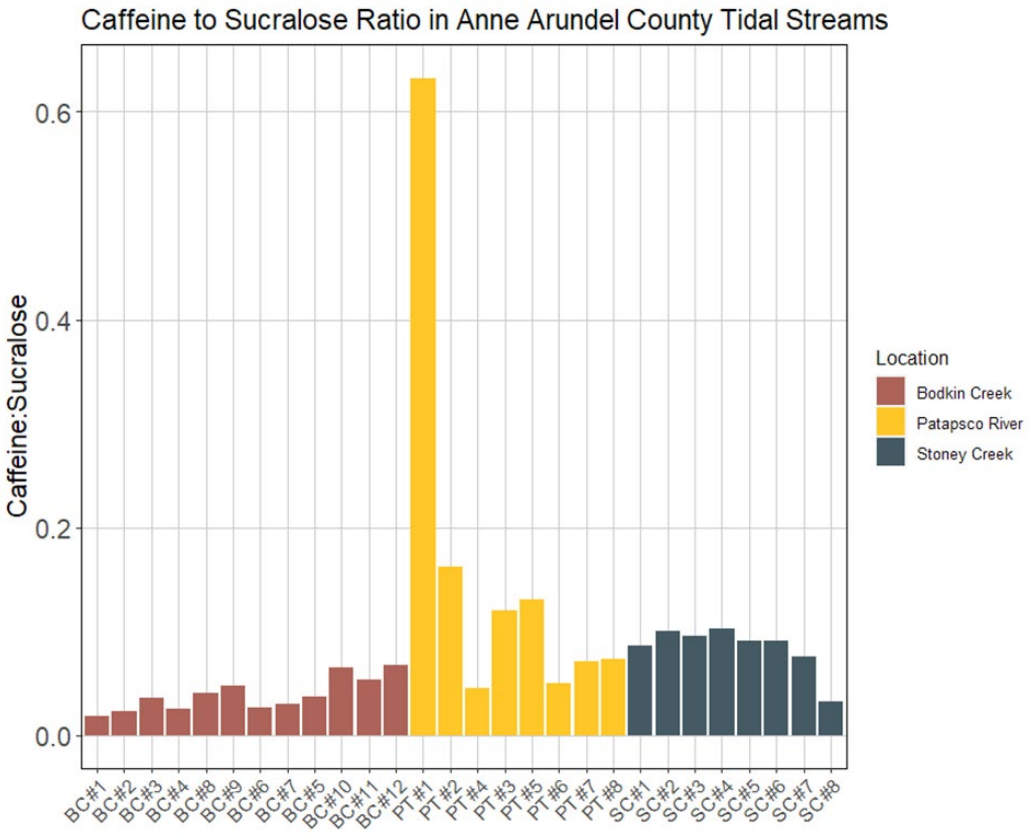



**Figure 34 Caffeine: Sucralose Ratio in Anne Arundel County Sites**

Caffeine to sucralose ratios in the Anne Arundel were consistent across sites with some variation in the PT sites. The low ratios observed indicate that there was more treated wastewater than untreated wastewater discharging into these streams. Cox Creek WWTP's effluent outfall was adjacent to PT# 1. A higher caffeine to sucralose ratio indicates that there was more labile caffeine in the effluent as caffeine is readily degraded in WWTP as opposed to sucralose (Table 1, Chapter 1). Downstream, (i.e. sites PT #2, 3, and 4) dilution of WWTP effluent was the likely cause of elevated ratios.

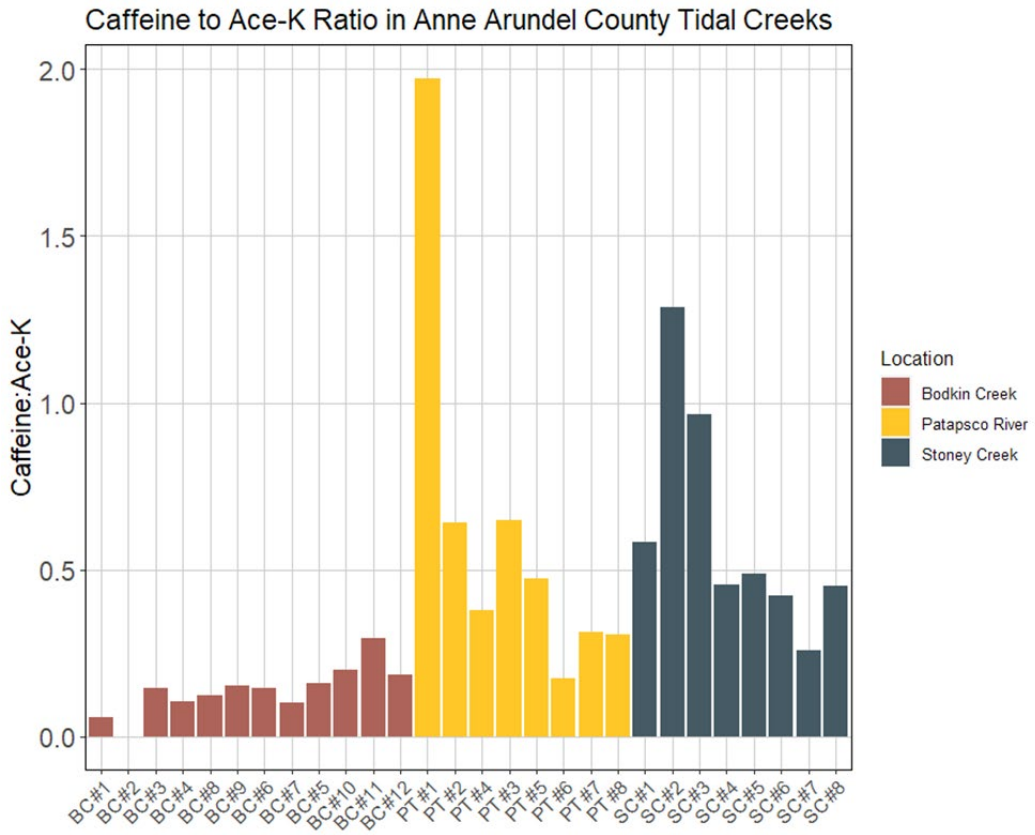



**Figure 35 Caffeine: Ace-K Ratio in Anne Arundel County Sites**

Caffeine to Ace-K ratios in the Patapsco River and Stoney Creek sites were more variable than their sucralose counterparts. Bodkin Creek sites show constant ratios ranging from 0.005 to 0.098. This low ratio indicates that most of the wastewater entering this stream was treated. In the Patapsco site near the WWTP effluent of Cox Creek (PT #1) and in Stoney Creek site 2, the caffeine to sucralose ratio was relatively high, which is indicative of untreated waste. High ratios in downstream Patapsco and Benedict sites were likely due to a dilution effect.

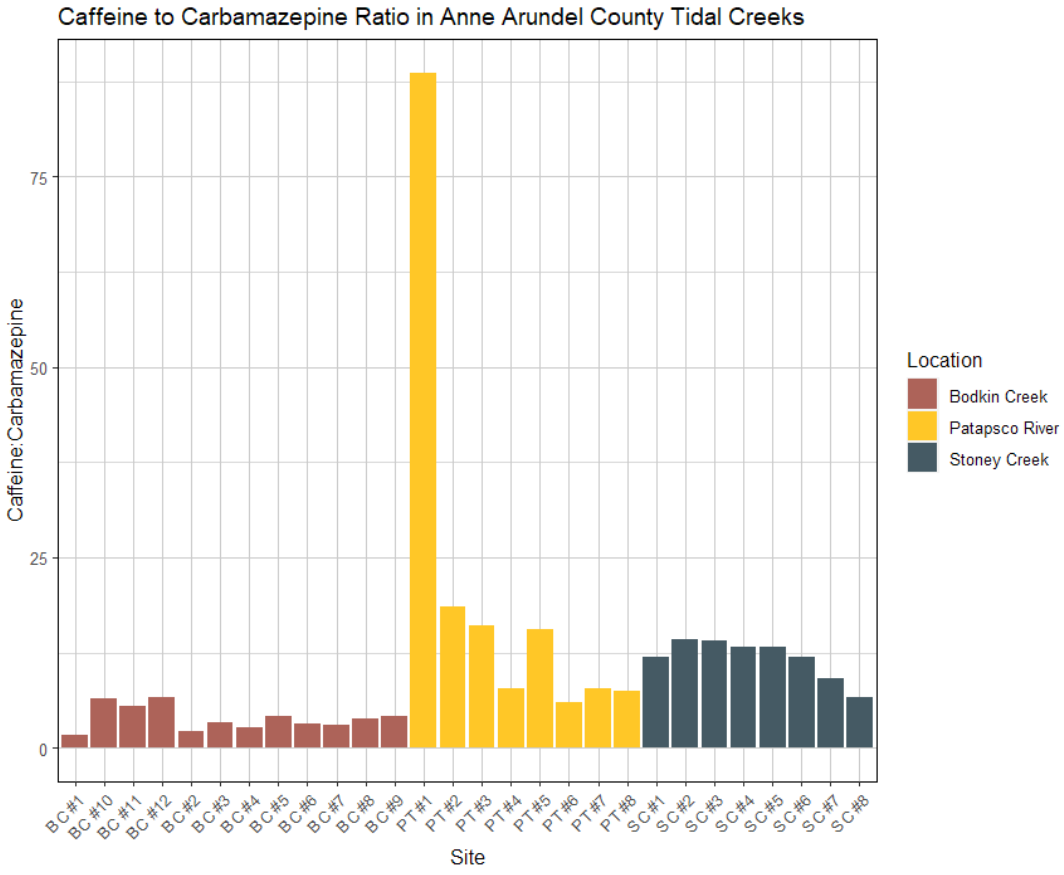



***Figure 35 Caffeine: Carbamazepine Ratio in Anne Arundel County Sites***

Within Bodkin and Stoney creeks, ratios of caffeine to carbamazepine were rather low. Again PT #1 near the effluent of Cox Creek WWTP had elevated caffeine levels. Carbamazepine is a prescription drug with a low likelihood of being found in the creeks but their detection instream has been associated with untreated waste from WWTP (Figure 35).

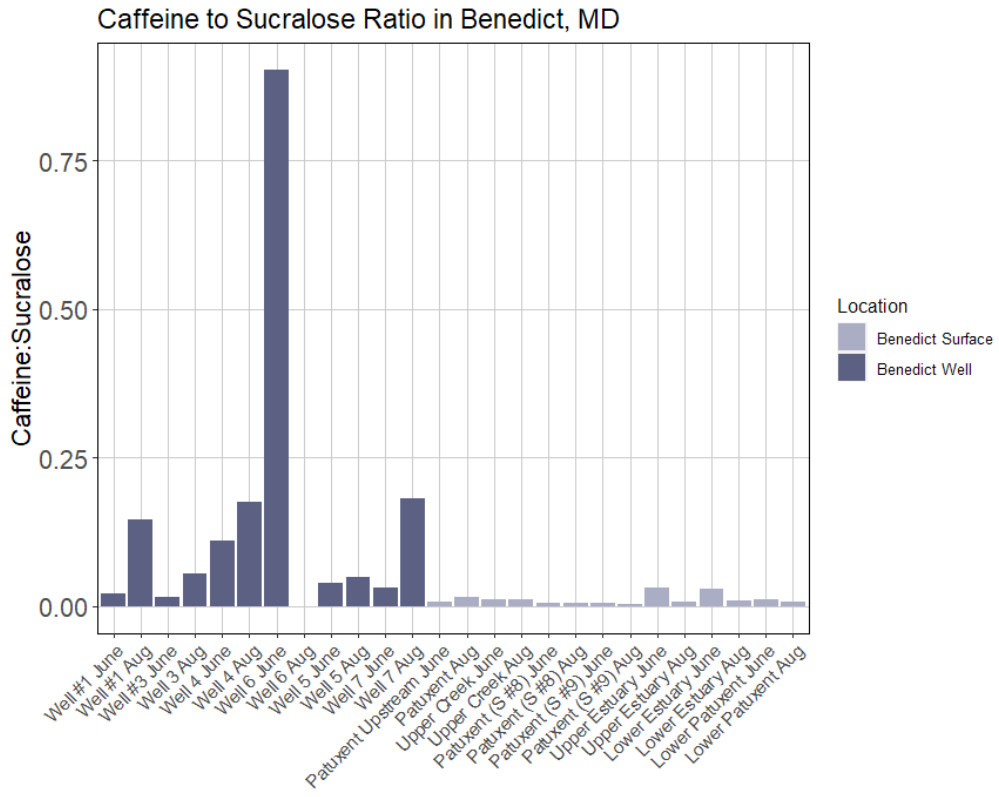



**Figure 36 Caffeine: Sucralose Ratio in Benedict, MD**

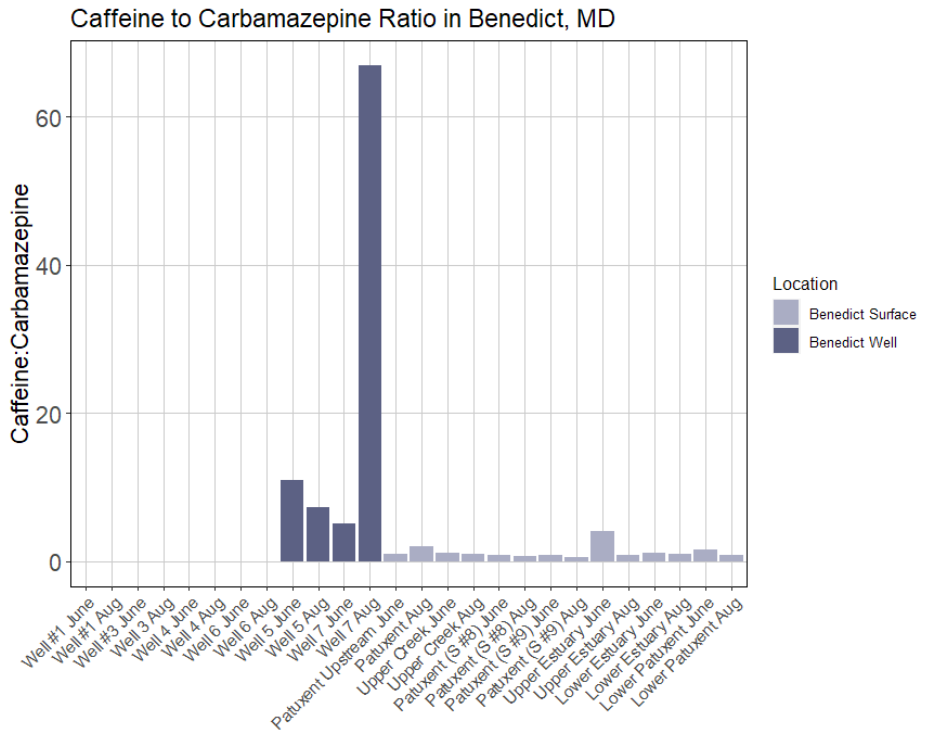



**Figure 37 Caffeine: Carbamazepine Ratios in Benedict, MD**

Within Benedict, surface water samples had similar caffeine to sucralose ratios while ratios in groundwater samples were more variable, with higher values in August (dry period) (Figure 36). Higher ratios in sites 6 and 7 may be explained by ongoing construction at these sites, including digging for the installation of a septic system in an area with a shallow water table. Disruptions to the soil can cause water to be blocked from its ordinary flow path and accumulate in the ground [Brassington, 2007]. Sites 1 and 3 were located in dense housing areas and thus had more potential for PPCP/AS contamination. Caffeine to carbamazepine ratios followed the same pattern, with the exception of some non-detects, which was expected for a prescription drug in a rural community with low population density (Figure 37).

Based on the previous Cantwell et., [2018] study, ratio values above 1 are indicative of untreated human wastewater. Only PT#1 and SC #1 met this threshold. However, $\delta^{15}N$/ $\delta^{18}O$ ratios and elevated carbamazepine and sucralose suggests that the caffeine:AS ratio is not an accurate way

to determine the presence of untreated wastewater. Further study is needed to determine chemical thresholds for water contamination.

Caffeine to carbamazepine ratios followed a similar trend to that of caffeine:sucralose in both Benedict and the Patapsco River, with PT #1 and Well 7 August having high values.

## 4.4 Conclusions

This study examined the presence and distribution of PPCP and AS receiving human wastewater from both septic system and WWTP sources in coastal catchments. Traditional water quality parameters including nutrients concentrations, and $\delta^{15}N$:$\delta^{18}O$ ratios were also examined to understand how PPCP and AS correlate.

Initially, it was hypothesized that septic dominated catchments would have relatively high PPCP and AS concentrations due to insufficient degradation. However the results from this study suggest that high PPCP and AS concentrations in septic dominated catchments (Bodkin Creek and Benidict, MD) were controlled, in part, by sewage wastewater inputs from WWTPs in the Stoney Creek and Patapsco River; the Cox Creek WWTP discharges at Stoney Creek, and the Patapsco WWTP in the Patapsco River. These sewered catchments had elevated PPCP and AS concentrations associated with WWTP effluent (Figure 33, Figure 34).

The second goal of this study was to determine the correlation of PPCP and AS with commonly used water quality indicators such as nitrate, TDN and dissolved oxygen concentrations. The results showed significant correlations, but they varied (positive or negative) according to the type of compound and by site. The inconsistencies in correlations, even when comparing catchments that have the same waste water disposal method, indicates that there is more study needed to fully understand what causes correlation between PPCPs and AS and water quality metrics.

In order to strengthen the conclusion that PPCP and AS are sourced from wastewater, isotopic analysis was conducted in the Anne Arundel County samples. The results from the $\delta^{15}N$ and $\delta^{18}O$ analysis (Figure 28) confirmed wastewater contamination on the water sampled in this study.

Lasty, this study aimed to determine the "freshness" of the wastewater found in each catchment by comparing concentrations of compounds readily removed during wastewater treatment compounds (liable) to compounds that are poorly removed (conservative). It was hypothesized that septic dominated catchments would contain a higher rate of fresh untreated wastewater, however the opposite was found. Sewered catchments, particularly sites near WWTP outfalls, had a higher rate of fresh untreated wastewater. This is indicative of incomplete treatment of wastewater by WWTPs.

This study showed high contamination of surface and groundwaters in Maryland and confirmed that human-derived wastewater is a substantial contributor. The freshness of wastewater and correlations between PPCP/AS and water quality remains an emerging field of research and this study confirms the complicated relationship between them.

In both study areas, sampling was limited by the number of sampling events, but the previously recommended standard human wastewater tracers were found universally. The ubiquitous presence of these tracers can guide future researchers in presence-absence studies of human wastewater. Future studies would benefit from multiple sampling events in varied conditions and a more robust understanding of stream connectivity, potentially saving valuable lab resources. Further research is needed to study PPCP and AS contamination in groundwater, particularly its connection to surface water. In short, wastewater contamination is a complex problem that needs to be more universally monitored to evaluate the extent to which human waste impacts freshwater.

# Chapter 5: Conclusions and Future Work

## 5.1 Summary of Findings

Previous studies assessing the contamination of PPCP and AS in water bodies have mainly focused on wastewater treatment plants discharge to large streams in urban areas. Fewer studies have analyzed the connection between PPCP and AS and septic systems. Thus, until now, very little was known about the influence of septic systems on PPCP and AS transport and distribution. This study sheds light on the behavior of PPCP and AS in septic dominated catchments in western MD. The large density of septic systems and recent reports of WWTP releasing untreated wastewater in the Western Shore MD [Condon and Dance, 2021], especially near an already degraded ecosystem like the Chesapeake Bay, has raised the concern regarding PPCP and AS pollution in the region for both policymakers and people who enjoy recreation on the Bay.

Overall the results of this study suggest that PPCP and AS are ubiquitous in the Western Shore of Maryland, regardless of land use or population size. A high septic density may be a good indicator of PPCP & AS presence and wastewater pollution but WWTP overflows and incomplete treatment suggest that septic systems are not alone in blame and a holistic approach is needed to reduce human wastewater inputs to the Chesapeake Bay and its coastal catchments.

## 5.2 Recognized limitations and future work

This study design had some inherent limitations which should be discussed. One of the main limitations was a lack of information about household usage of PPCP and AS in watersheds. Knowing whether PPCP and AS were being used in catchment but not detected in the surface or groundwater systems could have provided valuable information regarding compound specific attenuation characteristics. Another considerable limitation was the lack of

more specific demographic data, such as population age, in the small headwater catchments studied. This information could have helped determine the influence of demographics as a factor in PPCP and AS presence and distribution in catchments with septic systems. Also, information about the age of sewer and septic infrastructure would have helped in some analysis of sewered vs septic dominated catchments. Aging sewer systems may be more likely to release contaminants when compared to a well maintained septic system.

This study was limited to a narrow geological setting of the Chesapeake Bay watershed, the Western Shore of Maryland. Therefore, it is possible that the influence of septic systems on surface waters in other regions, which experience different precipitation rates and have different soil types, would be distinct and affect PPCP and AS concentrations differently as well. However, this study is among the first to examine PPCP and AS in urban headwater streams.

This project is only the beginning of the work needed to understand the impacts of PPCP and AS in streams, particularly headwater streams. More work is needed in this field focusing on coastal communities, as sea level rise is already affecting coastal wastewater infrastructure, causing septic leach field oversaturation with sea water hindering the system from utilizing soil microbial communities in the wastewater treatment process and premature degradation of sewer lines from saltwater intrusion [Vogelsong, 2019]. This problem will only grow worse with time while studies over the past 20 years have shown that contaminant pollution in surface waters is only increasing. However, while we wait for more studies and scientific information, policymakers and regulatory agencies ultimately have the responsibility to implement infrastructure changes to curb PPCP and AS pollution.

# 6. Appendices

## Appendix A: Supplemental Materials to Chapter 3

| **Table 1: Spearman's rank correlation (p-values) in headwater streams** | **Season** | **Ace-K** | **Atorvastatin** | **Caffeine** | **Carbamazepine** | **Cotinine** |
|---|---|---|---|---|---|---|
| **Season** | NA | **0.02** | 0.39 | 0.09 | 0.86 | **0.01** |
| **Ace-K** | **0.02** | NA | 0.24 | 0.86 | 0.39 | 0.05 |
| **Atorvastatin** | 0.39 | 0.24 | NA | **0.04** | **0.02** | **0.00** |
| **Caffeine** | 0.09 | 0.86 | **0.04** | NA | **0.03** | 0.23 |
| **Carbamazepine** | 0.86 | 0.39 | **0.02** | **0.03** | NA | **0.00** |
| **Cotinine** | **0.01** | 0.05 | **0.00** | 0.23 | **0.00** | NA |
| **DEET** | **0.00** | 0.06 | **0.01** | 0.75 | 0.18 | 0.14 |
| **Dichlorvos** | 0.05 | 0.86 | **0.00** | 0.39 | 0.06 | 0.61 |
| **Estrone** | **0.01** | 0.06 | **0.00** | 0.06 | **0.00** | **0.00** |
| **Ibuprofen** | **0.04** | 0.46 | 0.89 | **0.03** | 0.18 | 0.16 |
| **Paraxanthine** | 0.92 | 0.16 | 0.08 | 0.05 | **0.04** | 0.13 |
| **Sucralose** | 0.24 | **0.00** | 0.98 | 0.79 | **0.01** | 0.74 |
| **Sulfamethoxazole** | 0.45 | **0.05** | **0.00** | **0.04** | **0.00** | **0.02** |
| **Total PPCP & AS** | 1.00 | **0.00** | 0.69 | 0.55 | 0.28 | 0.86 |
| **Total PPCP** | 1.00 | **0.05** | 0.76 | 0.17 | 0.87 | 0.47 |
| **Total AS** | 1.00 | **0.00** | 0.63 | 0.40 | 0.20 | 0.82 |
| **Caffeine: Sucralose Ratio** | 0.72 | **0.02** | 0.10 | **0.00** | 0.87 | 0.48 |
| **Caffeine: Ace-K Ratio** | 0.65 | **0.00** | **0.05** | **0.00** | 0.45 | 0.50 |
| **Caffeine:Carbamazepine Ratio** | **0.02** | 0.70 | **0.01** | **0.00** | **0.00** | 0.40 |
| **Drainage Area** | 1.00 | **0.00** | 0.44 | 0.18 | 0.86 | 0.77 |
| **Septic Count** | 1.00 | **0.00** | 0.23 | 0.72 | 0.36 | 0.77 |
| **Septic Density** | 1.00 | **0.00** | 0.64 | 0.78 | 0.21 | 0.88 |
| **Mean Basin Slope** | 1.00 | **0.02** | 0.33 | 0.99 | 0.07 | 0.47 |
| **Urban Land Use** | 1.00 | 0.06 | 0.16 | 0.36 | 0.97 | 0.33 |
| **Agriculture Land Use** | 1.00 | 0.97 | 0.17 | 0.09 | 0.49 | 0.07 |
| **Forested Land Use** | 1.00 | 0.49 | 0.23 | 0.45 | 0.92 | 0.35 |
| **Water Land Use** | 1.00 | **0.01** | 0.54 | 0.29 | 0.92 | 0.98 |
| **Transportation Land Use** | 1.00 | 0.10 | 0.12 | 0.08 | 0.17 | 0.16 |
| **% Impervious Surfaces** | 1.00 | **0.00** | 0.98 | 0.92 | 0.30 | 0.83 |
| **Stream Width** | 0.21 | 0.22 | 0.19 | 0.29 | 0.10 | 0.19 |
| **Stream Depth** | 1.00 | 0.74 | 0.70 | 0.22 | 0.88 | 0.80 |
| **Calcium** | 0.90 | **0.03** | 0.82 | 0.58 | 0.39 | **0.03** |
| **Chloride** | 0.40 | 0.14 | 0.50 | 0.20 | 0.62 | 0.25 |
| **Fluoride** | 1.00 | 0.16 | 0.05 | 0.73 | 0.97 | 0.45 |
| **Magnesium** | 0.59 | 0.18 | 0.42 | 0.92 | 0.89 | 0.20 |
| **Nitrate** | 0.40 | 0.98 | 0.51 | 0.39 | 0.13 | 0.14 |
| **Potassium** | 0.40 | **0.01** | 0.30 | 0.48 | 0.69 | 0.69 |
| **Sodium** | 0.57 | 0.10 | 0.81 | 0.52 | 0.39 | 0.64 |
| **Sulfate** | 0.89 | 0.90 | 0.71 | 0.89 | 0.41 | 0.69 |
| **Minimum Septic Distance** | 1.00 | **0.00** | 0.90 | 0.18 | 0.42 | 0.75 |
| **Average Septic Distance** | 1.00 | **0.00** | 0.31 | 0.34 | 0.68 | 0.78 |
| **Median Septic Distance** | 1.00 | **0.00** | 0.41 | 0.48 | 0.72 | 0.65 |

| Table 1: Spearman's rank correlation (p-values) in headwater streams | DEET | Dichlorvos | Estrone | Ibuprofen | Paraxanthine | Sucralose |
|---|---|---|---|---|---|---|
| **Season** | **0.00** | 0.05 | **0.01** | **0.04** | 0.92 | 0.24 |
| **Ace-K** | 0.06 | 0.86 | 0.06 | 0.46 | 0.16 | **0.00** |
| **Atorvastatin** | **0.01** | **0.00** | **0.00** | 0.89 | 0.08 | 0.98 |
| **Caffeine** | 0.75 | 0.39 | 0.06 | **0.03** | 0.05 | 0.79 |
| **Carbamazepine** | 0.18 | 0.06 | **0.00** | 0.18 | **0.04** | **0.01** |
| **Cotinine** | 0.14 | 0.61 | **0.00** | 0.16 | 0.13 | 0.74 |
| **DEET** | NA | **0.00** | 0.57 | 0.17 | 0.44 | 0.20 |
| **Dichlorvos** | **0.00** | NA | 0.11 | **0.00** | 0.08 | 0.85 |
| **Estrone** | 0.57 | 0.11 | NA | 0.35 | **0.00** | 0.98 |
| **Ibuprofen** | 0.17 | **0.00** | 0.35 | NA | 0.34 | 0.65 |
| **Paraxanthine** | 0.44 | 0.08 | **0.00** | 0.34 | NA | 0.37 |
| **Sucralose** | 0.20 | 0.85 | 0.98 | 0.65 | 0.37 | NA |
| **Sulfamethoxazole** | 0.38 | 0.79 | **0.00** | 0.57 | **0.00** | **0.00** |
| **Total PPCP & AS** | 0.64 | 0.94 | 0.73 | 0.44 | 0.41 | **0.00** |
| **Total PPCP** | 0.78 | 0.97 | 0.94 | 0.19 | 0.45 | 0.49 |
| **Total AS** | 0.65 | 0.84 | 0.95 | 0.39 | 0.50 | **0.00** |
| **Caffeine:Sucralose Ratio** | 0.23 | 0.75 | 0.14 | 0.23 | 0.16 | **0.00** |
| **Caffeine: Ace-K Ratio** | 0.05 | 0.22 | 0.07 | 0.26 | 0.15 | **0.03** |
| **Caffeine: Carbamazepine Ratio** | 0.60 | 0.31 | 0.22 | 0.32 | 0.65 | **0.03** |
| **Drainage Area** | 0.98 | 0.91 | 0.32 | 0.70 | 0.81 | 0.44 |
| **Septic Count** | 0.62 | 0.94 | 0.79 | 0.24 | 0.63 | **0.00** |
| **Septic Density** | 0.64 | 0.97 | 0.77 | 0.60 | 0.41 | **0.00** |
| **Mean Basin Slope** | 0.65 | 0.84 | 0.59 | 0.20 | 0.70 | 0.59 |
| **Urban Land Use** | 0.86 | 0.71 | 0.44 | 0.96 | 0.48 | **0.00** |
| **Agriculture Land Use** | 0.77 | 0.67 | 0.05 | 0.59 | 1.00 | **0.04** |
| **Forested Land Use** | 0.89 | 0.66 | 0.27 | 0.95 | 0.60 | **0.00** |
| **Water Land Use** | 0.94 | 0.65 | 0.83 | 0.78 | 0.43 | 0.23 |
| **Transportation Land Use** | 0.99 | 0.83 | 0.33 | 0.54 | 0.44 | **0.00** |
| **% Impervious Surfaces** | 0.61 | 0.69 | 0.59 | 0.15 | 0.60 | 0.50 |
| **Stream Width** | 0.06 | 0.93 | 0.05 | 0.79 | 0.40 | 0.25 |
| **Stream Depth** | 0.76 | 0.19 | 0.35 | 0.31 | 0.34 | 0.39 |
| **Calcium** | 0.51 | 0.66 | 0.98 | 0.80 | 0.17 | 0.44 |
| **Chloride** | 0.25 | 0.64 | 0.64 | 0.58 | 0.36 | 0.06 |
| **Fluoride** | 0.15 | 0.30 | 0.34 | 0.22 | 0.80 | 0.11 |
| **Magnesium** | 0.71 | 0.52 | 0.73 | 0.98 | 0.32 | 0.14 |
| **Nitrate** | 0.82 | 0.69 | 0.36 | 0.43 | 0.33 | **0.04** |
| **Potassium** | 0.66 | 0.38 | 0.24 | 0.85 | 0.89 | 0.50 |
| **Sodium** | 0.45 | 0.97 | 0.44 | 0.78 | 0.64 | 0.27 |
| **Sulfate** | 0.73 | 0.88 | 0.43 | 0.49 | 0.81 | 0.06 |
| **Minimum Septic Distance** | 0.55 | 0.71 | 0.85 | 0.49 | 0.86 | **0.00** |
| **Average Septic Distance** | 0.59 | 0.85 | 0.91 | 0.33 | 0.98 | 0.96 |
| **Median Septic Distance** | 0.52 | 0.79 | 0.62 | 0.27 | 0.94 | 0.78 |

| Table 1: Spearman's rank correlation (p-values) in headwater streams | Sulfamethoxazole | Total PPCP & AS | Total PPCP | Total AS | Caffeine: Sucralose Ratio |
|---|---|---|---|---|---|
| **Season** | 0.45 | 1.00 | 1.00 | 1.00 | 0.72 |
| **Ace-K** | **0.05** | **0.00** | **0.05** | **0.00** | **0.02** |
| **Atorvastatin** | **0.00** | 0.69 | 0.76 | 0.63 | 0.10 |
| **Caffeine** | **0.04** | 0.55 | 0.17 | 0.40 | **0.00** |
| **Carbamazepine** | **0.00** | 0.28 | 0.87 | 0.20 | 0.87 |
| **Cotinine** | **0.02** | 0.86 | 0.47 | 0.82 | 0.48 |
| **DEET** | 0.38 | 0.64 | 0.78 | 0.65 | 0.23 |
| **Dichlorvos** | 0.79 | 0.94 | 0.97 | 0.84 | 0.75 |
| **Estrone** | **0.00** | 0.73 | 0.94 | 0.95 | 0.14 |
| **Ibuprofen** | 0.57 | 0.44 | 0.19 | 0.39 | 0.23 |
| **Paraxanthine** | **0.00** | 0.41 | 0.45 | 0.50 | 0.16 |
| **Sucralose** | **0.00** | **0.00** | 0.49 | **0.00** | **0.00** |
| **Sulfamethoxazole** | NA | **0.00** | 0.16 | **0.00** | 0.71 |
| **Total PPCP & AS** | **0.00** | NA | **0.00** | **0.00** | **0.00** |
| **Total PPCP** | 0.16 | **0.00** | NA | 0.11 | 0.42 |
| **Total AS** | **0.00** | **0.00** | 0.11 | NA | **0.00** |
| **Caffeine: Sucralose Ratio** | 0.71 | **0.00** | 0.42 | **0.00** | NA |
| **Caffeine: Ace-K Ratio** | 0.75 | 0.05 | 0.89 | **0.01** | **0.00** |
| **Caffeine:Carbamazepine Ratio** | **0.01** | **0.03** | 0.06 | **0.01** | **0.00** |
| **Drainage Area** | 0.51 | **0.04** | **0.01** | 0.16 | 0.63 |
| **Septic Count** | **0.00** | **0.00** | **0.00** | **0.00** | **0.04** |
| **Septic Density** | **0.00** | **0.00** | **0.00** | **0.00** | **0.00** |
| **Mean Basin Slope** | 0.40 | 0.40 | **0.00** | 0.53 | 0.91 |
| **Urban Land Use** | **0.00** | **0.00** | 0.84 | **0.00** | **0.00** |
| **Agriculture Land Use** | 0.77 | **0.01** | 0.90 | 0.12 | **0.03** |
| **Forested Land Use** | **0.01** | **0.00** | 0.43 | **0.00** | **0.02** |
| **Water Land Use** | 0.11 | **0.04** | **0.00** | 0.49 | 0.78 |
| **Transportation Land Use** | 0.51 | **0.01** | 0.07 | **0.00** | **0.00** |
| **% Impervious Surfaces** | 0.87 | 0.19 | **0.02** | **0.00** | 0.51 |
| **Stream Width** | **0.05** | 0.59 | 0.80 | 0.85 | 0.42 |
| **Stream Depth** | 0.23 | 0.54 | **0.00** | 0.55 | 0.21 |
| **Calcium** | 0.53 | 0.57 | **0.00** | 0.40 | 0.29 |
| **Chloride** | 0.42 | **0.03** | **0.01** | 0.25 | 0.16 |
| **Fluoride** | 0.66 | **0.01** | **0.01** | **0.04** | 0.10 |
| **Magnesium** | 0.19 | **0.04** | 0.08 | **0.04** | 0.36 |
| **Nitrate** | 0.32 | 0.38 | **0.01** | 0.39 | 0.71 |
| **Potassium** | 0.22 | 0.28 | 0.26 | 0.20 | 0.89 |
| **Sodium** | 0.46 | 0.07 | **0.00** | 0.70 | 0.55 |
| **Sulfate** | 0.17 | 0.70 | **0.00** | 0.57 | 0.26 |
| **Minimum Septic Distance** | 0.08 | **0.00** | 0.55 | **0.00** | **0.00** |
| **Average Septic Distance** | 0.25 | 0.84 | **0.00** | 0.84 | 0.91 |
| **Median Septic Distance** | 0.75 | 0.69 | **0.00** | 0.84 | 0.76 |

| Table 1: Spearman's rank correlation (p-values) in headwater streams | Caffeine:Ace-K Ratio | Caffeine:Carbamazepine Ratio | Drainage Area | Septic Count | Septic Density |
|---|---|---|---|---|---|
| **Season** | 0.65 | **0.02** | 1.00 | 1.00 | 1.00 |
| **Ace-K** | **0.00** | 0.70 | **0.00** | **0.00** | **0.00** |
| **Atorvastatin** | **0.05** | **0.01** | 0.44 | 0.23 | 0.64 |
| **Caffeine** | **0.00** | **0.00** | 0.18 | 0.72 | 0.78 |
| **Carbamazepine** | 0.45 | **0.00** | 0.86 | 0.36 | 0.21 |
| **Cotinine** | 0.50 | 0.40 | 0.77 | 0.77 | 0.88 |
| **DEET** | 0.05 | 0.60 | 0.98 | 0.62 | 0.64 |
| **Dichlorvos** | 0.22 | 0.31 | 0.91 | 0.94 | 0.97 |
| **Estrone** | 0.07 | 0.22 | 0.32 | 0.79 | 0.77 |
| **Ibuprofen** | 0.26 | 0.32 | 0.70 | 0.24 | 0.60 |
| **Paraxanthine** | 0.15 | 0.65 | 0.81 | 0.63 | 0.41 |
| **Sucralose** | **0.03** | **0.03** | 0.44 | **0.00** | **0.00** |
| **Sulfamethoxazole** | 0.75 | **0.01** | 0.51 | **0.00** | **0.00** |
| **Total PPCP & AS** | 0.05 | **0.03** | **0.04** | **0.00** | **0.00** |
| **Total PPCP** | 0.89 | 0.06 | **0.01** | **0.00** | **0.00** |
| **Total AS** | **0.01** | **0.01** | 0.16 | **0.00** | **0.00** |
| **Caffeine:Sucralose Ratio** | **0.00** | **0.00** | 0.63 | **0.04** | **0.00** |
| **Caffeine: Ace-K Ratio** | NA | **0.00** | 0.72 | **0.04** | 0.07 |
| **Caffeine:Carbamazepine Ratio** | **0.00** | NA | 0.10 | 0.47 | **0.05** |
| **Drainage Area** | 0.72 | 0.10 | NA | **0.00** | 0.32 |
| **Septic Count** | **0.04** | 0.47 | **0.00** | NA | **0.00** |
| **Septic Density** | 0.07 | **0.05** | 0.32 | **0.00** | NA |
| **Mean Basin Slope** | 0.34 | 0.08 | **0.00** | **0.00** | 0.53 |
| **Urban Land Use** | 0.14 | 0.15 | 0.55 | **0.00** | **0.00** |
| **Agriculture Land Use** | 0.34 | 0.11 | **0.00** | 0.52 | **0.01** |
| **Forested Land Use** | 0.46 | 0.19 | 0.23 | 0.11 | **0.00** |
| **Water Land Use** | 0.83 | 0.32 | **0.00** | **0.00** | **0.00** |
| **Transportation Land Use** | **0.03** | 0.31 | 0.49 | **0.02** | **0.01** |
| **% Impervious Surfaces** | 0.09 | 0.21 | **0.00** | **0.00** | 0.48 |
| **Stream Width** | 0.24 | 0.36 | 0.38 | 0.83 | 0.49 |
| **Stream Depth** | 0.34 | 0.30 | 0.50 | 0.54 | 0.37 |
| **Calcium** | 0.15 | 0.55 | **0.01** | **0.03** | 0.76 |
| **Chloride** | 0.68 | 0.23 | 0.08 | 0.52 | 0.06 |
| **Fluoride** | 0.25 | 0.88 | **0.00** | **0.00** | **0.00** |
| **Magnesium** | 0.75 | 0.68 | 0.62 | 0.06 | **0.01** |
| **Nitrate** | 0.39 | 0.74 | 0.61 | 0.44 | 0.17 |
| **Potassium** | 0.76 | 0.84 | 0.13 | **0.00** | **0.05** |
| **Sodium** | 0.77 | 0.31 | **0.03** | 0.42 | 0.14 |
| **Sulfate** | 0.99 | 0.58 | 0.73 | 0.73 | 0.36 |
| **Minimum Septic Distance** | **0.04** | **0.01** | **0.00** | **0.03** | **0.00** |
| **Average Septic Distance** | 0.53 | 0.53 | **0.00** | **0.00** | 0.32 |
| **Median Septic Distance** | 0.70 | 0.31 | **0.00** | **0.00** | 0.32 |

| Table 1: Spearman's rank correlation (p-values) in headwater streams | Mean Basin Slope | Urban Land Use | Agriculture Land Use | Forested Land Use | Water Land Use |
|---|---|---|---|---|---|
| **Season** | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| **Ace-K** | **0.02** | 0.06 | 0.97 | 0.49 | **0.01** |
| **Atorvastatin** | 0.33 | 0.16 | 0.17 | 0.23 | 0.54 |
| **Caffeine** | 0.99 | 0.36 | 0.09 | 0.45 | 0.29 |
| **Carbamazepine** | 0.07 | 0.97 | 0.49 | 0.92 | 0.92 |
| **Cotinine** | 0.47 | 0.33 | 0.07 | 0.35 | 0.98 |
| **DEET** | 0.65 | 0.86 | 0.77 | 0.89 | 0.94 |
| **Dichlorvos** | 0.84 | 0.71 | 0.67 | 0.66 | 0.65 |
| **Estrone** | 0.59 | 0.44 | 0.05 | 0.27 | 0.83 |
| **Ibuprofen** | 0.20 | 0.96 | 0.59 | 0.95 | 0.78 |
| **Paraxanthine** | 0.70 | 0.48 | 1.00 | 0.60 | 0.43 |
| **Sucralose** | 0.59 | **0.00** | **0.04** | **0.00** | 0.23 |
| **Sulfamethoxazole** | 0.40 | **0.00** | 0.77 | **0.01** | 0.11 |
| **Total PPCP & AS** | 0.40 | **0.00** | **0.01** | **0.00** | **0.04** |
| **Total PPCP** | **0.00** | 0.84 | 0.90 | 0.43 | **0.00** |
| **Total AS** | 0.53 | **0.00** | 0.12 | **0.00** | 0.49 |
| **Caffeine:Sucralose Ratio** | 0.91 | **0.00** | **0.03** | **0.02** | 0.78 |
| **Caffeine:Ace-K Ratio** | 0.34 | 0.14 | 0.34 | 0.46 | 0.83 |
| **Caffeine:Carbamazepine Ratio** | 0.08 | 0.15 | 0.11 | 0.19 | 0.32 |
| **Drainage Area** | **0.00** | 0.55 | **0.00** | 0.23 | **0.00** |
| **Septic Count** | **0.00** | **0.00** | 0.52 | 0.11 | **0.00** |
| **Septic Density** | 0.53 | **0.00** | **0.01** | **0.00** | **0.00** |
| **Mean Basin Slope** | NA | 0.92 | **0.02** | 0.40 | **0.00** |
| **Urban Land Use** | 0.92 | NA | **0.00** | **0.00** | **0.00** |
| **Agriculture Land Use** | **0.02** | **0.00** | NA | **0.00** | 0.07 |
| **Forested Land Use** | 0.40 | **0.00** | **0.00** | NA | **0.00** |
| **Water Land Use** | **0.00** | **0.00** | 0.07 | **0.00** | NA |
| **Transportation Land Use** | **0.00** | **0.00** | **0.00** | **0.00** | **0.02** |
| **% Impervious Surfaces** | **0.00** | **0.01** | **0.03** | **0.00** | 0.49 |
| **Stream Width** | **0.00** | 0.60 | 0.05 | 0.48 | 0.14 |
| **Stream Depth** | 0.33 | 0.06 | 0.09 | **0.00** | **0.00** |
| **Calcium** | 0.23 | 0.06 | **0.00** | **0.02** | 0.71 |
| **Chloride** | 0.64 | **0.01** | 0.05 | **0.00** | 0.15 |
| **Fluoride** | **0.00** | **0.00** | 1.00 | **0.01** | **0.03** |
| **Magnesium** | 0.25 | **0.00** | **0.00** | **0.00** | 0.07 |
| **Nitrate** | **0.00** | **0.00** | 0.88 | **0.00** | 0.51 |
| **Potassium** | 0.17 | 0.11 | 0.09 | 0.32 | **0.02** |
| **Sodium** | 0.91 | 0.16 | **0.02** | **0.00** | 0.18 |
| **Sulfate** | **0.00** | **0.00** | 0.77 | **0.00** | 0.25 |
| **Minimum Septic Distance** | 0.34 | 1.00 | 0.19 | 0.55 | **0.00** |
| **Average Septic Distance** | **0.00** | 0.84 | 0.70 | 0.43 | **0.00** |
| **Median Septic Distance** | **0.00** | 0.69 | **0.02** | 0.84 | **0.00** |

| Table 1: Spearman's rank correlation (p-values) in headwater streams | Transportation Land Use | % Impervious Surfaces | Stream Width | Stream Depth | Calcium |
|---|---|---|---|---|---|
| **Season** | 1.00 | 1.00 | 0.21 | 1.00 | 0.90 |
| **Ace-K** | 0.10 | **0.00** | 0.22 | 0.74 | **0.03** |
| **Atorvastatin** | 0.12 | 0.98 | 0.19 | 0.70 | 0.82 |
| **Caffeine** | 0.08 | 0.92 | 0.29 | 0.22 | 0.58 |
| **Carbamazepine** | 0.17 | 0.30 | 0.10 | 0.88 | 0.39 |
| **Cotinine** | 0.16 | 0.83 | 0.19 | 0.80 | **0.03** |
| **DEET** | 0.99 | 0.61 | 0.06 | 0.76 | 0.51 |
| **Dichlorvos** | 0.83 | 0.69 | 0.93 | 0.19 | 0.66 |
| **Estrone** | 0.33 | 0.59 | 0.05 | 0.35 | 0.98 |
| **Ibuprofen** | 0.54 | 0.15 | 0.79 | 0.31 | 0.80 |
| **Paraxanthine** | 0.44 | 0.60 | 0.40 | 0.34 | 0.17 |
| **Sucralose** | **0.00** | 0.50 | 0.25 | 0.39 | 0.44 |
| **Sulfamethoxazole** | 0.51 | 0.87 | **0.05** | 0.23 | 0.53 |
| **Total PPCP & AS** | **0.01** | 0.19 | 0.59 | 0.54 | 0.57 |
| **Total PPCP** | 0.07 | **0.02** | 0.80 | **0.00** | **0.00** |
| **Total AS** | **0.00** | **0.00** | 0.85 | 0.55 | 0.40 |
| **Caffeine:Sucralose Ratio** | **0.00** | 0.51 | 0.42 | 0.21 | 0.29 |
| **Caffeine:Ace-K Ratio** | **0.03** | 0.09 | 0.24 | 0.34 | 0.15 |
| **Caffeine:Carbamazepine Ratio** | 0.31 | 0.21 | 0.36 | 0.30 | 0.55 |
| **Drainage Area** | 0.49 | **0.00** | 0.38 | 0.50 | **0.01** |
| **Septic Count** | **0.02** | **0.00** | 0.83 | 0.54 | **0.03** |
| **Septic Density** | **0.01** | 0.48 | 0.49 | 0.37 | 0.76 |
| **Mean Basin Slope** | **0.00** | **0.00** | **0.00** | 0.33 | 0.23 |
| **Urban Land Use** | **0.00** | **0.01** | 0.60 | 0.06 | 0.06 |
| **Agriculture Land Use** | **0.00** | **0.03** | 0.05 | 0.09 | **0.00** |
| **Forested Land Use** | **0.00** | **0.00** | 0.48 | **0.00** | **0.02** |
| **Water Land Use** | **0.02** | 0.49 | 0.14 | **0.00** | 0.71 |
| **Transportation Land Use** | NA | 0.21 | 0.13 | 0.90 | **0.02** |
| **% Impervious Surfaces** | 0.21 | NA | **0.03** | **0.03** | **0.00** |
| **Stream Width** | 0.13 | **0.03** | NA | 0.21 | 0.39 |
| **Stream Depth** | 0.90 | **0.03** | 0.21 | NA | 0.66 |
| **Calcium** | **0.02** | **0.00** | 0.39 | 0.66 | NA |
| **Chloride** | 0.21 | 0.07 | 0.34 | 0.06 | **0.04** |
| **Fluoride** | **0.00** | **0.04** | 0.68 | 0.65 | 0.06 |
| **Magnesium** | **0.00** | 0.61 | **0.03** | 0.76 | **0.00** |
| **Nitrate** | 0.08 | **0.00** | 0.38 | 0.98 | **0.00** |
| **Potassium** | 0.06 | 0.54 | 0.53 | 0.27 | **0.00** |
| **Sodium** | 0.71 | **0.03** | 0.29 | **0.00** | 0.06 |
| **Sulfate** | **0.00** | **0.00** | 0.33 | 0.42 | **0.01** |
| **Minimum Septic Distance** | 0.11 | **0.00** | 0.09 | **0.00** | 0.95 |
| **Average Septic Distance** | 0.82 | **0.00** | 0.65 | 0.12 | **0.03** |
| **Median Septic Distance** | 1.00 | **0.00** | 0.11 | **0.03** | 0.13 |

| Table 1: Spearman's rank correlation (p-values) in headwater streams | Chloride | Fluoride | Lithium | Magnesium | Nitrate | Potassium |
|---|---|---|---|---|---|---|
| **Season** | 0.40 | 1.00 | NA | 0.59 | 0.40 | 0.40 |
| **Ace-K** | 0.14 | 0.16 | NA | 0.18 | 0.98 | **0.01** |
| **Atorvastatin** | 0.50 | 0.05 | NA | 0.42 | 0.51 | 0.30 |
| **Caffeine** | 0.20 | 0.73 | NA | 0.92 | 0.39 | 0.48 |
| **Carbamazepine** | 0.62 | 0.97 | NA | 0.89 | 0.13 | 0.69 |
| **Cotinine** | 0.25 | 0.45 | NA | 0.20 | 0.14 | 0.69 |
| **DEET** | 0.25 | 0.15 | NA | 0.71 | 0.82 | 0.66 |
| **Dichlorvos** | 0.64 | 0.30 | NA | 0.52 | 0.69 | 0.38 |
| **Estrone** | 0.64 | 0.34 | NA | 0.73 | 0.36 | 0.24 |
| **Ibuprofen** | 0.58 | 0.22 | NA | 0.98 | 0.43 | 0.85 |
| **Paraxanthine** | 0.36 | 0.80 | NA | 0.32 | 0.33 | 0.89 |
| **Sucralose** | 0.06 | 0.11 | NA | 0.14 | **0.04** | 0.50 |
| **Sulfamethoxazole** | 0.42 | 0.66 | NA | 0.19 | 0.32 | 0.22 |
| **Total PPCP & AS** | **0.03** | **0.01** | NA | **0.04** | 0.38 | 0.28 |
| **Total PPCP** | **0.01** | **0.01** | NA | 0.08 | **0.01** | 0.26 |
| **Total AS** | 0.25 | **0.04** | NA | **0.04** | 0.39 | 0.20 |
| **Caffeine:Sucralose Ratio** | 0.16 | 0.10 | NA | 0.36 | 0.71 | 0.89 |
| **Caffeine:Ace-K Ratio** | 0.68 | 0.25 | NA | 0.75 | 0.39 | 0.76 |
| **Caffeine:Carbamazepine Ratio** | 0.23 | 0.88 | NA | 0.68 | 0.74 | 0.84 |
| **Drainage Area** | 0.08 | **0.00** | NA | 0.62 | 0.61 | 0.13 |
| **Septic Count** | 0.52 | **0.00** | NA | 0.06 | 0.44 | **0.00** |
| **Septic Density** | 0.06 | **0.00** | NA | **0.01** | 0.17 | **0.05** |
| **Mean Basin Slope** | 0.64 | **0.00** | NA | 0.25 | **0.00** | 0.17 |
| **Urban Land Use** | **0.01** | **0.00** | NA | **0.00** | **0.00** | 0.11 |
| **Agriculture Land Use** | 0.05 | 1.00 | NA | **0.00** | 0.88 | 0.09 |
| **Forested Land Use** | **0.00** | **0.01** | NA | **0.00** | **0.00** | 0.32 |
| **Water Land Use** | 0.15 | **0.03** | NA | 0.07 | 0.51 | **0.02** |
| **Transportation Land Use** | 0.21 | **0.00** | NA | **0.00** | 0.08 | 0.06 |
| **% Impervious Surfaces** | 0.07 | **0.04** | NA | 0.61 | **0.00** | 0.54 |
| **Stream Width** | 0.34 | 0.68 | NA | **0.03** | 0.38 | 0.53 |
| **Stream Depth** | 0.06 | 0.65 | NA | 0.76 | 0.98 | 0.27 |
| **Calcium** | **0.04** | 0.06 | NA | **0.00** | **0.00** | **0.00** |
| **Chloride** | NA | 0.09 | NA | **0.03** | 0.51 | **0.00** |
| **Fluoride** | 0.09 | NA | NA | 0.72 | **0.04** | 0.56 |
| **Magnesium** | **0.03** | 0.72 | NA | NA | **0.02** | **0.00** |
| **Nitrate** | 0.51 | **0.04** | NA | **0.02** | NA | **0.05** |
| **Potassium** | **0.00** | 0.56 | NA | **0.00** | **0.05** | NA |
| **Sodium** | **0.00** | 0.98 | NA | **0.01** | 0.07 | **0.00** |
| **Sulfate** | 0.91 | 0.37 | NA | **0.03** | **0.00** | 0.06 |
| **Minimum Septic Distance** | 0.59 | 0.68 | NA | 0.08 | 0.53 | 0.27 |
| **Average Septic Distance** | 0.15 | 0.38 | NA | 0.44 | **0.00** | **0.02** |
| **Median Septic Distance** | 0.69 | 0.58 | NA | 0.30 | **0.00** | 0.07 |

| Table 1: Spearman's rank correlation (p-values) in headwater streams | Sodium | Sulfate | Minimum Septic Distance | Average Septic Distance | Median Septic Distance |
|---|---|---|---|---|---|
| **Season** | 0.57 | 0.89 | 1.00 | 1.00 | 1.00 |
| **Ace-K** | 0.10 | 0.90 | **0.00** | **0.00** | **0.00** |
| **Atorvastatin** | 0.81 | 0.71 | 0.90 | 0.31 | 0.41 |
| **Caffeine** | 0.52 | 0.89 | 0.18 | 0.34 | 0.48 |
| **Carbamazepine** | 0.39 | 0.41 | 0.42 | 0.68 | 0.72 |
| **Cotinine** | 0.64 | 0.69 | 0.75 | 0.78 | 0.65 |
| **DEET** | 0.45 | 0.73 | 0.55 | 0.59 | 0.52 |
| **Dichlorvos** | 0.97 | 0.88 | 0.71 | 0.85 | 0.79 |
| **Estrone** | 0.44 | 0.43 | 0.85 | 0.91 | 0.62 |
| **Ibuprofen** | 0.78 | 0.49 | 0.49 | 0.33 | 0.27 |
| **Paraxanthine** | 0.64 | 0.81 | 0.86 | 0.98 | 0.94 |
| **Sucralose** | 0.27 | 0.06 | **0.00** | 0.96 | 0.78 |
| **Sulfamethoxazole** | 0.46 | 0.17 | 0.08 | 0.25 | 0.75 |
| **Total PPCP & AS** | 0.07 | 0.70 | **0.00** | 0.84 | 0.69 |
| **Total PPCP** | **0.00** | **0.00** | 0.55 | **0.00** | **0.00** |
| **Total AS** | 0.70 | 0.57 | **0.00** | 0.84 | 0.84 |
| **Caffeine:Sucralose Ratio** | 0.55 | 0.26 | **0.00** | 0.91 | 0.76 |
| **Caffeine:Ace-K Ratio** | 0.77 | 0.99 | **0.04** | 0.53 | 0.70 |
| **Caffeine:Carbamazepine Ratio** | 0.31 | 0.58 | **0.01** | 0.53 | 0.31 |
| **Drainage Area** | **0.03** | 0.73 | **0.00** | **0.00** | **0.00** |
| **Septic Count** | 0.42 | 0.73 | **0.03** | **0.00** | **0.00** |
| **Septic Density** | 0.14 | 0.36 | **0.00** | 0.32 | 0.32 |
| **Mean Basin Slope** | 0.91 | **0.00** | 0.34 | **0.00** | **0.00** |
| **Urban Land Use** | 0.16 | **0.00** | 1.00 | 0.84 | 0.69 |
| **Agriculture Land Use** | **0.02** | 0.77 | 0.19 | 0.70 | **0.02** |
| **Forested Land Use** | **0.00** | **0.00** | 0.55 | 0.43 | 0.84 |
| **Water Land Use** | 0.18 | 0.25 | **0.00** | **0.00** | **0.00** |
| **Transportation Land Use** | 0.71 | **0.00** | 0.11 | 0.82 | 1.00 |
| **% Impervious Surfaces** | **0.03** | **0.00** | **0.00** | **0.00** | **0.00** |
| **Stream Width** | 0.29 | 0.33 | 0.09 | 0.65 | 0.11 |
| **Stream Depth** | **0.00** | 0.42 | **0.00** | 0.12 | **0.03** |
| **Calcium** | 0.06 | **0.01** | 0.95 | **0.03** | 0.13 |
| **Chloride** | **0.00** | 0.91 | 0.59 | 0.15 | 0.69 |
| **Fluoride** | 0.98 | 0.37 | 0.68 | 0.38 | 0.58 |
| **Magnesium** | **0.01** | **0.03** | 0.08 | 0.44 | 0.30 |
| **Nitrate** | 0.07 | **0.00** | 0.53 | **0.00** | **0.00** |
| **Potassium** | **0.00** | 0.06 | 0.27 | **0.02** | 0.07 |
| **Sodium** | NA | 0.09 | 0.36 | 0.60 | 0.36 |
| **Sulfate** | 0.09 | NA | 0.18 | **0.02** | **0.00** |
| **Minimum Septic Distance** | 0.36 | 0.18 | NA | 0.16 | 0.23 |
| **Average Septic Distance** | 0.60 | **0.02** | 0.16 | NA | **0.00** |
| **Median Septic Distance** | 0.36 | **0.00** | 0.23 | **0.00** | NA |

| Table 2: Spearman's rank correlation ($r_s$-values) in headwater streams | Season | Ace-K | Atorvastatin | Caffeine | Carbamazepine |
|---|---|---|---|---|---|
| **Season** | 1.00 | -0.32 | -0.17 | -0.23 | -0.03 |
| **Ace-K** | -0.32 | 1.00 | 0.26 | -0.03 | 0.14 |
| **Atorvastatin** | -0.17 | 0.26 | 1.00 | 0.39 | -0.47 |
| **Caffeine** | -0.23 | -0.03 | 0.39 | 1.00 | 0.32 |
| **Carbamazepine** | -0.03 | 0.14 | -0.47 | 0.32 | 1.00 |
| **Cotinine** | 0.34 | -0.28 | -0.54 | 0.17 | 0.49 |
| **DEET** | -0.65 | 0.32 | -0.50 | -0.05 | 0.23 |
| **Dichlorvos** | 0.30 | -0.03 | 0.62 | 0.14 | -0.33 |
| **Estrone** | -0.34 | 0.27 | 0.56 | -0.26 | -0.65 |
| **Ibuprofen** | -0.37 | 0.14 | 0.04 | 0.40 | 0.26 |
| **Paraxanthine** | 0.02 | -0.27 | -0.38 | 0.34 | 0.38 |
| **Sucralose** | -0.17 | 0.59 | 0.00 | -0.04 | 0.41 |
| **Sulfamethoxazole** | 0.11 | 0.31 | -0.63 | 0.30 | 0.76 |
| **Total PPCP & AS** | 0.00 | 0.51 | -0.08 | -0.08 | 0.16 |
| **Total PPCP** | 0.00 | 0.27 | 0.06 | 0.19 | -0.02 |
| **Total AS** | 0.00 | 0.58 | -0.10 | -0.12 | 0.19 |
| **Caffeine:Sucralose Ratio** | -0.05 | -0.35 | 0.33 | 0.79 | -0.03 |
| **Caffeine:Ace-K Ratio** | 0.07 | -0.43 | 0.43 | 0.87 | 0.12 |
| **Caffeine:Carbamazepine Ratio** | -0.36 | -0.07 | 0.53 | 0.75 | -0.50 |
| **Drainage Area** | 0.00 | 0.40 | -0.16 | 0.19 | -0.03 |
| **Septic Count** | 0.00 | 0.77 | -0.24 | 0.05 | 0.14 |
| **Septic Density** | 0.00 | 0.56 | -0.09 | -0.04 | 0.19 |
| **Mean Basin Slope** | 0.00 | 0.31 | -0.20 | 0.00 | -0.27 |
| **Urban Land Use** | 0.00 | 0.25 | -0.28 | -0.13 | 0.01 |
| **Agriculture Land Use** | 0.00 | 0.00 | 0.27 | 0.23 | 0.10 |
| **Forested Land Use** | 0.00 | -0.09 | 0.24 | 0.11 | -0.02 |
| **Water Land Use** | 0.00 | 0.35 | -0.12 | 0.15 | -0.02 |
| **Transportation Land Use** | 0.00 | -0.22 | 0.30 | 0.24 | 0.20 |
| **% Impervious Surfaces** | 0.00 | -0.47 | -0.01 | 0.01 | 0.16 |
| **Stream Width** | 0.22 | -0.22 | -0.39 | 0.19 | 0.32 |
| **Stream Depth** | 0.00 | -0.05 | -0.09 | 0.19 | 0.03 |
| **Calcium** | -0.02 | -0.31 | 0.05 | 0.09 | -0.15 |
| **Chloride** | -0.13 | 0.22 | 0.15 | 0.21 | -0.09 |
| **Fluoride** | 0.00 | -0.51 | 0.87 | 0.16 | 0.02 |
| **Magnesium** | 0.08 | 0.20 | -0.18 | 0.02 | 0.02 |
| **Nitrate** | -0.14 | 0.00 | 0.15 | 0.15 | 0.28 |
| **Potassium** | 0.13 | 0.38 | -0.23 | 0.12 | 0.07 |
| **Sodium** | -0.08 | 0.24 | 0.06 | 0.11 | -0.15 |
| **Sulfate** | -0.02 | 0.02 | -0.09 | 0.02 | 0.15 |
| **Minimum Septic Distance** | 0.00 | -0.38 | -0.02 | 0.19 | -0.12 |
| **Average Septic Distance** | 0.00 | 0.51 | -0.20 | 0.13 | 0.06 |
| **Median Septic Distance** | 0.00 | 0.38 | -0.17 | 0.10 | -0.05 |

| Table 2: Spearman's rank correlation ($r_s$-values) in headwater streams | Cotinine | DEET | Dichlorvos | Estrone | Ibuprofen | Paraxanthine |
|---|---|---|---|---|---|---|
| **Season** | 0.34 | -0.65 | 0.30 | -0.34 | -0.37 | 0.02 |
| **Ace-K** | -0.28 | 0.32 | -0.03 | 0.27 | 0.14 | -0.27 |
| **Atorvastatin** | -0.54 | -0.50 | 0.62 | 0.56 | 0.04 | -0.38 |
| **Caffeine** | 0.17 | -0.05 | 0.14 | -0.26 | 0.40 | 0.34 |
| **Carbamazepine** | 0.49 | 0.23 | -0.33 | -0.65 | 0.26 | 0.38 |
| **Cotinine** | 1.00 | 0.24 | 0.08 | -0.55 | -0.26 | 0.27 |
| **DEET** | 0.24 | 1.00 | -0.65 | 0.09 | 0.27 | -0.15 |
| **Dichlorvos** | 0.08 | -0.65 | 1.00 | 0.26 | -0.59 | -0.40 |
| **Estrone** | -0.55 | 0.09 | 0.26 | 1.00 | -0.17 | -0.60 |
| **Ibuprofen** | -0.26 | 0.27 | -0.59 | -0.17 | 1.00 | 0.23 |
| **Paraxanthine** | 0.27 | -0.15 | -0.40 | -0.60 | 0.23 | 1.00 |
| **Sucralose** | -0.05 | 0.21 | 0.03 | 0.00 | 0.09 | 0.17 |
| **Sulfamethoxazole** | 0.34 | -0.16 | -0.05 | -0.48 | 0.11 | 0.56 |
| **Total PPCP & AS** | -0.02 | 0.08 | 0.01 | 0.05 | 0.15 | 0.15 |
| **Total PPCP** | 0.10 | 0.05 | -0.01 | 0.01 | 0.24 | 0.14 |
| **Total AS** | -0.03 | 0.07 | 0.03 | 0.01 | 0.16 | 0.12 |
| **Caffeine:Sucralose Ratio** | 0.10 | -0.20 | 0.05 | -0.22 | 0.23 | 0.26 |
| **Caffeine:Ace-K Ratio** | 0.10 | -0.33 | 0.21 | -0.26 | 0.21 | 0.28 |
| **Caffeine:Carbamazepine Ratio** | -0.13 | 0.10 | 0.18 | 0.20 | 0.22 | -0.09 |
| **Drainage Area** | 0.04 | 0.00 | -0.02 | -0.14 | 0.07 | 0.04 |
| **Septic Count** | -0.04 | 0.08 | -0.01 | -0.04 | 0.22 | 0.09 |
| **Septic Density** | -0.02 | 0.08 | -0.01 | 0.04 | 0.10 | 0.15 |
| **Mean Basin Slope** | -0.10 | 0.07 | -0.03 | 0.08 | 0.24 | 0.07 |
| **Urban Land Use** | -0.14 | -0.03 | -0.06 | 0.11 | 0.01 | 0.13 |
| **Agriculture Land Use** | 0.25 | -0.05 | 0.07 | -0.27 | -0.10 | 0.00 |
| **Forested Land Use** | 0.13 | 0.02 | 0.07 | -0.15 | 0.01 | -0.10 |
| **Water Land Use** | 0.00 | 0.01 | -0.07 | 0.03 | 0.05 | 0.14 |
| **Transportation Land Use** | 0.19 | 0.00 | 0.04 | -0.14 | -0.12 | -0.14 |
| **% Impervious Surfaces** | -0.03 | -0.08 | -0.06 | 0.08 | -0.26 | -0.10 |
| **Stream Width** | 0.23 | -0.38 | -0.02 | -0.34 | -0.06 | -0.20 |
| **Stream Depth** | -0.04 | -0.05 | -0.23 | 0.15 | 0.20 | 0.20 |
| **Calcium** | -0.35 | -0.12 | -0.09 | 0.01 | 0.05 | 0.28 |
| **Chloride** | -0.19 | 0.21 | -0.09 | -0.08 | 0.12 | -0.19 |
| **Fluoride** | -0.34 | -0.66 | 0.51 | 0.43 | -0.67 | 0.20 |
| **Magnesium** | -0.21 | -0.07 | -0.13 | -0.06 | 0.01 | 0.20 |
| **Nitrate** | -0.26 | -0.04 | -0.08 | -0.16 | 0.18 | 0.21 |
| **Potassium** | -0.07 | 0.08 | -0.17 | -0.19 | 0.04 | 0.03 |
| **Sodium** | -0.08 | 0.14 | 0.01 | -0.13 | 0.06 | -0.10 |
| **Sulfate** | -0.07 | -0.07 | -0.03 | -0.13 | -0.15 | 0.05 |
| **Minimum Septic Distance** | 0.05 | -0.10 | -0.06 | -0.03 | -0.13 | -0.03 |
| **Average Septic Distance** | -0.04 | 0.09 | -0.03 | -0.02 | 0.18 | 0.00 |
| **Median Septic Distance** | -0.06 | 0.10 | -0.04 | 0.07 | 0.20 | 0.01 |

| Table 2: Spearman's rank correlation ($r_s$-values) in headwater streams | Sucralose | Sulfamethoxazole | Total PPCP & AS | Total PPCP | Total AS | Caffeine:Sucralose Ratio |
|---|---|---|---|---|---|---|
| **Season** | -0.17 | 0.11 | 0.00 | 0.00 | 0.00 | -0.05 |
| **Ace-K** | 0.59 | 0.31 | 0.51 | 0.27 | 0.58 | -0.35 |
| **Atorvastatin** | 0.00 | -0.63 | -0.08 | 0.06 | -0.10 | 0.33 |
| **Caffeine** | -0.04 | 0.30 | -0.08 | 0.19 | -0.12 | 0.79 |
| **Carbamazepine** | 0.41 | 0.76 | 0.16 | -0.02 | 0.19 | -0.03 |
| **Cotinine** | -0.05 | 0.34 | -0.02 | 0.10 | -0.03 | 0.10 |
| **DEET** | 0.21 | -0.16 | 0.08 | 0.05 | 0.07 | -0.20 |
| **Dichlorvos** | 0.03 | -0.05 | 0.01 | -0.01 | 0.03 | 0.05 |
| **Estrone** | 0.00 | -0.48 | 0.05 | 0.01 | 0.01 | -0.22 |
| **Ibuprofen** | 0.09 | 0.11 | 0.15 | 0.24 | 0.16 | 0.23 |
| **Paraxanthine** | 0.17 | 0.56 | 0.15 | 0.14 | 0.12 | 0.26 |
| **Sucralose** | 1.00 | 0.52 | 0.85 | 0.10 | 0.86 | -0.53 |
| **Sulfamethoxazole** | 0.52 | 1.00 | 0.61 | 0.21 | 0.60 | -0.06 |
| **Total PPCP & AS** | 0.85 | 0.61 | 1.00 | 0.36 | 0.95 | -0.49 |
| **Total PPCP** | 0.10 | 0.21 | 0.36 | 1.00 | 0.19 | 0.12 |
| **Total AS** | 0.86 | 0.60 | 0.95 | 0.19 | 1.00 | -0.54 |
| **Caffeine:Sucralose Ratio** | -0.53 | -0.06 | -0.49 | 0.12 | -0.54 | 1.00 |
| **Caffeine:Ace-K Ratio** | -0.32 | 0.05 | -0.28 | 0.02 | -0.35 | 0.92 |
| **Caffeine:Carbamazepine Ratio** | -0.35 | -0.41 | -0.34 | 0.29 | -0.41 | 0.73 |
| **Drainage Area** | -0.11 | 0.10 | -0.24 | 0.29 | -0.17 | 0.07 |
| **Septic Count** | 0.47 | 0.51 | 0.55 | 0.48 | 0.60 | -0.30 |
| **Septic Density** | 0.82 | 0.63 | 0.98 | 0.38 | 0.90 | -0.46 |
| **Mean Basin Slope** | -0.08 | -0.13 | -0.10 | 0.46 | -0.08 | -0.02 |
| **Urban Land Use** | 0.58 | 0.42 | 0.52 | -0.02 | 0.45 | -0.44 |
| **Agriculture Land Use** | -0.29 | -0.04 | -0.30 | 0.02 | -0.19 | 0.31 |
| **Forested Land Use** | -0.50 | -0.38 | -0.52 | -0.10 | -0.36 | 0.34 |
| **Water Land Use** | 0.17 | 0.24 | 0.25 | 0.58 | 0.08 | -0.04 |
| **Transportation Land Use** | -0.46 | -0.10 | -0.30 | 0.22 | -0.35 | 0.47 |
| **% Impervious Surfaces** | -0.10 | 0.03 | -0.16 | -0.28 | -0.34 | 0.10 |
| **Stream Width** | -0.22 | 0.36 | 0.10 | 0.05 | -0.03 | 0.16 |
| **Stream Depth** | -0.14 | 0.20 | 0.09 | 0.47 | -0.09 | 0.21 |
| **Calcium** | -0.13 | -0.11 | -0.09 | -0.51 | -0.13 | 0.18 |
| **Chloride** | -0.31 | -0.14 | -0.33 | -0.38 | -0.17 | 0.24 |
| **Fluoride** | -0.65 | -0.23 | -0.81 | -0.78 | -0.69 | 0.67 |
| **Magnesium** | 0.25 | 0.22 | 0.30 | -0.26 | 0.30 | -0.16 |
| **Nitrate** | 0.36 | 0.19 | 0.14 | -0.41 | 0.14 | -0.07 |
| **Potassium** | 0.11 | 0.21 | 0.16 | -0.17 | 0.19 | 0.02 |
| **Sodium** | -0.18 | -0.13 | -0.27 | -0.55 | -0.06 | 0.10 |
| **Sulfate** | 0.32 | 0.24 | 0.06 | -0.53 | 0.09 | -0.20 |
| **Minimum Septic Distance** | -0.58 | -0.26 | -0.69 | 0.07 | -0.81 | 0.41 |
| **Average Septic Distance** | -0.01 | 0.17 | 0.02 | 0.57 | 0.02 | 0.02 |
| **Median Septic Distance** | -0.04 | 0.05 | 0.05 | 0.69 | -0.02 | 0.05 |

| Table 2: Spearman's rank correlation ($r_s$-values) in headwater streams | Caffeine:Ace-K Ratio | Caffeine:Carbamazepine Ratio | Drainage Area | Septic Count | Septic Density |
|---|---|---|---|---|---|
| **Season** | 0.07 | -0.36 | 0.00 | 0.00 | 0.00 |
| **Ace-K** | -0.43 | -0.07 | 0.40 | 0.77 | 0.56 |
| **Atorvastatin** | 0.43 | 0.53 | -0.16 | -0.24 | -0.09 |
| **Caffeine** | 0.87 | 0.75 | 0.19 | 0.05 | -0.04 |
| **Carbamazepine** | 0.12 | -0.50 | -0.03 | 0.14 | 0.19 |
| **Cotinine** | 0.10 | -0.13 | 0.04 | -0.04 | -0.02 |
| **DEET** | -0.33 | 0.10 | 0.00 | 0.08 | 0.08 |
| **Dichlorvos** | 0.21 | 0.18 | -0.02 | -0.01 | -0.01 |
| **Estrone** | -0.26 | 0.20 | -0.14 | -0.04 | 0.04 |
| **Ibuprofen** | 0.21 | 0.22 | 0.07 | 0.22 | 0.10 |
| **Paraxanthine** | 0.28 | -0.09 | 0.04 | 0.09 | 0.15 |
| **Sucralose** | -0.32 | -0.35 | -0.11 | 0.47 | 0.82 |
| **Sulfamethoxazole** | 0.05 | -0.41 | 0.10 | 0.51 | 0.63 |
| **Total PPCP & AS** | -0.28 | -0.34 | -0.24 | 0.55 | 0.98 |
| **Total PPCP** | 0.02 | 0.29 | 0.29 | 0.48 | 0.38 |
| **Total AS** | -0.35 | -0.41 | -0.17 | 0.60 | 0.90 |
| **Caffeine:Sucralose Ratio** | 0.92 | 0.73 | 0.07 | -0.30 | -0.46 |
| **Caffeine:Ace-K Ratio** | 1.00 | 0.70 | -0.05 | -0.29 | -0.26 |
| **Caffeine:Carbamazepine Ratio** | 0.70 | 1.00 | 0.26 | -0.12 | -0.31 |
| **Drainage Area** | -0.05 | 0.26 | 1.00 | 0.62 | -0.12 |
| **Septic Count** | -0.29 | -0.12 | 0.62 | 1.00 | 0.62 |
| **Septic Density** | -0.26 | -0.31 | -0.12 | 0.62 | 1.00 |
| **Mean Basin Slope** | -0.14 | 0.28 | 0.61 | 0.55 | -0.08 |
| **Urban Land Use** | -0.21 | -0.23 | 0.07 | 0.36 | 0.60 |
| **Agriculture Land Use** | 0.14 | 0.26 | 0.34 | -0.08 | -0.30 |
| **Forested Land Use** | 0.11 | 0.21 | 0.14 | -0.19 | -0.60 |
| **Water Land Use** | -0.03 | 0.16 | 0.58 | 0.58 | 0.41 |
| **Transportation Land Use** | 0.31 | 0.16 | -0.08 | -0.27 | -0.30 |
| **% Impervious Surfaces** | 0.24 | -0.20 | -0.38 | -0.51 | -0.08 |
| **Stream Width** | 0.21 | -0.20 | 0.16 | 0.04 | 0.13 |
| **Stream Depth** | 0.15 | 0.19 | 0.10 | 0.09 | 0.13 |
| **Calcium** | 0.24 | 0.11 | -0.38 | -0.31 | -0.05 |
| **Chloride** | 0.07 | 0.23 | 0.26 | 0.10 | -0.28 |
| **Fluoride** | 0.50 | 0.07 | -0.90 | -0.90 | -0.95 |
| **Magnesium** | -0.05 | -0.08 | -0.07 | 0.28 | 0.38 |
| **Nitrate** | 0.15 | -0.07 | -0.08 | -0.12 | 0.22 |
| **Potassium** | -0.05 | 0.04 | 0.23 | 0.41 | 0.29 |
| **Sodium** | -0.05 | 0.20 | 0.32 | 0.12 | -0.22 |
| **Sulfate** | 0.00 | -0.11 | 0.05 | -0.05 | 0.14 |
| **Minimum Septic Distance** | 0.30 | 0.39 | 0.45 | -0.26 | -0.57 |
| **Average Septic Distance** | -0.09 | 0.10 | 0.76 | 0.79 | 0.12 |
| **Median Septic Distance** | -0.06 | 0.16 | 0.55 | 0.64 | 0.12 |

| Table 2: Spearman's rank correlation ($r_s$-values) in headwater streams | Transportation Land Use | % Impervious Surfaces | Stream Width | Stream Depth |
|---|---|---|---|---|
| **Season** | 0.00 | 0.00 | 0.22 | 0.00 |
| **Ace-K** | -0.22 | -0.47 | -0.22 | -0.05 |
| **Atorvastatin** | 0.30 | -0.01 | -0.39 | -0.09 |
| **Caffeine** | 0.24 | 0.01 | 0.19 | 0.19 |
| **Carbamazepine** | 0.20 | 0.16 | 0.32 | 0.03 |
| **Cotinine** | 0.19 | -0.03 | 0.23 | -0.04 |
| **DEET** | 0.00 | -0.08 | -0.38 | -0.05 |
| **Dichlorvos** | 0.04 | -0.06 | -0.02 | -0.23 |
| **Estrone** | -0.14 | 0.08 | -0.34 | 0.15 |
| **Ibuprofen** | -0.12 | -0.26 | -0.06 | 0.20 |
| **Paraxanthine** | -0.14 | -0.10 | -0.20 | 0.20 |
| **Sucralose** | -0.46 | -0.10 | -0.22 | -0.14 |
| **Sulfamethoxazole** | -0.10 | 0.03 | 0.36 | 0.20 |
| **Total PPCP & AS** | -0.30 | -0.16 | 0.10 | 0.09 |
| **Total PPCP** | 0.22 | -0.28 | 0.05 | 0.47 |
| **Total AS** | -0.35 | -0.34 | -0.03 | -0.09 |
| **Caffeine:Sucralose Ratio** | 0.47 | 0.10 | 0.16 | 0.21 |
| **Caffeine:Ace-K Ratio** | 0.31 | 0.24 | 0.21 | 0.15 |
| **Caffeine:Carbamazepine Ratio** | 0.16 | -0.20 | -0.20 | 0.19 |
| **Drainage Area** | -0.08 | -0.38 | 0.16 | 0.10 |
| **Septic Count** | -0.27 | -0.51 | 0.04 | 0.09 |
| **Septic Density** | -0.30 | -0.08 | 0.13 | 0.13 |
| **Mean Basin Slope** | -0.35 | -0.61 | -0.50 | 0.14 |
| **Urban Land Use** | -0.76 | 0.30 | 0.10 | 0.26 |
| **Agriculture Land Use** | 0.59 | -0.25 | 0.34 | -0.24 |
| **Forested Land Use** | 0.57 | -0.53 | -0.13 | -0.41 |
| **Water Land Use** | -0.28 | 0.08 | 0.26 | 0.46 |
| **Transportation Land Use** | 1.00 | 0.15 | 0.27 | 0.02 |
| **% Impervious Surfaces** | 0.15 | 1.00 | 0.38 | 0.31 |
| **Stream Width** | 0.27 | 0.38 | 1.00 | 0.23 |
| **Stream Depth** | 0.02 | 0.31 | 0.23 | 1.00 |
| **Calcium** | -0.33 | 0.41 | -0.18 | -0.07 |
| **Chloride** | 0.19 | -0.27 | -0.19 | -0.29 |
| **Fluoride** | 0.92 | 0.69 | 0.32 | -0.18 |
| **Magnesium** | -0.58 | 0.08 | -0.43 | -0.05 |
| **Nitrate** | -0.28 | 0.55 | 0.20 | 0.00 |
| **Potassium** | -0.28 | -0.09 | -0.13 | -0.17 |
| **Sodium** | -0.06 | -0.32 | -0.22 | -0.47 |
| **Sulfate** | -0.41 | 0.50 | 0.21 | -0.13 |
| **Minimum Septic Distance** | 0.19 | 0.48 | 0.30 | 0.39 |
| **Average Septic Distance** | 0.03 | -0.44 | -0.08 | 0.22 |
| **Median Septic Distance** | 0.00 | -0.40 | -0.28 | 0.30 |

| Table 2: Spearman's rank correlation ($r_s$-values) in headwater streams | Mean Basin Slope | Urban Land Use | Agriculture Land Use | Forested Land Use | Water Land Use |
|---|---|---|---|---|---|
| **Season** | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| **Ace-K** | 0.31 | 0.25 | 0.00 | -0.09 | 0.35 |
| **Atorvastatin** | -0.20 | -0.28 | 0.27 | 0.24 | -0.12 |
| **Caffeine** | 0.00 | -0.13 | 0.23 | 0.11 | 0.15 |
| **Carbamazepine** | -0.27 | 0.01 | 0.10 | -0.02 | -0.02 |
| **Cotinine** | -0.10 | -0.14 | 0.25 | 0.13 | 0.00 |
| **DEET** | 0.07 | -0.03 | -0.05 | 0.02 | 0.01 |
| **Dichlorvos** | -0.03 | -0.06 | 0.07 | 0.07 | -0.07 |
| **Estrone** | 0.08 | 0.11 | -0.27 | -0.15 | 0.03 |
| **Ibuprofen** | 0.24 | 0.01 | -0.10 | 0.01 | 0.05 |
| **Paraxanthine** | 0.07 | 0.13 | 0.00 | -0.10 | 0.14 |
| **Sucralose** | -0.08 | 0.58 | -0.29 | -0.50 | 0.17 |
| **Sulfamethoxazole** | -0.13 | 0.42 | -0.04 | -0.38 | 0.24 |
| **Total PPCP & AS** | -0.10 | 0.52 | -0.30 | -0.52 | 0.25 |
| **Total PPCP** | 0.46 | -0.02 | 0.02 | -0.10 | 0.58 |
| **Total AS** | -0.08 | 0.45 | -0.19 | -0.36 | 0.08 |
| **Caffeine:Sucralose Ratio** | -0.02 | -0.44 | 0.31 | 0.34 | -0.04 |
| **Caffeine:Ace-K Ratio** | -0.14 | -0.21 | 0.14 | 0.11 | -0.03 |
| **Caffeine:Carbamazepine Ratio** | 0.28 | -0.23 | 0.26 | 0.21 | 0.16 |
| **Drainage Area** | 0.61 | 0.07 | 0.34 | 0.14 | 0.58 |
| **Septic Count** | 0.55 | 0.36 | -0.08 | -0.19 | 0.58 |
| **Septic Density** | -0.08 | 0.60 | -0.30 | -0.60 | 0.41 |
| **Mean Basin Slope** | 1.00 | 0.01 | -0.27 | 0.10 | 0.44 |
| **Urban Land Use** | 0.01 | 1.00 | -0.55 | -0.93 | 0.58 |
| **Agriculture Land Use** | -0.27 | -0.55 | 1.00 | 0.65 | -0.22 |
| **Forested Land Use** | 0.10 | -0.93 | 0.65 | 1.00 | -0.58 |
| **Water Land Use** | 0.44 | 0.58 | -0.22 | -0.58 | 1.00 |
| **Transportation Land Use** | -0.35 | -0.76 | 0.59 | 0.57 | -0.28 |
| **% Impervious Surfaces** | -0.61 | 0.30 | -0.25 | -0.53 | 0.08 |
| **Stream Width** | -0.50 | 0.10 | 0.34 | -0.13 | 0.26 |
| **Stream Depth** | 0.14 | 0.26 | -0.24 | -0.41 | 0.46 |
| **Calcium** | -0.18 | 0.28 | -0.52 | -0.33 | -0.06 |
| **Chloride** | 0.07 | -0.40 | 0.29 | 0.53 | -0.21 |
| **Fluoride** | -0.91 | -0.95 | 0.00 | 0.78 | -0.73 |
| **Magnesium** | 0.17 | 0.52 | -0.65 | -0.47 | 0.27 |
| **Nitrate** | -0.54 | 0.54 | -0.02 | -0.49 | 0.10 |
| **Potassium** | 0.21 | 0.24 | -0.25 | -0.15 | 0.33 |
| **Sodium** | 0.02 | -0.21 | 0.35 | 0.45 | -0.20 |
| **Sulfate** | -0.44 | 0.64 | -0.05 | -0.52 | 0.18 |
| **Minimum Septic Distance** | 0.11 | 0.00 | 0.16 | -0.07 | 0.41 |
| **Average Septic Distance** | 0.79 | -0.02 | -0.05 | 0.10 | 0.58 |
| **Median Septic Distance** | 0.85 | -0.05 | -0.26 | 0.02 | 0.58 |

| Table 2: Spearman's rank correlation ($r_s$-values) in headwater streams | Calcium | Chloride | Fluoride | Magnesium | Nitrate | Potassium |
|---|---|---|---|---|---|---|
| **Season** | -0.02 | -0.13 | 0.00 | 0.08 | -0.14 | 0.13 |
| **Ace-K** | -0.31 | 0.22 | -0.51 | 0.20 | 0.00 | 0.38 |
| **Atorvastatin** | 0.05 | 0.15 | 0.87 | -0.18 | 0.15 | -0.23 |
| **Caffeine** | 0.09 | 0.21 | 0.16 | 0.02 | 0.15 | 0.12 |
| **Carbamazepine** | -0.15 | -0.09 | 0.02 | 0.02 | 0.28 | 0.07 |
| **Cotinine** | -0.35 | -0.19 | -0.34 | -0.21 | -0.26 | -0.07 |
| **DEET** | -0.12 | 0.21 | -0.66 | -0.07 | -0.04 | 0.08 |
| **Dichlorvos** | -0.09 | -0.09 | 0.51 | -0.13 | -0.08 | -0.17 |
| **Estrone** | 0.01 | -0.08 | 0.43 | -0.06 | -0.16 | -0.19 |
| **Ibuprofen** | 0.05 | 0.12 | -0.67 | 0.01 | 0.18 | 0.04 |
| **Paraxanthine** | 0.28 | -0.19 | 0.20 | 0.20 | 0.21 | 0.03 |
| **Sucralose** | -0.13 | -0.31 | -0.65 | 0.25 | 0.36 | 0.11 |
| **Sulfamethoxazole** | -0.11 | -0.14 | -0.23 | 0.22 | 0.19 | 0.21 |
| **Total PPCP & AS** | -0.09 | -0.33 | -0.81 | 0.30 | 0.14 | 0.16 |
| **Total PPCP** | -0.51 | -0.38 | -0.78 | -0.26 | -0.41 | -0.17 |
| **Total AS** | -0.13 | -0.17 | -0.69 | 0.30 | 0.14 | 0.19 |
| **Caffeine:Sucralose Ratio** | 0.18 | 0.24 | 0.67 | -0.16 | -0.07 | 0.02 |
| **Caffeine:Ace-K Ratio** | 0.24 | 0.07 | 0.50 | -0.05 | 0.15 | -0.05 |
| **Caffeine:Carbamazepine Ratio** | 0.11 | 0.23 | 0.07 | -0.08 | -0.07 | 0.04 |
| **Drainage Area** | -0.38 | 0.26 | -0.90 | -0.07 | -0.08 | 0.23 |
| **Septic Count** | -0.31 | 0.10 | -0.90 | 0.28 | -0.12 | 0.41 |
| **Septic Density** | -0.05 | -0.28 | -0.95 | 0.38 | 0.22 | 0.29 |
| **Mean Basin Slope** | -0.18 | 0.07 | -0.91 | 0.17 | -0.54 | 0.21 |
| **Urban Land Use** | 0.28 | -0.40 | -0.95 | 0.52 | 0.54 | 0.24 |
| **Agriculture Land Use** | -0.52 | 0.29 | 0.00 | -0.65 | -0.02 | -0.25 |
| **Forested Land Use** | -0.33 | 0.53 | 0.78 | -0.47 | -0.49 | -0.15 |
| **Water Land Use** | -0.06 | -0.21 | -0.73 | 0.27 | 0.10 | 0.33 |
| **Transportation Land Use** | -0.33 | 0.19 | 0.92 | -0.58 | -0.28 | -0.28 |
| **% Impervious Surfaces** | 0.41 | -0.27 | 0.69 | 0.08 | 0.55 | -0.09 |
| **Stream Width** | -0.18 | -0.19 | 0.32 | -0.43 | 0.20 | -0.13 |
| **Stream Depth** | -0.07 | -0.29 | -0.18 | -0.05 | 0.00 | -0.17 |
| **Calcium** | 1.00 | 0.30 | 0.64 | 0.71 | 0.44 | 0.52 |
| **Chloride** | 0.30 | 1.00 | 0.60 | 0.32 | 0.11 | 0.59 |
| **Fluoride** | 0.64 | 0.60 | 1.00 | -0.14 | -0.72 | -0.23 |
| **Magnesium** | 0.71 | 0.32 | -0.14 | 1.00 | 0.36 | 0.79 |
| **Nitrate** | 0.44 | 0.11 | -0.72 | 0.36 | 1.00 | 0.31 |
| **Potassium** | 0.52 | 0.59 | -0.23 | 0.79 | 0.31 | 1.00 |
| **Sodium** | 0.28 | 0.90 | -0.01 | 0.35 | 0.28 | 0.62 |
| **Sulfate** | 0.39 | -0.02 | -0.37 | 0.33 | 0.89 | 0.28 |
| **Minimum Septic Distance** | -0.01 | -0.08 | -0.16 | -0.26 | 0.10 | -0.16 |
| **Average Septic Distance** | -0.33 | 0.21 | -0.34 | 0.12 | -0.45 | 0.33 |
| **Median Septic Distance** | -0.23 | 0.06 | -0.21 | 0.16 | -0.59 | 0.27 |

| Table 2: Spearman's rank correlation ($r_s$-values) in headwater streams | Sodium | Sulfate | Minimum Septic Distance | Average Septic Distance | Median Septic Distance |
|---|---|---|---|---|---|
| **Season** | -0.08 | -0.02 | 0.00 | 0.00 | 0.00 |
| **Ace-K** | 0.24 | 0.02 | -0.38 | 0.51 | 0.38 |
| **Atorvastatin** | 0.06 | -0.09 | -0.02 | -0.20 | -0.17 |
| **Caffeine** | 0.11 | 0.02 | 0.19 | 0.13 | 0.10 |
| **Carbamazepine** | -0.15 | 0.15 | -0.12 | 0.06 | -0.05 |
| **Cotinine** | -0.08 | -0.07 | 0.05 | -0.04 | -0.06 |
| **DEET** | 0.14 | -0.07 | -0.10 | 0.09 | 0.10 |
| **Dichlorvos** | 0.01 | -0.03 | -0.06 | -0.03 | -0.04 |
| **Estrone** | -0.13 | -0.13 | -0.03 | -0.02 | 0.07 |
| **Ibuprofen** | 0.06 | -0.15 | -0.13 | 0.18 | 0.20 |
| **Paraxanthine** | -0.10 | 0.05 | -0.03 | 0.00 | 0.01 |
| **Sucralose** | -0.18 | 0.32 | -0.58 | -0.01 | -0.04 |
| **Sulfamethoxazole** | -0.13 | 0.24 | -0.26 | 0.17 | 0.05 |
| **Total PPCP & AS** | -0.27 | 0.06 | -0.69 | 0.02 | 0.05 |
| **Total PPCP** | -0.55 | -0.53 | 0.07 | 0.57 | 0.69 |
| **Total AS** | -0.06 | 0.09 | -0.81 | 0.02 | -0.02 |
| **Caffeine:Sucralose Ratio** | 0.10 | -0.20 | 0.41 | 0.02 | 0.05 |
| **Caffeine:Ace-K Ratio** | -0.05 | 0.00 | 0.30 | -0.09 | -0.06 |
| **Caffeine:Carbamazepine Ratio** | 0.20 | -0.11 | 0.39 | 0.10 | 0.16 |
| **Drainage Area** | 0.32 | 0.05 | 0.45 | 0.76 | 0.55 |
| **Septic Count** | 0.12 | -0.05 | -0.26 | 0.79 | 0.64 |
| **Septic Density** | -0.22 | 0.14 | -0.57 | 0.12 | 0.12 |
| **Mean Basin Slope** | 0.02 | -0.44 | 0.11 | 0.79 | 0.85 |
| **Urban Land Use** | -0.21 | 0.64 | 0.00 | -0.02 | -0.05 |
| **Agriculture Land Use** | 0.35 | -0.05 | 0.16 | -0.05 | -0.26 |
| **Forested Land Use** | 0.45 | -0.52 | -0.07 | 0.10 | 0.02 |
| **Water Land Use** | -0.20 | 0.18 | 0.41 | 0.58 | 0.58 |
| **Transportation Land Use** | -0.06 | -0.41 | 0.19 | 0.03 | 0.00 |
| **% Impervious Surfaces** | -0.32 | 0.50 | 0.48 | -0.44 | -0.40 |
| **Stream Width** | -0.22 | 0.21 | 0.30 | -0.08 | -0.28 |
| **Stream Depth** | -0.47 | -0.13 | 0.39 | 0.22 | 0.30 |
| **Calcium** | 0.28 | 0.39 | -0.01 | -0.33 | -0.23 |
| **Chloride** | 0.90 | -0.02 | -0.08 | 0.21 | 0.06 |
| **Fluoride** | -0.01 | -0.37 | -0.16 | -0.34 | -0.21 |
| **Magnesium** | 0.35 | 0.33 | -0.26 | 0.12 | 0.16 |
| **Nitrate** | 0.28 | 0.89 | 0.10 | -0.45 | -0.59 |
| **Potassium** | 0.62 | 0.28 | -0.16 | 0.33 | 0.27 |
| **Sodium** | 1.00 | 0.25 | -0.14 | 0.08 | -0.14 |
| **Sulfate** | 0.25 | 1.00 | 0.21 | -0.36 | -0.53 |
| **Minimum Septic Distance** | -0.14 | 0.21 | 1.00 | 0.17 | 0.14 |
| **Average Septic Distance** | 0.08 | -0.36 | 0.17 | 1.00 | 0.93 |
| **Median Septic Distance** | -0.14 | -0.53 | 0.14 | 0.93 | 1.00 |

**Table 3 Monthly Headwater Stream Field Measurements**

| Site | Month | Stream Width (cm) | Stream Depth L (cm) | Stream Depth C (cm) | Stream Depth R (cm) |
|---|---|---|---|---|---|
| **Cockey Creek** | May | 120.00 | 3.00 | 8.00 | 4.00 |
| **Cockey Creek** | June | 115.00 | 9.14 | 5.79 | 9.14 |
| **Cockey Creek** | July | 93.00 | 3.50 | 6.50 | 3.50 |
| **Cockey Creek** | August | 130.00 | 8.50 | 4.00 | 2.00 |
| **Cockey Creek** | September | NA | 5.00 | 5.50 | 4.50 |
| **Cockey Creek** | October | 96.00 | 3.50 | 5.00 | 5.00 |
| **Cockey Creek** | November | 40.00 | 10.00 | 11.00 | 4.50 |
| **Chelsea Beach** | May | NA | NA | NA | NA |
| **Chelsea Beach** | June | 121.92 | 0.30 | 0.70 | 0.50 |
| **Chelsea Beach** | July | 240.00 | 13.00 | 8.00 | 2.50 |
| **Chelsea Beach** | August | 300.00 | 14.00 | 15.00 | 9.00 |
| **Chelsea Beach** | September | NA | 27.00 | 28.00 | 16.00 |
| **Chelsea Beach** | October | NA | NA | NA | NA |
| **Chelsea Beach** | November | 195.58 | 7.00 | 7.00 | 3.00 |
| **Clements Creek** | May | 43.00 | 4.50 | 9.00 | 4.00 |
| **Clements Creek** | June | 27.43 | 1.52 | 6.10 | 1.52 |
| **Clements Creek** | July | 22.00 | 1.50 |  | 1.50 |
| **Clements Creek** | August | 31.50 | 2.00 | 2.00 | 3.00 |
| **Clements Creek** | September | NA | 2.50 | 4.00 | 2.50 |
| **Clements Creek** | October | 40.00 | 3.50 | 5.00 | 4.00 |
| **Clements Creek** | November | NA | 5.50 | 7.00 | 5.50 |
| **Main Creek** | June | 100.00 | 9.14 | 4.57 | 6.10 |
| **Main Creek** | August | NA | NA | NA | NA |
| **Main Creek** | September | NA | NA | NA | NA |
| **Main Creek** | October | NA | 2.50 | 5.00 | 2.00 |
| **Main Creek** | November | NA | 5.00 | 7.00 | 5.00 |
| **Old Man Creek** | May | 11.00 | NA | NA | NA |
| **Old Man Creek** | June | NA | NA | NA | NA |
| **Old Man Creek** | July | 83.00 | 7.00 | 14.00 | 7.00 |
| **Old Man Creek** | August | 83.00 | 9.00 | 12.00 | 7.00 |
| **Old Man Creek** | September | NA | NA | NA | NA |
| **Old Man Creek** | October | 87.00 | 4.50 | 10.00 | 5.50 |
| **Old Man Creek** | November | NA | 7.50 | 12.00 | 5.50 |
| **Rock Creek** | May | 45.72 | 7.62 | 11.43 | 7.62 |
| **Rock Creek** | June | 70.10 | 9.14 | 9.14 | 8.53 |
| **Rock Creek** | July | 98.00 | 2.00 | 3.00 | 9.00 |
| **Rock Creek** | August | 60.00 | 5.00 | 6.00 | 10.00 |
| **Rock Creek** | September | NA | 9.50 | 11.50 | 13.00 |
| **Rock Creek** | October | 174.00 | 4.50 | 4.50 | 5.50 |
| **Rock Creek** | November | 180.34 | 14.00 | 20.00 | 28.00 |
| **SERC** | May | 68.58 | 0.51 | 3.81 | 1.27 |
| **SERC** | August | NA | NA | NA | NA |
| **SERC** | September | NA | NA | NA | NA |

**Table 3 Monthly Headwater Stream Field Measurements**

| Site | Month | Stream Width (cm) | Stream Depth L (cm) | Stream Depth C (cm) | Stream Depth R (cm) |
|---|---|---|---|---|---|
| **SERC** | October | NA | NA | NA | NA |
| **SERC** | November | 66.00 | 1.50 | 2.00 | 2.00 |
| **Swan Creek** | May | 79.00 | 2.00 | 4.00 | 6.00 |
| **Swan Creek** | July | NA | 3.00 | 3.00 | 3.00 |
| **Swan Creek** | August | 40.00 | 2.00 | 2.00 | 1.50 |
| **Swan Creek** | September | NA | NA | NA | NA |
| **Swan Creek** | October | NA | NA | NA | NA |
| **Swan Creek** | November | NA | 8.00 | 8.00 | 7.00 |
| **Chartwell Creek** | May | 220.98 | | | |
| **Chartwell Creek** | June | NA | NA | NA | NA |
| **Chartwell Creek** | July | NA | NA | NA | NA |
| **Chartwell Creek** | August | NA | 10.00 | 13.00 | 10.00 |
| **Chartwell Creek** | September | NA | 13.00 | 7.00 | 7.00 |
| **Chartwell Creek** | October | NA | 12.00 | 10.00 | 18.00 |
| **Chartwell Creek** | November | NA | 15.00 | 15.00 | 18.00 |
| **Wilelinor** | May | 45.00 | 13.00 | 9.50 | 4.00 |
| **Wilelinor** | June | 30.48 | NA | NA | NA |
| **Wilelinor** | July | 100.00 | 8.00 | 26.00 | 12.00 |
| **Wilelinor** | August | 138.00 | 9.00 | 17.50 | 12.00 |
| **Wilelinor** | September | NA | 4.00 | 15.00 | 8.50 |
| **Wilelinor** | October | 165.00 | 9.00 | 14.00 | 11.00 |
| **Wilelinor** | November | 106.00 | 9.00 | 13.00 | 12.00 |

**Table 3 Monthly Headwater Stream Field Measurements**

| Site | Month | Stream Depth Average (cm) | Velocity L (m/s) | Velocity C (m/s) | Velocity R (m/s) | Velocity Average (m/s) |
|---|---|---|---|---|---|---|
| **Cockey Creek** | May | 5.00 | NA | NA | NA | 0.25 |
| **Cockey Creek** | June | 8.03 | NA | NA | NA | 0.25 |
| **Cockey Creek** | July | 4.50 | NA | NA | NA | 0.26 |
| **Cockey Creek** | August | 4.83 | 0.14 | 0.23 | 0.17 | 0.18 |
| **Cockey Creek** | September | 5.00 | NA | NA | | 0.29 |
| **Cockey Creek** | October | 4.50 | NA | NA | NA | NA |
| **Cockey Creek** | November | 8.50 | NA | NA | NA | 0.17 |
| **Chelsea Beach** | May | NA | NA | NA | NA | 0.02 |
| **Chelsea Beach** | June | 0.50 | NA | NA | NA | 0.08 |
| **Chelsea Beach** | July | 7.83 | NA | NA | NA | 0.13 |
| **Chelsea Beach** | August | 12.67 | 0.07 | 0.04 | 0.07 | 0.06 |
| **Chelsea Beach** | September | 23.67 | NA | NA | NA | 0.03 |
| **Chelsea Beach** | October | 23.50 | NA | NA | NA | 0.01 |
| **Chelsea Beach** | November | 5.67 | NA | NA | NA | 0.22 |
| **Clements Creek** | May | 5.83 | 0.02 | 0.07 | 0.06 | 0.05 |

**Table 3 Monthly Headwater Stream Field Measurements**

| Site | Month | Stream Depth Average (cm) | Velocity L (m/s) | Velocity C (m/s) | Velocity R (m/s) | Velocity Average (m/s) |
|---|---|---|---|---|---|---|
| **Clements Creek** | June | 3.05 | NA | NA | NA | 0.13 |
| **Clements Creek** | July | 1.50 | NA | NA | NA | 0.07 |
| **Clements Creek** | August | 2.33 | NA | NA | NA | 0.04 |
| **Clements Creek** | September | 3.00 | NA | NA | NA | 0.07 |
| **Clements Creek** | October | 4.17 | NA | NA | NA | 0.25 |
| **Clements Creek** | November | 6.00 | NA | NA | NA | 0.04 |
| **Main Creek** | June | 6.60 | NA | NA | NA | 0.14 |
| **Main Creek** | July | NA | NA | NA | NA | 0.31 |
| **Main Creek** | August | 1.50 | NA | NA | NA | 0.01 |
| **Main Creek** | September | 1.00 | NA | NA | NA | 0.18 |
| **Main Creek** | October | 3.17 | NA | NA | NA | 0.11 |
| **Main Creek** | November | 5.67 | NA | NA | NA | NA |
| **Old Man Creek** | May | 14.00 | NA | NA | NA | 0.08 |
| **Old Man Creek** | June | NA | NA | NA | NA | NA |
| **Old Man Creek** | July | 9.33 | NA | NA | NA | 0.10 |
| **Old Man Creek** | August | 9.33 | 0.02 | 0.04 | 0.17 | 0.08 |
| **Old Man Creek** | September | 6.00 | NA | NA | NA | 0.09 |
| **Old Man Creek** | October | 6.67 | NA | NA | NA | 0.06 |
| **Old Man Creek** | November | 8.33 | NA | NA | NA | 0.05 |
| **Rock Creek** | May | 8.89 | NA | NA | NA | 0.44 |
| **Rock Creek** | June | 8.94 | NA | NA | NA | 0.10 |
| **Rock Creek** | July | 4.67 | NA | NA | NA | 0.17 |
| **Rock Creek** | August | 7.00 | 0.14 | 0.27 | 0.23 | 0.21 |
| **Rock Creek** | September | 11.33 | NA | NA | NA | 0.18 |
| **Rock Creek** | October | 4.83 | NA | NA | NA | 0.09 |
| **Rock Creek** | November | 20.67 | NA | NA | NA | NA |
| **SERC** | May | NA | NA | NA | NA | 0.11 |
| **SERC** | August | NA | NA | NA | NA | NA |
| **SERC** | September | 5.08 | NA | NA | NA | 0.03 |
| **SERC** | October | 6.00 | NA | NA | NA | 0.01 |
| **SERC** | November | 1.83 | NA | NA | NA | NA |
| **Swan Creek** | May | 0.10 | NA | NA | NA | 0.10 |
| **Swan Creek** | July | 3.00 | NA | NA | NA | 0.09 |
| **Swan Creek** | August | 1.83 | 0.03 | 0.03 | 0.01 | 0.02 |
| **Swan Creek** | September | 0.50 | NA | NA | NA | 0.09 |
| **Swan Creek** | October | 7.00 | NA | NA | NA | NA |
| **Swan Creek** | November | 7.67 | NA | NA | NA | NA |
| **Chartwell Creek** | May | 14.50 | NA | NA | NA | 0.10 |
| **Chartwell Creek** | June | 15.24 | NA | NA | NA | 0.09 |

**Table 3 Monthly Headwater Stream Field Measurements**

| Site | Month | Stream Depth Average (cm) | Velocity L (m/s) | Velocity C (m/s) | Velocity R (m/s) | Velocity Average (m/s) |
|---|---|---|---|---|---|---|
| **Chartwell Creek** | July | 12.70 | NA | NA | NA | 0.13 |
| **Chartwell Creek** | August | 11.00 | 0.29 | 0.33 | 0.25 | 0.29 |
| **Chartwell Creek** | September | 9.00 | NA | NA | NA | 0.15 |
| **Chartwell Creek** | October | 13.33 | NA | NA | NA | 0.09 |
| **Chartwell Creek** | November | 16.00 | NA | NA | NA | 0.11 |
| **Wilelinor** | May | 8.83 | 0.30 | 0.28 | 0.17 | 0.25 |
| **Wilelinor** | June | 2.00 | NA | NA | NA | 0.10 |
| **Wilelinor** | July | 15.33 | NA | NA | NA | 0.17 |
| **Wilelinor** | August | 12.83 | 0.09 | 0.23 | 0.22 | 0.18 |
| **Wilelinor** | September | 9.17 | NA | NA | NA | 0.25 |
| **Wilelinor** | October | 11.33 | NA | NA | NA | 0.18 |
| **Wilelinor** | November | 11.33 | NA | NA | NA | 0.25 |

**Table 4 Monthly Headwater Stream PPCP/AS Concentrations**

| Sample Site | Month | Ace-K (µg/L) | Acetaminophen (µg/L) | Atorvastatin (µg/L) |
|---|---|---|---|---|
| **Chartwell Creek** | March | NA | n.d. | 0.00 |
| **Chartwell Creek** | April | NA | NA | NA |
| **Chartwell Creek** | May | 0.28 | n.d. | n.d. |
| **Chartwell Creek** | June | 0.18 | n.d. | n.d. |
| **Chartwell Creek** | July | 0.24 | 0.00 | 0.00 |
| **Chartwell Creek** | August | 0.22 | n.d. | n.d. |
| **Chartwell Creek** | September | 0.20 | NA | NA |
| **Chartwell Creek** | October | 0.19 | 0.00 | 0.00 |
| **Chartwell Creek** | November | 0.17 | n.d. | 0.00 |
| **Chelsea Beach** | March | NA | NA | NA |
| **Chelsea Beach** | April | NA | n.d. | 0.00 |
| **Chelsea Beach** | May | 0.22 | n.d. | n.d. |
| **Chelsea Beach** | June | 0.16 | n.d. | n.d. |
| **Chelsea Beach** | July | 0.19 | 0.00 | 0.00 |
| **Chelsea Beach** | August | 0.19 | n.d. | n.d. |
| **Chelsea Beach** | September | 0.19 | NA | NA |
| **Chelsea Beach** | October | 1.43 | 0.00 | 0.00 |
| **Chelsea Beach** | November | 0.20 | n.d. | 0.00 |
| **Clements Creek** | March | NA | NA | NA |
| **Clements Creek** | April | NA | NA | NA |
| **Clements Creek** | May | 0.28 | n.d. | n.d. |
| **Clements Creek** | June | 0.23 | n.d. | n.d. |
| **Clements Creek** | July | 0.19 | 0.00 | 0.00 |
| **Clements Creek** | August | 0.18 | n.d. | n.d. |
| **Clements Creek** | September | 0.17 | NA | NA |
| **Clements Creek** | October | 0.17 | 0.00 | 0.00 |
| **Clements Creek** | November | 0.13 | n.d. | 0.00 |
| **Cockey Creek** | March | NA | n.d. | 0.02 |
| **Cockey Creek** | April | NA | n.d. | 0.00 |
| **Cockey Creek** | May | 0.08 | n.d. | n.d. |
| **Cockey Creek** | June | 0.07 | n.d. | n.d. |
| **Cockey Creek** | July | 0.11 | 0.00 | 0.00 |
| **Cockey Creek** | August | 0.09 | n.d. | n.d. |
| **Cockey Creek** | September | 0.09 | NA | NA |
| **Cockey Creek** | October | 0.06 | 0.00 | 0.00 |
| **Cockey Creek** | November | 0.11 | n.d. | 0.01 |
| **Main Creek** | March | NA | NA | NA |
| **Main Creek** | April | NA | NA | NA |
| **Main Creek** | May | 0.33 | n.d. | n.d. |

**Table 4 Monthly Headwater Stream PPCP/AS Concentrations**

| Sample Site | Month | Ace-K (µg/L) | Acetaminophen (µg/L) | Atorvastatin (µg/L) |
|---|---|---|---|---|
| **Main Creek** | June | 0.22 | n.d. | n.d. |
| **Main Creek** | July | 0.21 | 0.00 | 0.00 |
| **Main Creek** | August | 0.16 | n.d. | n.d. |
| **Main Creek** | September | 0.15 | NA | NA |
| **Main Creek** | October | 0.06 | 0.00 | 0.00 |
| **Main Creek** | November | 0.07 | n.d. | 0.00 |
| **Old Man Creek** | March | NA | n.d. | 0.00 |
| **Old Man Creek** | April | NA | NA | NA |
| **Old Man Creek** | May | 0.30 | n.d. | n.d. |
| **Old Man Creek** | June | 0.16 | n.d. | n.d. |
| **Old Man Creek** | July | 0.14 | 0.00 | 0.00 |
| **Old Man Creek** | August | 0.14 | n.d. | n.d. |
| **Old Man Creek** | September | 0.12 | NA | NA |
| **Old Man Creek** | October | 0.11 | 0.00 | 0.00 |
| **Old Man Creek** | November | 0.10 | n.d. | 0.00 |
| **Rock Creek** | March | NA | NA | NA |
| **Rock Creek** | April | NA | NA | NA |
| **Rock Creek** | May | 0.06 | n.d. | n.d. |
| **Rock Creek** | June | 0.03 | n.d. | n.d. |
| **Rock Creek** | July | 0.03 | 0.00 | n.d. |
| **Rock Creek** | August | 0.03 | n.d. | n.d. |
| **Rock Creek** | September | 0.03 | NA | NA |
| **Rock Creek** | October | 0.03 | 0.00 | 0.00 |
| **Rock Creek** | November | 0.04 | n.d. | 0.00 |
| **SERC** | March | NA | NA | NA |
| **SERC** | April | NA | NA | NA |
| **SERC** | May | 0.12 | n.d. | n.d. |
| **SERC** | June | NA | NA | NA |
| **SERC** | July | 0.05 | 0.00 | 0.00 |
| **SERC** | August | 0.19 | n.d. | n.d. |
| **SERC** | September | 0.11 | NA | NA |
| **SERC** | October | 0.16 | 0.00 | 0.00 |
| **SERC** | November | 0.10 | n.d. | 0.00 |
| **Swan Creek** | March | NA | NA | NA |
| **Swan Creek** | April | NA | NA | NA |
| **Swan Creek** | May | 0.31 | n.d. | n.d. |
| **Swan Creek** | June | 0.16 | n.d. | n.d. |
| **Swan Creek** | July | 0.29 | 0.00 | 0.00 |
| **Swan Creek** | August | 0.09 | n.d. | n.d. |

**Table 4 Monthly Headwater Stream PPCP/AS Concentrations**

| Sample Site | Month | Ace-K (µg/L) | Acetaminophen (µg/L) | Atorvastatin (µg/L) |
|---|---|---|---|---|
| **Swan Creek** | September | 0.11 | NA | NA |
| **Swan Creek** | October | 0.09 | 0.00 | 0.00 |
| **Swan Creek** | November | 0.18 | n.d. | 0.00 |
| **Wilelinor** | March | NA | NA | NA |
| **Wilelinor** | April | NA | NA | NA |
| **Wilelinor** | May | 0.08 | n.d. | n.d. |
| **Wilelinor** | June | 0.19 | n.d. | n.d. |
| **Wilelinor** | July | 0.13 | 0.00 | 0.00 |
| **Wilelinor** | August | 0.06 | n.d. | n.d. |
| **Wilelinor** | September | 0.05 | NA | NA |
| **Wilelinor** | October | 0.04 | 0.00 | 0.00 |
| **Wilelinor** | November | 0.04 | n.d. | n.d. |

**Table 4 Monthly Headwater Stream PPCP/AS Concentrations**

| Sample Site | Month | Caffeine (µg/L) | Carbamazepine (µg/L) | Cotinine (µg/L) | DEET (µg/L) |
|---|---|---|---|---|---|
| **Chartwell Creek** | March | 0.11 | 0.07 | 0.02 | 0.04 |
| **Chartwell Creek** | April | NA | NA | NA | NA |
| **Chartwell Creek** | May | 0.02 | 0.02 | 0.00 | n.d. |
| **Chartwell Creek** | June | 0.03 | 0.00 | 0.01 | 0.02 |
| **Chartwell Creek** | July | 0.72 | 0.01 | 0.01 | n.d. |
| **Chartwell Creek** | August | 0.04 | 0.01 | 0.00 | 0.02 |
| **Chartwell Creek** | September | NA | NA | NA | NA |
| **Chartwell Creek** | October | 0.02 | 0.02 | 0.01 | 0.00 |
| **Chartwell Creek** | November | 0.06 | 0.05 | 0.01 | 0.02 |
| **Chelsea Beach** | March | NA | NA | NA | NA |
| **Chelsea Beach** | April | 0.10 | 0.08 | 0.02 | 0.04 |
| **Chelsea Beach** | May | 0.03 | 0.03 | 0.00 | n.d. |
| **Chelsea Beach** | June | 0.03 | 0.02 | 0.01 | 0.03 |
| **Chelsea Beach** | July | 0.15 | 0.03 | 0.01 | 0.00 |
| **Chelsea Beach** | August | 0.02 | 0.04 | 0.00 | n.d. |
| **Chelsea Beach** | September | NA | NA | NA | NA |
| **Chelsea Beach** | October | 0.01 | 0.04 | 0.01 | 0.00 |
| **Chelsea Beach** | November | 0.07 | 0.07 | 0.02 | 0.02 |
| **Clements Creek** | March | NA | NA | NA | NA |
| **Clements Creek** | April | NA | NA | NA | NA |
| **Clements Creek** | May | 0.01 | n.d. | 0.00 | 0.03 |

**Table 4 Monthly Headwater Stream PPCP/AS Concentrations**

| Sample Site | Month | Caffeine (µg/L) | Carbamazepine (µg/L) | Cotinine (µg/L) | DEET (µg/L) |
|---|---|---|---|---|---|
| **Clements Creek** | June | 0.00 | 0.00 | 0.01 | 0.05 |
| **Clements Creek** | July | 0.30 | n.d. | 0.01 | 0.01 |
| **Clements Creek** | August | 0.01 | n.d. | 0.00 | 0.02 |
| **Clements Creek** | September | NA | NA | NA | NA |
| **Clements Creek** | October | 0.02 | 0.00 | 0.01 | 0.01 |
| **Clements Creek** | November | 0.06 | n.d. | 0.01 | 0.02 |
| **Cockey Creek** | March | 0.19 | 0.06 | 0.02 | 0.02 |
| **Cockey Creek** | April | 0.13 | 0.06 | 0.02 | 0.03 |
| **Cockey Creek** | May | 0.04 | 0.01 | 0.00 | n.d. |
| **Cockey Creek** | June | 0.07 | 0.00 | 0.01 | 0.03 |
| **Cockey Creek** | July | 0.11 | 0.01 | 0.01 | 0.00 |
| **Cockey Creek** | August | 0.04 | 0.01 | 0.00 | 0.02 |
| **Cockey Creek** | September | NA | NA | NA | NA |
| **Cockey Creek** | October | 0.01 | 0.00 | 0.01 | 0.00 |
| **Cockey Creek** | November | 0.09 | 0.04 | 0.02 | 0.03 |
| **Main Creek** | March | NA | NA | NA | NA |
| **Main Creek** | April | NA | NA | NA | NA |
| **Main Creek** | May | 0.02 | 0.03 | 0.00 | n.d. |
| **Main Creek** | June | 0.00 | 0.02 | 0.01 | 0.04 |
| **Main Creek** | July | 0.22 | 0.03 | 0.01 | n.d. |
| **Main Creek** | August | 0.02 | 0.03 | 0.00 | n.d. |
| **Main Creek** | September | NA | NA | NA | NA |
| **Main Creek** | October | 0.01 | 0.04 | 0.01 | 0.01 |
| **Main Creek** | November | 0.04 | 0.05 | 0.02 | 0.02 |
| **Old Man Creek** | March | 0.09 | 0.06 | 0.02 | 0.04 |
| **Old Man Creek** | April | NA | NA | NA | NA |
| **Old Man Creek** | May | 0.02 | 0.01 | 0.00 | 0.03 |
| **Old Man Creek** | June | 0.00 | 0.00 | 0.01 | 0.03 |
| **Old Man Creek** | July | 0.60 | 0.01 | 0.01 | 0.00 |
| **Old Man Creek** | August | 0.02 | 0.01 | 0.00 | 0.02 |
| **Old Man Creek** | September | NA | NA | NA | NA |
| **Old Man Creek** | October | 0.02 | 0.02 | 0.01 | 0.00 |
| **Old Man Creek** | November | 0.01 | 0.04 | 0.01 | 0.02 |
| **Rock Creek** | March | NA | NA | NA | NA |
| **Rock Creek** | April | NA | NA | NA | NA |
| **Rock Creek** | May | 0.02 | n.d. | 0.00 | n.d. |

**Table 4 Monthly Headwater Stream PPCP/AS Concentrations**

| Sample Site | Month | Caffeine (µg/L) | Carbamazepine (µg/L) | Cotinine (µg/L) | DEET (µg/L) |
|---|---|---|---|---|---|
| **Rock Creek** | June | 0.00 | 0.00 | 0.01 | 0.03 |
| **Rock Creek** | July | 0.38 | n.d. | 0.00 | n.d. |
| **Rock Creek** | August | 0.01 | n.d. | 0.00 | n.d. |
| **Rock Creek** | September | NA | NA | NA | NA |
| **Rock Creek** | October | 0.01 | 0.00 | 0.01 | 0.00 |
| **Rock Creek** | November | 0.05 | 0.04 | 0.01 | 0.01 |
| **SERC** | March | NA | NA | NA | NA |
| **SERC** | April | NA | NA | NA | NA |
| **SERC** | May | 0.02 | 0.01 | 0.00 | n.d. |
| **SERC** | June | NA | NA | NA | NA |
| **SERC** | July | 0.28 | 0.01 | 0.01 | n.d. |
| **SERC** | August | 0.01 | 0.01 | 0.00 | n.d. |
| **SERC** | September | NA | NA | NA | NA |
| **SERC** | October | 0.02 | 0.00 | 0.01 | 0.00 |
| **SERC** | November | 0.01 | 0.03 | 0.01 | 0.02 |
| **Swan Creek** | March | NA | NA | NA | NA |
| **Swan Creek** | April | NA | NA | NA | NA |
| **Swan Creek** | May | 0.02 | n.d. | 0.00 | n.d. |
| **Swan Creek** | June | 0.01 | 0.00 | 0.01 | 0.02 |
| **Swan Creek** | July | 0.68 | 0.01 | 0.01 | n.d. |
| **Swan Creek** | August | 0.13 | n.d. | 0.01 | 0.02 |
| **Swan Creek** | September | NA | NA | NA | NA |
| **Swan Creek** | October | 0.02 | 0.02 | 0.01 | 0.00 |
| **Swan Creek** | November | 0.04 | 0.05 | 0.01 | 0.03 |
| **Wilelinor** | March | NA | NA | NA | NA |
| **Wilelinor** | April | NA | NA | NA | NA |
| **Wilelinor** | May | 0.22 | 0.01 | 0.00 | n.d. |
| **Wilelinor** | June | 0.00 | 0.21 | 0.01 | 0.10 |
| **Wilelinor** | July | 0.57 | 0.02 | 0.01 | n.d. |
| **Wilelinor** | August | 0.04 | 0.03 | 0.00 | 0.03 |
| **Wilelinor** | September | NA | NA | NA | NA |
| **Wilelinor** | October | 0.01 | 0.03 | 0.01 | 0.00 |
| **Wilelinor** | November | 0.06 | 0.06 | 0.01 | 0.02 |

**Table 4 Monthly Headwater Stream PPCP/AS Concentrations**

| Sample Site | Month | Dichlorvos (µg/L) | Diclofenac (µg/L) | Estrone (µg/L) | Ibuprofen (µg/L) |
|---|---|---|---|---|---|
| **Chartwell Creek** | March | 0.00 | n.d. | 0.00 | n.d. |
| **Chartwell Creek** | April | NA | NA | NA | NA |
| **Chartwell Creek** | May | 0.00 | 0.00 | 0.04 | 0.32 |
| **Chartwell Creek** | June | n.d. | n.d. | 0.02 | 0.00 |
| **Chartwell Creek** | July | n.d. | 0.00 | 0.02 | n.d. |
| **Chartwell Creek** | August | 0.00 | 0.00 | 0.01 | 0.00 |
| **Chartwell Creek** | September | NA | NA | NA | NA |
| **Chartwell Creek** | October | 0.01 | n.d. | 0.01 | 0.00 |
| **Chartwell Creek** | November | 0.00 | n.d. | 0.00 | 0.30 |
| **Chelsea Beach** | March | NA | NA | NA | NA |
| **Chelsea Beach** | April | 0.00 | n.d. | 0.00 | n.d. |
| **Chelsea Beach** | May | 0.00 | 0.00 | 0.02 | n.d. |
| **Chelsea Beach** | June | n.d. | n.d. | 0.01 | 0.14 |
| **Chelsea Beach** | July | 0.02 | 0.00 | 0.01 | n.d. |
| **Chelsea Beach** | August | 0.00 | 0.00 | 0.01 | n.d. |
| **Chelsea Beach** | September | NA | NA | NA | NA |
| **Chelsea Beach** | October | 0.00 | n.d. | 0.01 | 0.00 |
| **Chelsea Beach** | November | 0.00 | n.d. | 0.00 | n.d. |
| **Clements Creek** | March | NA | NA | NA | NA |
| **Clements Creek** | April | NA | NA | NA | NA |
| **Clements Creek** | May | 0.00 | 0.00 | 0.03 | 0.03 |
| **Clements Creek** | June | n.d. | n.d. | 0.02 | 0.00 |
| **Clements Creek** | July | n.d. | 0.00 | 0.01 | 0.14 |
| **Clements Creek** | August | 0.00 | 0.00 | 0.01 | 0.17 |
| **Clements Creek** | September | NA | NA | NA | NA |
| **Clements Creek** | October | 0.01 | n.d. | 0.02 | 0.00 |
| **Clements Creek** | November | 0.00 | n.d. | 0.00 | n.d. |
| **Cockey Creek** | March | 0.00 | n.d. | 0.00 | n.d. |
| **Cockey Creek** | April | 0.00 | n.d. | 0.00 | n.d. |
| **Cockey Creek** | May | 0.00 | 0.00 | 0.01 | n.d. |
| **Cockey Creek** | June | n.d. | n.d. | 0.06 | 0.00 |
| **Cockey Creek** | July | 0.02 | 0.00 | 0.00 | n.d. |
| **Cockey Creek** | August | 0.00 | 0.00 | 0.01 | n.d. |
| **Cockey Creek** | September | NA | NA | NA | NA |
| **Cockey Creek** | October | 0.01 | n.d. | 0.01 | 0.00 |

**Table 4 Monthly Headwater Stream PPCP/AS Concentrations**

| Sample Site | Month | Dichlorvos (µg/L) | Diclofenac (µg/L) | Estrone (µg/L) | Ibuprofen (µg/L) |
|---|---|---|---|---|---|
| **Cockey Creek** | November | 0.00 | n.d. | 0.00 | 0.12 |
| **Main Creek** | March | NA | NA | NA | NA |
| **Main Creek** | April | NA | NA | NA | NA |
| **Main Creek** | May | 0.00 | 0.00 | 0.03 | 0.00 |
| **Main Creek** | June | n.d. | n.d. | 0.05 | 0.00 |
| **Main Creek** | July | n.d. | 0.00 | 0.01 | n.d. |
| **Main Creek** | August | 0.00 | 0.00 | 0.01 | 0.03 |
| **Main Creek** | September | NA | NA | NA | NA |
| **Main Creek** | October | 0.00 | n.d. | 0.00 | 0.00 |
| **Main Creek** | November | n.d. | n.d. | 0.00 | n.d. |
| **Old Man Creek** | March | 0.00 | n.d. | 0.00 | n.d. |
| **Old Man Creek** | April | NA | NA | NA | NA |
| **Old Man Creek** | May | 0.00 | 0.00 | 0.03 | 0.20 |
| **Old Man Creek** | June | n.d. | n.d. | 0.04 | 0.04 |
| **Old Man Creek** | July | 0.01 | 0.00 | 0.02 | 0.01 |
| **Old Man Creek** | August | 0.00 | 0.00 | 0.01 | 0.25 |
| **Old Man Creek** | September | NA | NA | NA | NA |
| **Old Man Creek** | October | 0.01 | n.d. | 0.01 | 0.00 |
| **Old Man Creek** | November | 0.00 | n.d. | 0.00 | 0.11 |
| **Rock Creek** | March | NA | NA | NA | NA |
| **Rock Creek** | April | NA | NA | NA | NA |
| **Rock Creek** | May | 0.00 | 0.00 | 0.03 | 0.02 |
| **Rock Creek** | June | n.d. | n.d. | 0.06 | 0.00 |
| **Rock Creek** | July | 0.01 | 0.00 | 0.02 | n.d. |
| **Rock Creek** | August | 0.00 | 0.00 | 0.01 | n.d. |
| **Rock Creek** | September | NA | NA | NA | NA |
| **Rock Creek** | October | 0.00 | n.d. | 0.00 | 0.00 |
| **Rock Creek** | November | 0.00 | n.d. | 0.00 | n.d. |
| **SERC** | March | NA | NA | NA | NA |
| **SERC** | April | NA | NA | NA | NA |
| **SERC** | May | 0.00 | 0.00 | 0.02 | n.d. |
| **SERC** | June | NA | NA | NA | NA |
| **SERC** | July | 0.02 | 0.00 | 0.02 | n.d. |
| **SERC** | August | 0.00 | 0.00 | 0.00 | n.d. |
| **SERC** | September | NA | NA | NA | NA |
| **SERC** | October | 0.04 | n.d. | 0.01 | 0.01 |

**Table 4 Monthly Headwater Stream PPCP/AS Concentrations**

| Sample Site | Month | Dichlorvos (µg/L) | Diclofenac (µg/L) | Estrone (µg/L) | Ibuprofen (µg/L) |
|---|---|---|---|---|---|
| **SERC** | November | 0.00 | n.d. | 0.00 | 0.13 |
| **Swan Creek** | March | NA | NA | NA | NA |
| **Swan Creek** | April | NA | NA | NA | NA |
| **Swan Creek** | May | 0.00 | 0.00 | 0.07 | 0.00 |
| **Swan Creek** | June | n.d. | n.d. | 0.03 | 0.10 |
| **Swan Creek** | July | 0.02 | 0.00 | 0.04 | 0.24 |
| **Swan Creek** | August | 0.00 | 0.00 | 0.01 | 0.00 |
| **Swan Creek** | September | NA | NA | NA | NA |
| **Swan Creek** | October | 0.02 | n.d. | 0.02 | 0.09 |
| **Swan Creek** | November | 0.00 | n.d. | 0.00 | 0.14 |
| **Wilelinor** | March | NA | NA | NA | NA |
| **Wilelinor** | April | NA | NA | NA | NA |
| **Wilelinor** | May | 0.00 | 0.00 | 0.02 | n.d. |
| **Wilelinor** | June | n.d. | n.d. | 0.03 | 0.00 |
| **Wilelinor** | July | 0.02 | 0.00 | 0.04 | n.d. |
| **Wilelinor** | August | 0.00 | 0.00 | 0.00 | 0.24 |
| **Wilelinor** | September | NA | NA | NA | NA |
| **Wilelinor** | October | 0.00 | n.d. | 0.01 | 0.00 |
| **Wilelinor** | November | 0.00 | n.d. | 0.00 | n.d. |

**Table 4 Monthly Headwater Stream PPCP/AS Concentrations**

| Sample Site | Month | Paraxanthine (µg/L) | Sucralose (µg/L) | Sulfamethoxazole (µg/L) |
|---|---|---|---|---|
| **Chartwell Creek** | March | 0.10 | 2.56 | 0.04 |
| **Chartwell Creek** | April | NA | NA | NA |
| **Chartwell Creek** | May | n.d. | 1.96 | 0.01 |
| **Chartwell Creek** | June | 0.00 | 1.62 | 0.00 |
| **Chartwell Creek** | July | 0.01 | 2.12 | 0.01 |
| **Chartwell Creek** | August | n.d. | 1.64 | 0.00 |
| **Chartwell Creek** | September | NA | NA | NA |
| **Chartwell Creek** | October | 0.01 | 1.81 | 0.01 |
| **Chartwell Creek** | November | n.d. | 1.80 | 0.02 |
| **Chelsea Beach** | March | NA | NA | NA |
| **Chelsea Beach** | April | 0.08 | 2.35 | 0.03 |
| **Chelsea Beach** | May | n.d. | 1.57 | 0.01 |

**Table 4 Monthly Headwater Stream PPCP/AS Concentrations**

| Sample Site | Month | Paraxanthine (µg/L) | Sucralose (µg/L) | Sulfamethoxazole (µg/L) |
|---|---|---|---|---|
| **Chelsea Beach** | June | 0.00 | 0.99 | 0.00 |
| **Chelsea Beach** | July | 0.01 | 2.05 | 0.01 |
| **Chelsea Beach** | August | n.d. | 1.62 | 0.01 |
| **Chelsea Beach** | September | NA | NA | NA |
| **Chelsea Beach** | October | 0.01 | 1.97 | 0.02 |
| **Chelsea Beach** | November | 0.00 | 2.04 | 0.02 |
| **Clements Creek** | March | NA | NA | NA |
| **Clements Creek** | April | NA | NA | NA |
| **Clements Creek** | May | n.d. | 1.01 | 0.00 |
| **Clements Creek** | June | 0.00 | 0.88 | 0.00 |
| **Clements Creek** | July | 0.03 | 0.87 | 0.00 |
| **Clements Creek** | August | n.d. | 0.96 | 0.00 |
| **Clements Creek** | September | NA | NA | NA |
| **Clements Creek** | October | 0.01 | 0.83 | 0.00 |
| **Clements Creek** | November | n.d. | 0.85 | n.d. |
| **Cockey Creek** | March | n.d. | n.d. | n.d. |
| **Cockey Creek** | April | 0.07 | 0.64 | n.d. |
| **Cockey Creek** | May | 0.00 | 0.31 | 0.00 |
| **Cockey Creek** | June | 0.00 | 0.03 | 0.00 |
| **Cockey Creek** | July | 0.01 | 0.34 | 0.00 |
| **Cockey Creek** | August | n.d. | 0.34 | 0.00 |
| **Cockey Creek** | September | NA | NA | NA |
| **Cockey Creek** | October | 0.01 | 0.21 | 0.00 |
| **Cockey Creek** | November | 0.06 | 0.49 | n.d. |
| **Main Creek** | March | NA | NA | NA |
| **Main Creek** | April | NA | NA | NA |
| **Main Creek** | May | n.d. | 3.23 | 0.01 |
| **Main Creek** | June | 0.00 | 4.39 | 0.00 |
| **Main Creek** | July | 0.01 | 4.83 | 0.01 |
| **Main Creek** | August | n.d. | 2.33 | 0.01 |
| **Main Creek** | September | NA | NA | NA |
| **Main Creek** | October | 0.01 | 3.05 | 0.01 |
| **Main Creek** | November | 0.06 | 2.46 | 0.02 |
| **Old Man Creek** | March | 0.07 | 2.18 | 0.03 |
| **Old Man Creek** | April | NA | NA | NA |
| **Old Man Creek** | May | n.d. | 2.31 | 0.01 |

**Table 4 Monthly Headwater Stream PPCP/AS Concentrations**

| Sample Site | Month | Paraxanthine (µg/L) | Sucralose (µg/L) | Sulfamethoxazole (µg/L) |
|---|---|---|---|---|
| **Old Man Creek** | June | 0.00 | 1.34 | 0.01 |
| **Old Man Creek** | July | 0.01 | 3.03 | 0.00 |
| **Old Man Creek** | August | n.d. | 2.16 | 0.00 |
| **Old Man Creek** | September | NA | NA | NA |
| **Old Man Creek** | October | 0.01 | 2.21 | 0.01 |
| **Old Man Creek** | November | n.d. | 2.28 | n.d. |
| **Rock Creek** | March | NA | NA | NA |
| **Rock Creek** | April | NA | NA | NA |
| **Rock Creek** | May | n.d. | n.d. | n.d. |
| **Rock Creek** | June | 0.00 | 0.06 | 0.00 |
| **Rock Creek** | July | 0.01 | n.d. | 0.00 |
| **Rock Creek** | August | n.d. | n.d. | 0.00 |
| **Rock Creek** | September | NA | NA | NA |
| **Rock Creek** | October | 0.01 | 0.07 | 0.00 |
| **Rock Creek** | November | n.d. | 0.08 | n.d. |
| **SERC** | March | NA | NA | NA |
| **SERC** | April | NA | NA | NA |
| **SERC** | May | n.d. | 2.16 | 0.01 |
| **SERC** | June | NA | NA | NA |
| **SERC** | July | 0.01 | 2.40 | 0.00 |
| **SERC** | August | n.d. | 1.81 | 0.00 |
| **SERC** | September | NA | NA | NA |
| **SERC** | October | 0.01 | 0.59 | 0.00 |
| **SERC** | November | n.d. | 1.21 | n.d. |
| **Swan Creek** | March | NA | NA | NA |
| **Swan Creek** | April | NA | NA | NA |
| **Swan Creek** | May | n.d. | 4.12 | 0.00 |
| **Swan Creek** | June | 0.00 | 6.59 | 0.00 |
| **Swan Creek** | July | 0.01 | 5.61 | 0.00 |
| **Swan Creek** | August | n.d. | 1.36 | 0.00 |
| **Swan Creek** | September | NA | NA | NA |
| **Swan Creek** | October | 0.01 | 5.67 | 0.01 |
| **Swan Creek** | November | n.d. | 5.68 | 0.02 |
| **Wilelinor** | March | NA | NA | NA |
| **Wilelinor** | April | NA | NA | NA |
| **Wilelinor** | May | n.d. | 0.28 | 0.00 |

| Table 4 Monthly Headwater Stream PPCP/AS Concentrations | | | | |
|---|---|---|---|---|
| **Sample Site** | **Month** | **Paraxanthine (µg/L)** | **Sucralose (µg/L)** | **Sulfamethoxazole (µg/L)** |
| **Wilelinor** | June | 0.00 | 4.47 | 0.00 |
| **Wilelinor** | July | 0.01 | 0.24 | 0.00 |
| **Wilelinor** | August | n.d. | 0.27 | 0.00 |
| **Wilelinor** | September | NA | NA | NA |
| **Wilelinor** | October | 0.01 | 0.23 | 0.01 |
| **Wilelinor** | November | n.d. | 0.25 | 0.01 |

**Table 4 Monthly Headwater Stream PPCP/AS Concentrations**

| Sample Site | Month | Caffeine:Sucralose Ratio | Caffeine:Ace-K Ratio | Caffeine:Carbamazepine Ratio |
|---|---|---|---|---|
| **Chartwell Creek** | March | 0.04 | NA | 1.52 |
| **Chartwell Creek** | April | NA | NA | NA |
| **Chartwell Creek** | May | 0.01 | 0.08 | 1.43 |
| **Chartwell Creek** | June | 0.02 | 0.15 | 6.94 |
| **Chartwell Creek** | July | 0.34 | 2.96 | 55.52 |
| **Chartwell Creek** | August | 0.02 | 0.16 | 2.74 |
| **Chartwell Creek** | September | NA | NA | NA |
| **Chartwell Creek** | October | 0.01 | 0.10 | 0.96 |
| **Chartwell Creek** | November | 0.03 | 0.33 | 1.27 |
| **Chelsea Beach** | March | NA | NA | NA |
| **Chelsea Beach** | April | 0.04 | NA | 1.28 |
| **Chelsea Beach** | May | 0.02 | 0.13 | 0.83 |
| **Chelsea Beach** | June | 0.04 | 0.22 | 1.58 |
| **Chelsea Beach** | July | 0.07 | 0.79 | 4.86 |
| **Chelsea Beach** | August | 0.01 | 0.11 | 0.56 |
| **Chelsea Beach** | September | NA | NA | NA |
| **Chelsea Beach** | October | 0.01 | 0.01 | 0.29 |
| **Chelsea Beach** | November | 0.03 | 0.35 | 0.99 |
| **Clements Creek** | March | NA | NA | NA |
| **Clements Creek** | April | NA | NA | NA |
| **Clements Creek** | May | 0.01 | 0.05 | NA |
| **Clements Creek** | June | 0.01 | 0.02 | 1.76 |
| **Clements Creek** | July | 0.35 | 1.57 | NA |
| **Clements Creek** | August | 0.01 | 0.07 | NA |

**Table 4 Monthly Headwater Stream PPCP/AS Concentrations**

| Sample Site | Month | Caffeine:Sucralose Ratio | Caffeine:Ace-K Ratio | Caffeine:Carbamazepine Ratio |
|---|---|---|---|---|
| **Clements Creek** | September | NA | NA | NA |
| **Clements Creek** | October | 0.02 | 0.10 | NA |
| **Clements Creek** | November | 0.07 | 0.45 | NA |
| **Cockey Creek** | March | NA | NA | 3.07 |
| **Cockey Creek** | April | 0.21 | NA | 2.31 |
| **Cockey Creek** | May | 0.12 | 0.47 | 3.70 |
| **Cockey Creek** | June | 2.60 | 0.96 | 28.90 |
| **Cockey Creek** | July | 0.31 | 1.00 | 9.07 |
| **Cockey Creek** | August | 0.10 | 0.38 | 4.08 |
| **Cockey Creek** | September | NA | NA | NA |
| **Cockey Creek** | October | 0.05 | 0.19 | NA |
| **Cockey Creek** | November | 0.18 | 0.84 | 2.01 |
| **Main Creek** | March | NA | NA | NA |
| **Main Creek** | April | NA | NA | NA |
| **Main Creek** | May | 0.01 | 0.06 | 0.59 |
| **Main Creek** | June | 0.00 | 0.00 | 0.00 |
| **Main Creek** | July | 0.05 | 1.07 | 8.02 |
| **Main Creek** | August | 0.01 | 0.12 | 0.64 |
| **Main Creek** | September | NA | NA | NA |
| **Main Creek** | October | 0.00 | 0.09 | 0.15 |
| **Main Creek** | November | 0.01 | 0.55 | 0.66 |
| **Old Man Creek** | March | 0.04 | NA | 1.50 |
| **Old Man Creek** | April | NA | NA | NA |
| **Old Man Creek** | May | NA | 0.05 | 1.57 |
| **Old Man Creek** | June | 0.00 | 0.03 | NA |
| **Old Man Creek** | July | 0.20 | 4.23 | 54.25 |
| **Old Man Creek** | August | 0.01 | 0.11 | 1.77 |
| **Old Man Creek** | September | NA | NA | NA |
| **Old Man Creek** | October | 0.01 | 0.14 | 0.91 |
| **Old Man Creek** | November | 0.00 | 0.11 | 0.27 |
| **Rock Creek** | March | NA | NA | NA |
| **Rock Creek** | April | NA | NA | NA |
| **Rock Creek** | May | NA | 0.39 | NA |
| **Rock Creek** | June | 0.00 | 0.00 | NA |
| **Rock Creek** | July | NA | 12.39 | NA |
| **Rock Creek** | August | NA | 0.42 | NA |

**Table 4 Monthly Headwater Stream PPCP/AS Concentrations**

| Sample Site | Month | Caffeine:Sucralose Ratio | Caffeine:Ace-K Ratio | Caffeine:Carbamazepine Ratio |
|---|---|---|---|---|
| **Rock Creek** | September | NA | NA | NA |
| **Rock Creek** | October | 0.13 | 0.31 | NA |
| **Rock Creek** | November | 0.68 | 1.18 | 1.22 |
| **SERC** | March | NA | NA | NA |
| **SERC** | April | NA | NA | NA |
| **SERC** | May | 0.01 | 0.14 | 1.56 |
| **SERC** | June | NA | NA | NA |
| **SERC** | July | 0.12 | 5.15 | 25.92 |
| **SERC** | August | 0.01 | 0.08 | 1.56 |
| **SERC** | September | NA | NA | NA |
| **SERC** | October | 0.03 | 0.09 | NA |
| **SERC** | November | 0.00 | 0.05 | 0.19 |
| **Swan Creek** | March | NA | NA | NA |
| **Swan Creek** | April | NA | NA | NA |
| **Swan Creek** | May | 0.00 | 0.07 | NA |
| **Swan Creek** | June | 0.00 | 0.05 | NA |
| **Swan Creek** | July | 0.12 | 2.36 | 58.36 |
| **Swan Creek** | August | 0.09 | 1.43 | NA |
| **Swan Creek** | September | NA | NA | NA |
| **Swan Creek** | October | 0.00 | 0.18 | 0.90 |
| **Swan Creek** | November | 0.01 | 0.23 | 0.87 |
| **Wilelinor** | March | NA | NA | NA |
| **Wilelinor** | April | NA | NA | NA |
| **Wilelinor** | May | 0.78 | 2.64 | 20.62 |
| **Wilelinor** | June | 0.00 | 0.02 | 0.02 |
| **Wilelinor** | July | 2.37 | 4.43 | 24.92 |
| **Wilelinor** | August | 0.15 | 0.66 | 1.35 |
| **Wilelinor** | September | NA | NA | NA |
| **Wilelinor** | October | 0.05 | 0.33 | 0.43 |
| **Wilelinor** | November | 0.23 | 1.51 | 1.04 |

**Table 8 Headwater Streams Detection Frequency and Maximum and Minimum Concentrations**

| Compound | Detection Frequency (%) | Minimum Concentration (µg/L) | Maximum Concentration (µg/L) |
|---|---|---|---|
| **Ace-K** | 100 | 0.025 | 1.434 |
| **Acetaminophen** | 31 | 0.000 | 0.000 |
| **Atorvastatin** | 52 | 0.000 | 0.016 |
| **Caffeine** | 100 | 0.004 | 0.718 |
| **Carbamazepine** | 86 | 0.002 | 0.205 |
| **Cotinine** | 100 | 0.000 | 0.021 |
| **DEET** | 72 | 0.001 | 0.103 |
| **Dichlorvos** | 80 | 0.003 | 0.045 |
| **Diclofenac** | 47 | 0.000 | 0.000 |
| **Estrone** | 100 | 0.000 | 0.075 |
| **Ibuprofen** | 61 | 0.003 | 0.317 |
| **Paraxanthine** | 58 | 0.000 | 0.099 |
| **Sucralose** | 94 | 0.026 | 6.586 |
| **Sulfamethoxazole** | 88 | 0.000 | 0.039 |

**Table 5 June 8th Storm Chartwell Creek PPCP/AS Concentrations**

| June 8th Storm | Acetaminophen (µg/L) | Atorvastatin (µg/L) | Caffeine (µg/L) | Carbamazepine (µg/L) | Cotinine (µg/L) |
|---|---|---|---|---|---|
| **Pre Storm** | n.d. | n.d. | 0.04 | 0.01 | 0.00 |
| **5:50 PM** | n.d. | 0.00 | 0.06 | 0.01 | 0.00 |
| **1:50 AM** | n.d. | 0.00 | 0.04 | 0.01 | 0.00 |
| **2:50 AM** | 0.01 | 0.00 | 0.11 | 0.01 | 0.00 |
| **3:50 AM** | n.d. | 0.00 | 0.08 | 0.01 | 0.00 |
| **6:50 AM** | n.d. | 0.00 | 0.06 | 0.01 | 0.00 |
| **10:50 AM** | n.d. | 0.00 | 0.08 | 0.01 | 0.00 |
| **1:50 PM** | 0.01 | 0.00 | 0.06 | 0.01 | 0.00 |
| **Post Storm** | n.d. | 0.00 | 0.04 | 0.01 | 0.00 |
| **Environmental Blank** | n.d. | 0.00 | 0.02 | n.d. | 0.00 |

**Table 5 June 8th Storm Chartwell Creek PPCP/AS Concentrations**

| June 8th Storm | DEET (µg/L) | Dichlorvos (µg/L) | Diclofenac (µg/L) | Estrone (µg/L) | Ibuprofen (µg/L) | Paraxanthine (µg/L) | Sucralose (µg/L) | Sulfamethoxazole (µg/L) |
|---|---|---|---|---|---|---|---|---|
| **Pre Storm** | 0.14 | n.d. | n.d. | 0.02 | n.d. | 0.01 | 2.24 | 0.01 |
| **5:50 PM** | n.d. | 0.01 | n.d. | 0.03 | n.d. | 0.01 | 2.20 | 0.01 |
| **1:50 AM** | n.d. | 0.01 | n.d. | 0.02 | n.d. | 0.01 | 1.65 | 0.01 |
| **2:50 AM** | n.d. | 0.02 | n.d. | 0.04 | 0.04 | 0.02 | 1.23 | 0.01 |
| **3:50 AM** | n.d. | 0.01 | n.d. | 0.03 | 0.02 | 0.01 | 1.06 | 0.00 |
| **6:50 AM** | n.d. | 0.01 | n.d. | 0.03 | 0.01 | 0.01 | 1.62 | 0.00 |
| **10:50 AM** | n.d. | 0.02 | n.d. | 0.04 | 0.04 | 0.01 | 1.03 | 0.01 |
| **1:50 PM** | n.d. | 0.02 | n.d. | 0.03 | 0.01 | 0.01 | 0.63 | 0.00 |
| **Post Storm** | 0.06 | 0.01 | n.d. | 0.02 | 0.01 | 0.01 | 1.24 | 0.00 |
| **Environmental Blank** | n.d. | n.d. | n.d. | 0.01 | n.d. | 0.01 | n.d. | 0.00 |

**Table 6 September 1st Storm Chartwell Creek PPCP/AS Concentrations**

| Sept 1st Storm | Acetaminophen (µg/L) | Atorvastatin (µg/L) | Caffeine (µg/L) | Carbamazepine (µg/L) | Cotinine (µg/L) | DEET (µg/L) | Dichlorvos (µg/L) |
|---|---|---|---|---|---|---|---|
| **Pre Storm** | n.d. | n.d. | 0.02 | 0.01 | 0.00 | 0.02 | n.d. |
| **1:07 PM** | n.d. | n.d. | 0.02 | 0.01 | 0.00 | 0.00 | 0.00 |
| **2:07 PM** | n.d. | n.d. | 0.06 | 0.01 | 0.00 | 0.00 | 0.18 |
| **4:07 PM** | n.d. | n.d. | 0.03 | 0.01 | 0.00 | 0.00 | 0.07 |
| **Post Storm** | n.d. | n.d. | 0.02 | 0.01 | 0.00 | 0.02 | n.d. |
| **Environmental Blank** | n.d. | n.d. | 0.01 | n.d. | 0.00 | 0.00 | n.d. |

**Table 6 September 1st Storm Chartwell Creek PPCP/AS Concentrations**

| Sept 1st Storm | Diclofenac (µg/L) | Estrone (µg/L) | Ibuprofen (µg/L) | Paraxanthine (µg/L) | Sucralose (µg/L) | Sulfamethoxazole (µg/L) |
|---|---|---|---|---|---|---|
| **Pre Storm** | n.d. | 0.01 | n.d. | n.d. | 0.71 | 0.00 |
| **1:07 PM** | n.d. | 0.01 | n.d. | n.d. | 0.74 | 0.00 |
| **2:07 PM** | n.d. | 0.01 | n.d. | n.d. | 0.42 | 0.00 |
| **4:07 PM** | n.d. | 0.01 | n.d. | n.d. | 0.61 | 0.00 |
| **Post Storm** | n.d. | 0.01 | n.d. | n.d. | 0.69 | 0.00 |
| **Environmental Blank** | n.d. | 0.02 | n.d. | n.d. | n.d. | n.d. |

**Table 7 September 22nd Storm Chartwell Creek PPCP/AS Concentrations**

| Sept 22nd Storm | Acetaminophen (µg/L) | Atorvastatin (µg/L) | Caffeine (µg/L) | Carbamazepine (µg/L) | Cotinine (µg/L) |
|---|---|---|---|---|---|
| **Pre Storm** | n.d. | 0.00 | 0.01 | 0.01 | 0.00 |
| **6:47 PM** | n.d. | n.d. | 0.02 | 0.01 | 0.00 |
| **3:47 AM** | n.d. | n.d. | 0.03 | 0.01 | 0.00 |
| **4:47 AM** | n.d. | 0.00 | 0.02 | 0.01 | 0.00 |
| **5:47 AM** | n.d. | 0.00 | 0.07 | 0.01 | 0.00 |
| **6:47 AM** | n.d. | n.d. | 0.04 | 0.01 | 0.00 |
| **8:47 AM** | n.d. | n.d. | 0.08 | 0.01 | 0.00 |
| **1:47 PM** | n.d. | n.d. | 0.02 | 0.01 | 0.00 |
| **Post Storm** | n.d. | 0.00 | 0.02 | 0.01 | 0.00 |

| Sept 22nd Storm | DEET (µg/L) | Dichlorvos (µg/L) | Diclofenac (µg/L) | Estrone (µg/L) | Ibuprofen (µg/L) | Paraxanthine (µg/L) | Sucralose (µg/L) | Sulfamethoxazole (µg/L) |
|---|---|---|---|---|---|---|---|---|
| **Pre Storm** | 0.05 | n.d. | n.d. | 0.01 | n.d. | 0.01 | 0.96 | 0.00 |
| **6:47 PM** | n.d. | 0.02 | n.d. | 0.01 | n.d. | 0.01 | 1.02 | 0.00 |
| **3:47 AM** | n.d. | 0.02 | n.d. | 0.01 | n.d. | 0.01 | 1.01 | 0.00 |
| **4:47 AM** | n.d. | 0.02 | n.d. | 0.01 | n.d. | 0.01 | 0.85 | 0.00 |
| **5:47 AM** | n.d. | 0.02 | n.d. | 0.02 | n.d. | 0.01 | 0.40 | 0.01 |
| **6:47 AM** | n.d. | 0.02 | n.d. | 0.01 | n.d. | 0.01 | 0.35 | 0.00 |
| **8:47 AM** | n.d. | 0.02 | n.d. | 0.01 | n.d. | 0.01 | 0.51 | 0.00 |
| **1:47 PM** | n.d. | 0.02 | n.d. | 0.01 | n.d. | 0.01 | 0.68 | 0.00 |
| **Post Storm** | 0.03 | 0.01 | n.d. | 0.02 | n.d. | 0.01 | 0.76 | 0.00 |

# Appendix B: Supplemental Materials to Chapter 4

**Table 9 Anne Arundel County Field Measurements**

| Site | Layer | Station ID | Catchment Area ($km^2$) | Total Depth (m) | Temperature (˚C) | Secchi Disk (m) |
|---|---|---|---|---|---|---|
| Bodkin Creek | Surface | BC#1 S | 4.56 | 1.40 | 18.30 | 0.90 |
| Bodkin Creek | Surface | BC#2 S | 9.93 | 3.00 | 17.30 | 1.00 |
| Bodkin Creek | Surface | BC#3 S | 10.84 | 3.3. | 17.30 | 0.75 |
| Bodkin Creek | Surface | BC#4 S | 0.54 | 3.10 | 16.90 | 0.80 |
| Bodkin Creek | Surface | BC#5 S | 12.61 | 3.00 | 16.50 | 0.80 |
| Bodkin Creek | Surface | BC#6 S | 2.85 | 2.70 | 17.90 | 0.80 |
| Bodkin Creek | Surface | BC#7 S | 3.24 | 2.90 | 17.40 | 0.80 |
| Bodkin Creek | Surface | BC#8 S | 2.32 | 2.90 | 16.50 | 0.80 |
| Bodkin Creek | Surface | BC#9 S | 2.50 | 2.90 | 16.00 | 1.30 |
| Bodkin Creek | Surface | BC#10 S | 16.27 | 3.00 | 15.80 | 0.70 |
| Bodkin Creek | Surface | BC#11 S | 3.73 | 2.90 | 16.50 | 0.80 |
| Bodkin Creek | Surface | BC#12 S | 3.73 | 4.00 | 16.10 | 0.80 |
| Bodkin Creek | Bottom | BC#1 B | NA | 1.40 | 17.80 | 0.90 |
| Bodkin Creek | Bottom | BC#2 B | NA | 3.00 | 16.80 | 1.00 |
| Bodkin Creek | Bottom | BC#3 B | NA | 3.3. | 16.40 | 0.75 |
| Bodkin Creek | Bottom | BC#4 B | NA | 3.10 | 16.50 | 0.80 |
| Bodkin Creek | Bottom | BC#5 B | NA | 3.00 | 16.00 | 0.80 |
| Bodkin Creek | Bottom | BC#6 B | NA | 2.70 | 16.70 | 0.80 |
| Bodkin Creek | Bottom | BC#7 B | NA | 2.90 | 15.60 | 0.80 |
| Bodkin Creek | Bottom | BC#8 B | NA | 2.90 | 15.70 | 0.80 |
| Bodkin Creek | Bottom | BC#9 B | NA | 2.90 | 14.40 | 1.30 |
| Bodkin Creek | Bottom | BC#10 B | NA | 3.00 | 14.20 | 0.70 |
| Bodkin Creek | Bottom | BC#11 B | NA | 2.90 | 14.20 | 0.80 |
| Bodkin Creek | Bottom | BC#12 B | NA | 4.00 | 14.00 | 0.80 |
| Stoney Creek | Surface | SC#1 S | 4.70 | 2.10 | 17.22 | 0.40 |
| Stoney Creek | Surface | SC#2 S | 1.00 | 1.90 | 17.29 | 0.80 |
| Stoney Creek | Surface | SC#3 S | 8.84 | 3.10 | 16.91 | 0.70 |
| Stoney Creek | Surface | SC#4 S | 12.81 | 4.40 | 15.45 | 1.10 |
| Stoney Creek | Surface | SC#5 S | 1.48 | 3.10 | 17.19 | 0.70 |
| Stoney Creek | Surface | SC#6 S | 3.12 | 4.20 | 15.53 | 1.00 |
| Stoney Creek | Surface | SC#7 S | 17.70 | 5.00 | 15.35 | 0.90 |
| Stoney Creek | Surface | SC#8 S | 19.47 | 5.50 | 15.19 | 1.10 |
| Stoney Creek | Bottom | SC#1 B | NA | 2.10 | 16.77 | 0.40 |
| Stoney Creek | Bottom | SC#2 B | NA | 1.90 | 16.67 | 0.80 |
| Stoney Creek | Bottom | SC#3 B | NA | 3.10 | 16.17 | 0.70 |
| Stoney Creek | Bottom | SC#4 B | NA | 4.40 | 15.89 | 1.10 |
| Stoney Creek | Bottom | SC#5 B | NA | 3.10 | 16.21 | 0.70 |
| Stoney Creek | Bottom | SC#6 B | NA | 4.20 | 15.53 | 1.00 |
| Stoney Creek | Bottom | SC#7 B | NA | 5.00 | 15.59 | 0.90 |
| Stoney Creek | Bottom | SC#8 B | NA | 5.50 | 14.24 | 1.10 |
| Patapsco River | Surface | PT#1 S | 0.21 | 6.20 | 14.91 | 1.00 |
| Patapsco River | Surface | PT#2 S | 98.30 | 6.90 | 14.90 | 1.10 |
| Patapsco River | Surface | PT#3 S | 0.97 | 6.10 | 15.15 | 1.10 |

**Table 9 Anne Arundel County Field Measurements**

| Site | Layer | Station ID | Catchment Area ($km^2$) | Total Depth (m) | Temperature (˚C) | Secchi Disk (m) |
|---|---|---|---|---|---|---|
| Patapsco River | Surface | PT#4 S | 0.33 | 4.70 | 14.99 | 1.10 |
| Patapsco River | Surface | PT#5 S | 0.14 | 4.80 | 15.15 | 1.10 |
| Patapsco River | Surface | PT#6 S | 0.09 | 5.60 | 14.24 | 0.80 |
| Patapsco River | Surface | PT#7 S | 3.77 | 5.70 | 14.31 | 0.90 |
| Patapsco River | Surface | PT#8 S | 0.09 | 4.50 | 14.46 | 1.20 |
| Patapsco River | Bottom | PT#1 B | NA | 6.20 | 12.42 | 1.00 |
| Patapsco River | Bottom | PT#2 B | NA | 6.90 | 11.48 | 1.10 |
| Patapsco River | Bottom | PT#3 B | NA | 6.10 | 12.35 | 1.10 |
| Patapsco River | Bottom | PT#4 B | NA | 4.70 | 13.36 | 1.10 |
| Patapsco River | Bottom | PT#5 B | NA | 4.80 | 13.36 | 1.10 |
| Patapsco River | Bottom | PT#6 B | NA | 5.60 | 12.45 | 0.80 |
| Patapsco River | Bottom | PT#7 B | NA | 5.70 | 12.35 | 0.90 |
| Patapsco River | Bottom | PT#8 B | NA | 4.50 | 12.92 | 1.20 |
| Cox Creek WWTP | Surface | WWTP | NA | NA | NA | NA |

**Table 10 Anne Arundel County Water Quality Measurements**

| Station ID | Dissolved Oxygen (%) | pH | Specific Conductivity (mS/cm) | $\delta^{15}$ N | $\delta^{18}$ O | $\delta^{15}$ N:$\delta^{18}$ O |
|---|---|---|---|---|---|---|
| BC#1 S | 97.80 | 7.44 | 6.66 | 7.83 | 4.02 | 1.95 |
| BC#2 S | 95.70 | 7.48 | 6.82 | NA | NA | NA |
| BC#3 S | 100.70 | 7.63 | 6.80 | NA | NA | NA |
| BC#4 S | 101.90 | 7.83 | 7.11 | NA | NA | NA |
| BC#5 S | 100.50 | 7.88 | 6.93 | NA | NA | NA |
| BC#6 S | 102.10 | 7.64 | 6.42 | 8.17 | 4.50 | 1.82 |
| BC#7 S | 104.80 | 7.89 | 6.76 | NA | NA | NA |
| BC#8 S | 93.10 | 7.57 | 7.08 | 8.16 | 4.63 | 1.76 |
| BC#9 S | 94.20 | 7.73 | 6.93 | NA | NA | NA |
| BC#10 S | 96.90 | 7.76 | 6.82 | 7.18 | 4.11 | 1.75 |
| BC#11 S | 99.70 | 7.82 | 6.72 | NA | NA | NA |
| BC#12 S | 97.60 | 7.80 | 6.79 | 6.57 | 2.37 | 2.77 |
| BC#1 B | 92.40 | 7.45 | 7.17 | NA | NA | NA |
| BC#2 B | 83.00 | 7.38 | 7.39 | NA | NA | NA |
| BC#3 B | 81.80 | 7.42 | 7.36 | NA | NA | NA |
| BC#4 B | 89.30 | 7.51 | 7.31 | NA | NA | NA |
| BC#5 B | 86.20 | 7.47 | 7.16 | NA | NA | NA |
| BC#6 B | 70.80 | 7.28 | 7.04 | NA | NA | NA |
| BC#7 B | 75.20 | 7.35 | 6.94 | NA | NA | NA |
| BC#8 B | 73.40 | 7.33 | 7.23 | NA | NA | NA |
| BC#9 B | 84.20 | 7.48 | 6.98 | NA | NA | NA |
| BC#10 B | 84.90 | 7.48 | 7.05 | NA | NA | NA |
| BC#11 B | 87.00 | 7.53 | 6.83 | NA | NA | NA |
| BC#12 B | 75.50 | 7.33 | 7.40 | 7.07 | 0.96 | 7.36 |
| SC#1 S | 84.70 | 7.43 | 7.15 | NA | NA | NA |
| SC#2 S | 84.10 | 7.46 | 7.98 | NA | NA | NA |
| SC#3 S | 90.60 | 7.52 | 7.25 | 8.07 | 9.65 | 0.84 |
| SC#4 S | 102.00 | 7.96 | 7.82 | 8.33 | 5.73 | 1.45 |
| SC#5 S | 94.80 | 7.69 | 7.93 | 7.88 | 5.86 | 1.34 |
| SC#6 S | 104.30 | 8.03 | 7.55 | NA | NA | NA |
| SC#7 S | 100.90 | 7.29 | 7.13 | 7.52 | 5.13 | 1.47 |
| SC#8 S | 97.70 | 7.85 | 7.28 | 8.09 | 5.98 | 1.35 |
| SC#1 B | 88.50 | 7.58 | 8.44 | NA | NA | NA |
| SC#2 B | 84.60 | 7.52 | 8.46 | NA | NA | NA |
| SC#3 B | 89.20 | 7.66 | 8.51 | NA | NA | NA |
| SC#4 B | 85.30 | 7.56 | 8.53 | NA | NA | NA |
| SC#5 B | 91.80 | 7.74 | 8.34 | NA | NA | NA |
| SC#6 B | 7.50 | 7.44 | 8.52 | NA | NA | NA |
| SC#7 B | 89.70 | 7.66 | 8.38 | NA | NA | NA |
| SC#8 B | 54.10 | 7.18 | 9.12 | 7.06 | 4.52 | 1.56 |
| PT#1 S | 98.20 | 7.94 | 7.51 | NA | NA | NA |
| PT#2 S | 100.60 | 7.93 | 8.16 | 7.77 | 0.91 | 8.54 |

**Table 10 Anne Arundel County Water Quality Measurements**

| Station ID | Dissolved Oxygen (%) | pH | Specific Conductivity (mS/cm) | $\delta^{15}$ N | $\delta^{18}$ O | $\delta^{15}$ N:$\delta^{18}$ O |
|---|---|---|---|---|---|---|
| PT#3 S | 102.80 | 8.00 | 7.77 | 7.45 | 2.68 | 2.78 |
| PT#4 S | 98.50 | 7.82 | 7.25 | 6.94 | 3.84 | 1.81 |
| PT#5 S | 100.70 | 7.99 | 7.06 | NA | NA | NA |
| PT#6 S | 89.60 | 7.65 | 5.71 | NA | NA | NA |
| PT#7 S | 89.00 | 7.62 | 6.12 | NA | NA | NA |
| PT#8 S | 95.40 | 7.77 | 6.75 | 7.01 | 2.69 | 2.61 |
| PT#1 B | 56.20 | 7.16 | 12.51 | NA | NA | NA |
| PT#2 B | 54.30 | 7.20 | 14.91 | NA | NA | NA |
| PT#3 B | 66.90 | 7.30 | 13.09 | NA | NA | NA |
| PT#4 B | 59.80 | 7.24 | 10.60 | NA | NA | NA |
| PT#5 B | 60.90 | 7.23 | 10.32 | NA | NA | NA |
| PT#6 B | 48.80 | 7.21 | 11.67 | NA | NA | NA |
| PT#7 B | 53.50 | 7.16 | 12.21 | NA | NA | NA |
| PT#8 B | 70.80 | 7.31 | 10.33 | NA | NA | NA |
| Cox Creek WWTP | NA | NA | NA | 6.45 | 3.57 | 1.81 |

**Table 10 Anne Arundel County Water Quality Measurements**

| Station ID | DOC (mg/L) | $NH_4$ (N mg/L) | $NO_3$- (N mg/L) | TDN (N mg/L) | TDP (mg)/L |
|---|---|---|---|---|---|
| BC#1 S | 2.87 | 0.06 | 0.63 | 1.08 | 0.01 |
| BC#2 S | 3.18 | 0.06 | 0.70 | 1.07 | 0.01 |
| BC#3 S | 3.07 | 0.04 | 0.69 | 1.08 | 0.01 |
| BC#4 S | 2.79 | 0.03 | 0.68 | 1.08 | 0.01 |
| BC#5 S | 2.54 | 0.03 | 0.69 | 1.09 | 0.01 |
| BC#6 S | 3.15 | 0.06 | 0.60 | 1.07 | 0.01 |
| BC#7 S | 2.92 | 0.03 | 0.62 | 1.08 | 0.02 |
| BC#8 S | 3.06 | 0.05 | 0.63 | 1.06 | 0.01 |
| BC#9 S | 2.33 | 0.03 | 0.73 | 1.12 | 0.01 |
| BC#10 S | 2.47 | 0.05 | 0.76 | 1.17 | 0.01 |
| BC#11 S | 2.44 | 0.04 | 0.81 | 1.14 | 0.01 |
| BC#12 S | 2.17 | 0.04 | 0.91 | 1.16 | 0.01 |
| BC#1 B | 2.74 | 0.13 | 0.60 | 1.11 | 0.01 |
| BC#2 B | 2.55 | 0.10 | 0.69 | 1.09 | 0.01 |
| BC#3 B | 2.57 | 0.12 | 0.69 | 1.08 | 0.01 |
| BC#4 B | 2.59 | 0.13 | 0.65 | 1.07 | 0.01 |
| BC#5 B | 2.54 | 0.13 | 0.69 | 1.12 | 0.01 |
| BC#6 B | 2.74 | 0.21 | 0.63 | 1.15 | 0.01 |
| BC#7 B | 2.43 | 0.12 | 0.68 | 1.12 | 0.01 |
| BC#8 B | 3.02 | 0.13 | 0.63 | 1.13 | 0.01 |
| BC#9 B | 2.27 | 0.09 | 0.82 | 1.25 | 0.01 |
| BC#10 B | 2.38 | 0.10 | 0.88 | 1.24 | 0.02 |
| BC#11 B | 2.22 | 0.09 | 0.89 | 1.24 | 0.02 |
| BC#12 B | 2.39 | 0.12 | 0.79 | 1.24 | 0.02 |
| SC#1 S | 4.80 | 0.09 | 0.63 | 1.14 | 0.01 |
| SC#2 S | 3.71 | 0.09 | 0.58 | 1.06 | 0.01 |
| SC#3 S | 4.16 | 0.08 | 0.64 | 1.07 | 0.01 |
| SC#4 S | 2.65 | 0.04 | 0.73 | 1.12 | 0.01 |
| SC#5 S | 3.31 | 0.10 | 0.62 | 1.06 | 0.01 |
| SC#6 S | 2.59 | 0.04 | 0.81 | 1.15 | 0.01 |
| SC#7 S | 2.39 | 0.04 | 0.85 | 1.16 | 0.01 |
| SC#8 S | 2.30 | 0.05 | 0.77 | 1.17 | 0.01 |
| SC#1 B | 3.11 | 0.08 | 0.62 | 1.07 | 0.01 |
| SC#2 B | 3.09 | 0.10 | 0.57 | 1.08 | 0.01 |
| SC#3 B | 2.81 | 0.07 | 0.64 | 1.07 | 0.01 |
| SC#4 B | 2.83 | 0.07 | 0.66 | 1.07 | 0.01 |
| SC#5 B | 2.71 | 0.06 | 0.71 | 1.08 | 0.01 |
| SC#6 B | 2.50 | 0.10 | 0.69 | 1.09 | 0.01 |

**Table 10 Anne Arundel County Water Quality Measurements**

| Station ID | DOC (mg/L) | $NH_4$ (N mg/L) | $NO_3$- (N mg/L) | TDN (N mg/L) | TDP (mg)/L |
|---|---|---|---|---|---|
| SC#7 B | 2.65 | 0.07 | 0.68 | 1.08 | 0.01 |
| SC#8 B | 2.43 | 0.12 | 0.68 | 1.10 | 0.01 |
| PT#1 S | 2.61 | 0.08 | 0.82 | 1.34 | 0.01 |
| PT#2 S | 2.37 | 0.14 | 0.79 | 1.31 | 0.01 |
| PT#3 S | 2.49 | 0.08 | 0.83 | 1.25 | 0.01 |
| PT#4 S | 2.44 | 0.06 | 0.79 | 1.22 | 0.01 |
| PT#5 S | 2.30 | 0.05 | 0.82 | 1.22 | 0.01 |
| PT#6 S | 2.20 | 0.07 | 0.90 | 1.31 | 0.02 |
| PT#7 S | 2.08 | 0.08 | 0.95 | 1.25 | 0.02 |
| PT#8 S | 2.22 | 0.06 | 0.89 | 1.27 | 0.01 |
| PT#1 B | 4.66 | 1.42 | 0.68 | 2.47 | 0.09 |
| PT#2 B | 2.40 | 0.26 | 0.54 | 1.11 | 0.03 |
| PT#3 B | 2.32 | 0.23 | 0.62 | 1.15 | 0.02 |
| PT#4 B | 2.30 | 0.21 | 0.77 | 1.32 | 0.02 |
| PT#5 B | 2.42 | 0.28 | 0.64 | 1.28 | 0.02 |
| PT#6 B | 2.34 | 0.19 | 0.64 | 1.14 | 0.03 |
| PT#7 B | 2.45 | 0.23 | 0.66 | 1.12 | 0.03 |
| PT#8 B | 2.33 | 0.13 | 0.78 | 1.14 | 0.02 |
| Cox Creek WWTP | 5.36 | 0.06 | 0.30 | 0.95 | 0.52 |

**Table 10 Anne Arundel County PPCP/AS Concentrations**

| Station ID | Ace-K (µg/L) | Acetaminophen (µg/L) | Atorvastatin (µg/L) | Carbamazepine (µg/L) | Caffeine (µg/L) |
|---|---|---|---|---|---|
| BC#1 S | 0.20 | NA | NA | 0.01 | 0.02 |
| BC#2 S | NA | NA | NA | 0.01 | 0.01 |
| BC#3 S | 0.15 | NA | NA | 0.01 | 0.02 |
| BC#4 S | 0.20 | NA | NA | 0.01 | 0.02 |
| BC#5 S | 0.22 | NA | NA | 0.01 | 0.03 |
| BC#6 S | 0.20 | NA | NA | 0.01 | 0.04 |
| BC#7 S | 0.21 | NA | NA | 0.01 | 0.02 |
| BC#8 S | 0.21 | NA | NA | 0.01 | 0.03 |
| BC#9 S | 0.18 | NA | NA | 0.01 | 0.02 |
| BC#10 S | 0.17 | NA | NA | 0.01 | 0.05 |
| BC#11 S | 0.17 | NA | NA | 0.01 | 0.04 |
| BC#12 S | 0.17 | NA | NA | 0.01 | 0.03 |
| BC#1 B | 0.22 | NA | NA | 0.01 | 0.00 |
| BC#2 B | 0.20 | NA | NA | 0.01 | 0.02 |
| BC#3 B | 0.17 | NA | NA | 0.01 | 0.02 |
| BC#4 B | 0.20 | NA | NA | 0.01 | 0.03 |
| BC#5 B | 0.19 | NA | NA | 0.01 | 0.04 |
| BC#6 B | 0.19 | NA | NA | 0.01 | 0.02 |
| BC#7 B | 0.16 | NA | NA | 0.01 | 0.02 |
| BC#8 B | 0.24 | NA | 0.00 | 0.01 | 0.02 |
| BC#9 B | 0.19 | NA | 0.00 | 0.01 | 0.04 |
| BC#10 B | 0.24 | NA | 0.00 | 0.01 | 0.04 |
| BC#11 B | 0.15 | 0.00 | 0.00 | 0.01 | 0.06 |
| BC#12 B | 0.30 | 0.00 | 0.00 | 0.01 | 0.06 |
| SC#1 S | 0.22 | NA | NA | 0.01 | 0.12 |
| SC#2 S | 0.22 | NA | NA | 0.01 | 0.05 |
| SC#3 S | 0.23 | NA | NA | 0.01 | 0.07 |
| SC#4 S | 0.31 | 0.00 | NA | 0.01 | 0.07 |
| SC#5 S | 0.26 | 0.00 | NA | 0.01 | 0.17 |
| SC#6 S | 0.28 | 0.00 | NA | 0.01 | 0.09 |
| SC#7 S | 0.26 | 0.00 | NA | 0.01 | 0.08 |
| SC#8 S | 0.31 | 0.00 | NA | 0.03 | 0.18 |
| SC#1 B | 0.22 | NA | NA | 0.01 | 0.14 |
| SC#2 B | 0.35 | NA | NA | 0.05 | 0.68 |
| SC#3 B | 0.25 | NA | NA | 0.03 | 0.39 |
| SC#4 B | 0.29 | NA | NA | 0.01 | 0.20 |

**Table 10 Anne Arundel County PPCP/AS Concentrations**

| Station ID | Ace-K (µg/L) | Acetaminophen (µg/L) | Atorvastatin (µg/L) | Carbamazepine (µg/L) | Caffeine (µg/L) |
|---|---|---|---|---|---|
| SC#5 B | 0.33 | NA | NA | 0.01 | 0.11 |
| SC#6 B | 0.24 | 0.00 | NA | 0.01 | 0.13 |
| SC#7 B | 0.29 | 0.00 | NA | 0.01 | 0.06 |
| SC#8 B | 0.31 | 0.00 | NA | 0.01 | 0.10 |
| PT#1 S | 0.26 | 0.01 | 0.00 | 0.01 | 0.13 |
| PT#2 S | 0.40 | 0.02 | 0.00 | 0.01 | 0.28 |
| PT#3 S | 0.27 | 0.01 | 0.00 | 0.01 | 0.21 |
| PT#4 S | 0.32 | 0.00 | 0.00 | 0.03 | 0.13 |
| PT#5 S | 0.28 | 0.00 | 0.00 | 0.01 | 0.10 |
| PT#6 S | 0.31 | NA | NA | 0.01 | 0.03 |
| PT#7 S | 0.19 | NA | 0.00 | 0.01 | 0.03 |
| PT#8 S | 0.23 | NA | 0.00 | 0.01 | 0.08 |
| PT#1 B | 2.12 | 0.66 | 0.02 | 0.05 | 4.55 |
| PT#2 B | 0.26 | 0.01 | 0.00 | 0.01 | 0.14 |
| PT#3 B | 0.26 | 0.01 | 0.00 | 0.01 | 0.14 |
| PT#4 B | 0.46 | 0.03 | 0.00 | 0.01 | 0.17 |
| PT#5 B | 0.40 | 0.01 | 0.00 | 0.01 | 0.22 |
| PT#6 B | 0.24 | 0.00 | 0.00 | 0.01 | 0.06 |
| PT#7 B | 0.18 | 0.00 | 0.00 | 0.01 | 0.08 |
| PT#8 B | 0.17 | 0.00 | 0.00 | 0.01 | 0.05 |
| Cox Creek WWTP | NA | 2.95 | 0.57 | 3.02 | 37.18 |

**Table 10 Anne Arundel County PPCP/AS Concentrations**

| Station ID | Cotinine (µg/L) | DEET (µg/L) | Diclofenac (µg/L) | Ibuprofen (µg/L) |
|---|---|---|---|---|
| BC#1 S | NA | 0.05 | 0.00 | NA |
| BC#2 S | NA | 0.03 | 0.00 | NA |
| BC#3 S | NA | 0.03 | 0.00 | NA |
| BC#4 S | NA | 0.03 | 0.00 | NA |
| BC#5 S | NA | 0.03 | 0.00 | NA |
| BC#6 S | NA | 0.04 | 0.00 | NA |
| BC#7 S | NA | 0.03 | 0.00 | NA |
| BC#8 S | NA | 0.07 | NA | NA |
| BC#9 S | NA | 0.04 | 0.00 | NA |
| BC#10 S | NA | 0.03 | 0.00 | NA |
| BC#11 S | NA | 0.04 | 0.00 | NA |
| BC#12 S | NA | 0.03 | 0.00 | NA |
| BC#1 B | NA | 0.04 | 0.00 | NA |
| BC#2 B | NA | 0.03 | 0.00 | NA |
| BC#3 B | NA | 0.03 | 0.00 | NA |
| BC#4 B | NA | 0.03 | 0.00 | NA |
| BC#5 B | NA | 0.04 | 0.00 | NA |
| BC#6 B | NA | 0.03 | 0.00 | NA |
| BC#7 B | NA | 0.03 | 0.00 | NA |
| BC#8 B | NA | 0.05 | 0.00 | NA |
| BC#9 B | NA | 0.04 | 0.00 | NA |
| BC#10 B | NA | 0.02 | 0.00 | NA |
| BC#11 B | NA | 0.03 | 0.00 | NA |
| BC#12 B | NA | 0.02 | 0.00 | NA |
| SC#1 S | NA | 0.04 | 0.00 | NA |
| SC#2 S | NA | 0.02 | 0.00 | NA |
| SC#3 S | NA | 0.02 | 0.00 | NA |
| SC#4 S | NA | 0.02 | 0.00 | NA |
| SC#5 S | NA | 0.08 | 0.00 | NA |
| SC#6 S | NA | 0.02 | 0.00 | NA |
| SC#7 S | NA | 0.02 | 0.00 | NA |
| SC#8 S | NA | 0.03 | 0.00 | NA |
| SC#1 B | NA | 0.03 | 0.00 | NA |
| SC#2 B | NA | 0.10 | 0.00 | NA |
| SC#3 B | NA | 0.06 | 0.00 | NA |
| SC#4 B | NA | 0.03 | 0.00 | NA |

**Table 10 Anne Arundel County PPCP/AS Concentrations**

| Station ID | Cotinine (µg/L) | DEET (µg/L) | Diclofenac (µg/L) | Ibuprofen (µg/L) |
|---|---|---|---|---|
| SC#5 B | NA | 0.02 | 0.00 | NA |
| SC#6 B | NA | 0.02 | 0.00 | NA |
| SC#7 B | NA | 0.01 | 0.00 | NA |
| SC#8 B | NA | 0.02 | 0.00 | 0.01 |
| PT#1 S | NA | 0.02 | 0.00 | NA |
| PT#2 S | NA | 0.03 | 0.00 | NA |
| PT#3 S | NA | 0.03 | 0.00 | NA |
| PT#4 S | NA | 0.03 | 0.00 | NA |
| PT#5 S | NA | 0.03 | 0.00 | NA |
| PT#6 S | NA | 0.03 | 0.00 | NA |
| PT#7 S | NA | 0.03 | 0.00 | NA |
| PT#8 S | NA | 0.03 | 0.00 | NA |
| PT#1 B | 0.49 | 0.10 | 0.02 | 2.05 |
| PT#2 B | NA | 0.05 | 0.00 | NA |
| PT#3 B | NA | 0.03 | 0.00 | NA |
| PT#4 B | NA | 0.02 | 0.00 | NA |
| PT#5 B | NA | 0.03 | 0.00 | NA |
| PT#6 B | NA | 0.03 | 0.00 | NA |
| PT#7 B | NA | 0.02 | 0.00 | NA |
| PT#8 B | NA | 0.03 | 0.00 | NA |
| WWTP | 1.77 | 13.11 | 0.40 | NA |

**Table 10 Anne Arundel County PPCP/AS Concentrations**

| Station ID | Paraxanthine (µg/L) | Sucralose (µg/L) | Sulfamethoxazole (µg/L) |
|---|---|---|---|
| BC#1 S | 0.01 | 0.75 | 0.01 |
| BC#2 S | 0.01 | 0.77 | 0.00 |
| BC#3 S | 0.01 | 0.61 | 0.01 |
| BC#4 S | 0.01 | 0.80 | 0.00 |
| BC#5 S | 0.02 | 0.80 | 0.00 |
| BC#6 S | 0.02 | 1.43 | 0.00 |
| BC#7 S | 0.01 | 0.66 | 0.00 |
| BC#8 S | 0.01 | 0.78 | 0.00 |
| BC#9 S | 0.01 | 0.67 | 0.00 |
| BC#10 S | 0.02 | 0.72 | 0.00 |
| BC#11 S | 0.02 | 1.00 | 0.00 |
| BC#12 S | 0.01 | 0.75 | 0.00 |
| BC#1 B | 0.01 | 0.56 | 0.00 |
| BC#2 B | 0.01 | 0.59 | 0.00 |
| BC#3 B | 0.01 | 0.70 | 0.00 |
| BC#4 B | 0.01 | 0.83 | 0.00 |
| BC#5 B | 0.01 | 0.96 | 0.00 |
| BC#6 B | 0.01 | 0.66 | 0.00 |
| BC#7 B | 0.01 | 0.62 | 0.00 |
| BC#8 B | 0.01 | 0.61 | 0.00 |
| BC#9 B | 0.02 | 0.52 | 0.00 |
| BC#10 B | 0.02 | 0.53 | NA |
| BC#11 B | 0.02 | 0.77 | 0.00 |
| BC#12 B | 0.02 | 0.56 | 0.00 |
| SC#1 S | 0.01 | 1.16 | 0.00 |
| SC#2 S | 0.02 | 0.68 | 0.00 |
| SC#3 S | 0.00 | 0.86 | 0.00 |
| SC#4 S | 0.03 | 1.03 | 0.00 |
| SC#5 S | 0.02 | 1.79 | 0.00 |
| SC#6 S | 0.02 | 1.04 | 0.00 |
| SC#7 S | 0.00 | 1.03 | 0.00 |
| SC#8 S | 0.01 | 7.68 | 0.01 |
| SC#1 B | 0.02 | 1.81 | 0.00 |
| SC#2 B | 0.08 | 6.61 | 0.00 |
| SC#3 B | 0.06 | 3.95 | 0.00 |
| SC#4 B | 0.01 | 1.62 | 0.00 |

**Table 10 Anne Arundel County PPCP/AS Concentrations**

| Station ID | Paraxanthine (µg/L) | Sucralose (µg/L) | Sulfamethoxazole (µg/L) |
|---|---|---|---|
| SC#5 B | 0.01 | 1.39 | 0.00 |
| SC#6 B | 0.01 | 1.35 | 0.00 |
| SC#7 B | NA | 0.85 | 0.00 |
| SC#8 B | 0.01 | 1.06 | 0.00 |
| PT#1 S | 0.03 | 0.74 | 0.00 |
| PT#2 S | 0.07 | 1.33 | 0.00 |
| PT#3 S | 0.04 | 1.67 | 0.00 |
| PT#4 S | 0.03 | 5.27 | 0.01 |
| PT#5 S | 0.02 | 1.15 | 0.00 |
| PT#6 S | 0.01 | 0.97 | NA |
| PT#7 S | 0.01 | 0.95 | NA |
| PT#8 S | 0.01 | 0.97 | NA |
| PT#1 B | 1.23 | 6.65 | 0.00 |
| PT#2 B | 0.03 | 1.26 | NA |
| PT#3 B | 0.03 | 1.23 | NA |
| PT#4 B | 0.03 | 1.19 | 0.00 |
| PT#5 B | 0.05 | 1.32 | NA |
| PT#6 B | 0.02 | 0.97 | NA |
| PT#7 B | 0.01 | 0.66 | NA |
| PT#8 B | 0.02 | 0.73 | NA |
| WWTP | 23.89 | 673.61 | NA |

| Table 11: Spearman's rank correlation (p-values) Benedict, MD Well | Sucralose | Sulfameth-oxazole | Paraxanthine | Dichlorvos | DEET | Carbam-azepine | Caffeine | $NH_4$ | $NO_3$ | TDN | ON | $PO_4$ | TDP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Sucralose** | NA | **0.00** | NA | NA | 0.67 | **0.00** | 0.33 | 0.61 | 0.92 | 0.21 | **0.00** | **0.01** | **0.01** |
| **Sulfamethoxazole** | **0.00** | NA | NA | NA | **0.00** | **0.00** | 0.96 | 0.87 | 0.82 | 0.07 | **0.01** | **0.01** | **0.01** |
| **Paraxanthine** | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| **Dichlorvos** | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| **DEET** | 0.67 | **0.00** | NA | NA | NA | 0.67 | NA | 0.33 | **0.00** | **0.00** | 0.67 | 0.67 | 0.67 |
| **Carbamazepine** | **0.00** | **0.00** | NA | NA | 0.67 | NA | 0.40 | 0.51 | 0.70 | 0.17 | **0.00** | **0.01** | **0.02** |
| **Caffeine** | 0.33 | 0.96 | NA | NA | NA | 0.40 | NA | 0.44 | 0.66 | 0.26 | 0.16 | 0.16 | 0.21 |
| **$NH_4$** | 0.61 | 0.87 | NA | NA | 0.33 | 0.51 | 0.44 | NA | **0.02** | **0.02** | 0.35 | 0.84 | 0.93 |
| **$NO_3$** | 0.92 | 0.82 | NA | NA | **0.00** | 0.70 | 0.66 | **0.02** | NA | **0.00** | 0.34 | 0.12 | 0.12 |
| **TDN** | 0.21 | 0.07 | NA | NA | **0.00** | 0.17 | 0.26 | **0.02** | **0.00** | NA | **0.01** | **0.01** | **0.01** |
| **ON** | **0.00** | **0.01** | NA | NA | 0.67 | **0.00** | 0.16 | 0.35 | 0.34 | **0.01** | NA | **0.01** | **0.01** |
| **$PO_4$** | **0.01** | **0.01** | NA | NA | 0.67 | **0.01** | 0.16 | 0.84 | 0.12 | **0.01** | **0.01** | NA | **0.00** |
| **TDP** | **0.01** | **0.01** | NA | NA | 0.67 | **0.02** | 0.21 | 0.93 | 0.12 | **0.01** | **0.01** | **0.00** | NA |

| Table 12: Spearman's rank correlation ($r_s$-values) Benedict, MD Well | Sucralose | Sulfameth-oxazole | Paraxanthine | Dichlorvos | DEET | Carbam-azepine | Caffeine | $NH_4$ | $NO_3$ | TDN | ON | $PO_4$ | TDP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Sucralose** | 1.00 | 0.80 | NA | NA | 0.50 | 0.96 | 0.49 | -0.15 | -0.03 | -0.36 | -0.74 | -0.67 | -0.65 |
| **Sulfamethoxazole** | 0.80 | 1.00 | NA | NA | -1.00 | 0.82 | 0.03 | -0.06 | -0.08 | -0.56 | -0.71 | -0.77 | -0.75 |
| **Paraxanthine** | NA | NA | 1.00 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| **Dichlorvos** | NA | NA | NA | 1.00 | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| **DEET** | 0.50 | -1.00 | NA | NA | 1.00 | 0.50 | NA | 0.87 | 1.00 | 1.00 | -0.50 | 0.50 | 0.50 |
| **Carbamazepine** | 0.96 | 0.82 | NA | NA | 0.50 | 1.00 | 0.43 | -0.19 | -0.11 | -0.39 | -0.74 | -0.64 | -0.63 |
| **Caffeine** | 0.49 | 0.03 | NA | NA | NA | 0.43 | 1.00 | -0.39 | -0.23 | -0.55 | -0.66 | -0.66 | -0.60 |
| **$NH_4$** | -0.15 | -0.06 | NA | NA | 0.87 | -0.19 | -0.39 | 1.00 | 0.61 | 0.62 | 0.27 | 0.06 | 0.03 |
| **$NO_3$** | -0.03 | -0.08 | NA | NA | 1.00 | -0.11 | -0.23 | 0.61 | 1.00 | 0.78 | 0.28 | 0.44 | 0.44 |
| **TDN** | -0.36 | -0.56 | NA | NA | 1.00 | -0.39 | -0.55 | 0.62 | 0.78 | 1.00 | 0.70 | 0.66 | 0.65 |
| **ON** | -0.74 | -0.71 | NA | NA | -0.50 | -0.74 | -0.66 | 0.27 | 0.28 | 0.70 | 1.00 | 0.70 | 0.68 |
| **$PO_4$** | -0.67 | -0.77 | NA | NA | 0.50 | -0.64 | -0.66 | 0.06 | 0.44 | 0.66 | 0.70 | 1.00 | 0.98 |
| **TDP** | -0.65 | -0.75 | NA | NA | 0.50 | -0.63 | -0.60 | 0.03 | 0.44 | 0.65 | 0.68 | 0.98 | 1.00 |

**Table 13: Stoney Creek Detection Frequency and Maximum and Minimum Concentrations**

| Compound | Detection Frequency (%) | Minimum Concentration (µg/L) | Maximum Concentration (µg/L) |
|---|---|---|---|
| **Ace-K** | 100 | 0.22 | 0.35 |
| **Acetaminophen** | 50 | 0.00 | 0.00 |
| **Atorvastatin** | 0 | NA | NA |
| **Carbamazepine** | 100 | 0.01 | 0.05 |
| **Caffeine** | 100 | 0.05 | 0.68 |
| **Cotinine** | 0 | NA | 0.00 |
| **DEET** | 100 | 0.01 | 0.10 |
| **Diclofenac** | 100 | 0.00 | 0.00 |
| **Ibuprofen** | 6 | 0.01 | NA |
| **Paraxanthine** | 94 | 0.00 | 0.08 |
| **Sucralose** | 100 | 0.68 | 7.68 |
| **Sulfamethoxazole** | 100 | 0.00 | 0.01 |

**Table 14: Bodkin Creek Detection Frequency and Maximum and Minimum Concentrations**

| Compound | Detection Frequency (%) | Minimum Concentration (µg/L) | Maximum Concentration (µg/L) |
|---|---|---|---|
| **Ace-K** | 96 | 0.15 | 0.30 |
| **Acetaminophen** | 8 | 0.00 | 0.00 |
| **Atorvastatin** | 21 | 0.00 | 0.00 |
| **Carbamazepine** | 100 | 0.01 | 0.01 |
| **Caffeine** | 100 | 0.00 | 0.06 |
| **Cotinine** | 50 | 0.00 | 0.00 |
| **DEET** | 100 | 0.02 | 0.07 |
| **Diclofenac** | 96 | 0.00 | 0.00 |
| **Ibuprofen** | 0 | 0.00 | 0.00 |
| **Paraxanthine** | 100 | 0.01 | 0.02 |
| **Sucralose** | 100 | 0.52 | 1.43 |
| **Sulfamethoxazole** | 96 | 0.00 | 0.01 |

**Table 15: Patapsco River Detection Frequency and Maximum and Minimum Concentrations**

| Compound | Detection Frequency (%) | Minimum Concentration (µg/L) | Maximum Concentration (µg/L) |
|---|---|---|---|
| **Ace-K** | 100 | 0.17 | 2.12 |
| **Acetaminophen** | 81 | 0.00 | 0.66 |
| **Atorvastatin** | 94 | 0.00 | 0.02 |
| **Carbamazepine** | 100 | 0.01 | 0.05 |
| **Caffeine** | 100 | 0.03 | 4.55 |
| **Cotinine** | 6 | 0.49 | 0.49 |
| **DEET** | 100 | 0.02 | 0.10 |
| **Diclofenac** | 100 | 0.00 | 0.02 |
| **Ibuprofen** | 6 | 2.05 | 2.05 |
| **Paraxanthine** | 100 | 0.01 | 1.23 |
| **Sucralose** | 100 | 0.66 | 6.65 |
| **Sulfamethoxazole** | 44 | 0.00 | 0.01 |

**Table 16 Benedict, MD PPCP/AS Concentrations**

| Site | Date | Acetaminophen (µg/L) | Atorvastatin (µg/L) | Caffeine (µg/L) | Carbamazepine (µg/L) | Cotinine (µg/L) |
|---|---|---|---|---|---|---|
| **Well 1** | **June 24th** | BLD | BLD | 0.035 | BQL | BLQ |
| **Well 1** | **August 4th** | BLD | BLD | 0.057 | BQL | BLQ |
| **Well 3** | **June 24th** | BLD | BLD | 0.024 | BQL | BLQ |
| **Well 3** | **August 4th** | BLD | BLD | 0.117 | BQL | BLQ |
| **Well 4** | **June 24th** | BLD | BLD | 0.018 | BQL | BLQ |
| **Well 4** | **August 4th** | BLD | BLD | 0.040 | BQL | BLQ |
| **Well 6** | **June 24th** | BLD | BLD | 0.138 | BQL | BLQ |
| **Well 6** | **August 4th** | BLD | BLD | 0.080 | BQL | BLQ |
| **Well 5** | **June 24th** | BLD | BLD | 0.050 | 0.005 | BLQ |
| **Well 5** | **August 4th** | BLD | BLD | 0.045 | 0.006 | BLQ |
| **Well 7** | **June 24th** | BLD | BLD | 0.026 | 0.005 | BLQ |
| **Well 7** | **August 4th** | BLD | BLD | 0.082 | BQL | BLQ |
| **Surface 8** | **June 24th** | BLD | BLD | BQL | 0.021 | BLQ |
| **Surface 8** | **August 4th** | BLD | BLD | BQL | 0.013 | BLQ |
| **Surface 9** | **June 24th** | BLD | BLD | BQL | 0.013 | BLQ |
| **Surface 9** | **August 4th** | BLD | BLD | BQL | 0.012 | BLQ |
| **Surface 10** | **June 24th** | BLD | BLD | 0.015 | 0.015 | BLQ |
| **Surface 10** | **August 4th** | BLD | BLD | 0.024 | 0.012 | BLQ |
| **Surface 11** | **June 24th** | BLD | BLD | 0.022 | 0.013 | BLQ |
| **Surface 11** | **August 4th** | BLD | BLD | BQL | 0.011 | BLQ |
| **Surface 12** | **June 24th** | BLD | BLD | BQL | 0.008 | BLQ |
| **Surface 12** | **August 4th** | BLD | BLD | BQL | 0.010 | BLQ |
| **Surface 13** | **June 24th** | BLD | BLD | 0.051 | 0.013 | BLQ |
| **Surface 13** | **August 4th** | BLD | BLD | BQL | 0.011 | BLQ |
| **Surface 14** | **June 24th** | BLD | BLD | 0.012 | 0.010 | BLQ |
| **Surface 14** | **August 4th** | BLD | BLD | 0.011 | 0.011 | BLQ |

**Table 16 Benedict, MD PPCP/AS Concentrations**

| Site | Date | DEET (µg/L) | Dichlorvos (µg/L) | Estrone (µg/L) | Ibuprofen (µg/L) | Paraxan-thine (µg/L) | Sucralose (µg/L) | Sulfameth-oxazole (µg/L) |
|---|---|---|---|---|---|---|---|---|
| **Well 1** | **June 24th** | BLQ | BLQ | BLD | BLD | BLQ | 1.668 | 0.003 |
| **Well 1** | **August 4th** | 0.009 | BLQ | BLD | BLD | BLQ | 0.390 | BLQ |
| **Well 3** | **June 24th** | 0.024 | BLQ | BLD | BLD | BLQ | 1.541 | 0.003 |
| **Well 3** | **August 4th** | 0.057 | BLQ | BLD | BLD | 0.064 | 2.097 | 0.003 |
| **Well 4** | **June 24th** | BLQ | BLQ | BLD | BLD | BLQ | 0.163 | BLQ |
| **Well 4** | **August 4th** | 0.011 | BLQ | BLD | BLD | BLQ | 0.226 | BLQ |
| **Well 6** | **June 24th** | BLQ | BLQ | BLD | BLD | 0.046 | 0.153 | BLQ |
| **Well 6** | **August 4th** | BLQ | BLQ | BLD | BLD | BLQ |  | BLQ |
| **Well 5** | **June 24th** | BLQ | BLQ | BLD | BLD | BLQ | 1.285 | 0.005 |
| **Well 5** | **August 4th** | 0.020 | BLQ | BLD | BLD | BLQ | 0.911 | 0.003 |
| **Well 7** | **June 24th** | BLQ | BLQ | BLD | BLD | BLQ | 0.862 | 0.004 |
| **Well 7** | **August 4th** | BLQ | 0.012 | BLD | BLD | BLQ | 0.452 | 0.003 |
| **Surface 8** | **June 24th** | 0.015 | BLQ | BLD | BLD | BLQ | 3.631 | 0.008 |
| **Surface 8** | **August 4th** | 0.008 | BLQ | BLD | BLD | BLQ | 1.653 | BLQ |
| **Surface 9** | **June 24th** | BLQ | BLQ | BLD | BLD | BLQ | 1.699 | 0.006 |
| **Surface 9** | **August 4th** | BLQ | BLQ | BLD | BLD | BLQ | 1.555 | BLQ |
| **Surface 10** | **June 24th** | 0.008 | BLQ | BLD | BLD | BLQ | 2.147 | 0.008 |
| **Surface 10** | **August 4th** | BLQ | BLQ | BLD | BLD | BLQ | 1.537 | 0.002 |
| **Surface 11** | **June 24th** | BLQ | BLQ | BLD | BLD | BLQ | 1.782 | 0.008 |
| **Surface 11** | **August 4th** | BLQ | 0.008 | BLD | BLD | BLQ | 1.165 | 0.003 |
| **Surface 12** | **June 24th** | BLQ | BLQ | BLD | BLD | BLQ | 0.290 | BLQ |
| **Surface 12** | **August 4th** | BLQ | BLQ | BLD | BLD | BLQ | 1.080 | 0.003 |
| **Surface 13** | **June 24th** | BLQ | BLQ | BLD | BLD | BLQ | 1.602 | 0.008 |
| **Surface 13** | **August 4th** | BLQ | BLQ | BLD | BLD | BLQ | 1.180 | 0.004 |
| **Surface 14** | **June 24th** | BLQ | BLQ | BLD | BLD | BLQ | 1.075 | 0.003 |
| **Surface 14** | **August 4th** | BLQ | BLQ | BLD | BLD | BLQ | 1.053 | 0.003 |

**Table 17 Benedict, MD Water Quality Measurements**

| Site | Date | $NH_4$ (N mg/L) | $NO_2$ (N mg/L) | $NO_3$ (N mg/L) | TDN (N mg/L) | ON (N mg/L) | $PO_4$ (P mg/L) | TDP (N mg/L) |
|---|---|---|---|---|---|---|---|---|
| **Well 1** | **June 24th** | 0.009 | 0.001 | 2.430 | | | 0.005 | |
| **Well 1** | **August 4th** | 0.012 | 0.001 | 1.960 | 2.130 | 0.158 | 0.026 | 0.047 |
| **Well 3** | **June 24th** | 0.009 | 0.002 | 1.390 | 1.450 | 0.051 | 0.032 | 0.063 |
| **Well 3** | **August 4th** | 0.077 | 0.014 | 0.977 | 1.330 | 0.276 | 0.006 | 0.029 |
| **Well 4** | **June 24th** | 0.010 | 0.165 | 0.802 | 0.960 | 0.148 | 0.004 | 0.024 |
| **Well 4** | **August 4th** | 0.009 | 0.046 | 1.680 | 1.640 | 0.000 | 0.019 | 0.031 |
| **Well 6** | **June 24th** | 0.009 | 0.001 | 2.570 | 2.610 | 0.031 | 0.003 | 0.005 |
| **Well 6** | **August 4th** | 0.009 | 0.001 | 1.880 | 1.930 | 0.041 | 0.003 | 0.007 |
| **Well 5** | **June 24th** | 0.009 | 0.001 | 0.621 | 1.050 | 0.420 | 0.155 | 0.185 |
| **Well 5** | **August 4th** | 0.030 | 0.007 | 1.480 | 1.700 | 0.190 | 0.087 | 0.124 |
| **Well 7** | **June 24th** | 0.294 | 0.001 | 0.018 | 2.370 | 2.058 | 0.021 | 0.126 |
| **Well 7** | **August 4th** | 0.677 | 0.001 | 0.005 | 2.040 | 1.358 | 0.013 | 0.174 |
| **Surface 8** | **June 24th** | 0.038 | 0.003 | 0.089 | 0.390 | 0.263 | 0.027 | 0.041 |
| **Surface 8** | **August 4th** | 0.009 | 0.038 | 0.043 | 0.380 | 0.328 | 0.080 | 0.113 |
| **Surface 9** | **June 24th** | 0.018 | 0.001 | 0.009 | 0.310 | 0.283 | 0.021 | 0.035 |
| **Surface 9** | **August 4th** | 0.009 | 0.047 | 0.057 | 0.370 | 0.304 | 0.078 | 0.103 |
| **Surface 10** | **June 24th** | 0.009 | 0.001 | 0.009 | 0.290 | 0.272 | 0.022 | 0.036 |
| **Surface 10** | **August 4th** | 0.009 | 0.037 | 0.056 | 0.370 | 0.305 | 0.081 | 0.109 |
| **Surface 11** | **June 24th** | 0.009 | 0.001 | 0.009 | 0.270 | 0.252 | 0.020 | 0.038 |
| **Surface 11** | **August 4th** | 0.009 | 0.005 | 0.011 | 0.340 | 0.320 | 0.064 | 0.094 |
| **Surface 12** | **June 24th** | 0.403 | 0.011 | 0.396 | 1.140 | 0.341 | 0.214 | 0.316 |
| **Surface 12** | **August 4th** | 0.009 | 0.001 | 0.004 | 0.350 | 0.338 | 0.057 | 0.087 |
| **Surface 13** | **June 24th** | 0.009 | 0.001 | 0.002 | 0.280 | 0.269 | 0.012 | 0.029 |
| **Surface 13** | **August 4th** | 0.009 | 0.001 | 0.004 | 0.250 | 0.237 | 0.033 | 0.054 |
| **Surface 14** | **June 24th** | 0.064 | 0.003 | 0.069 | 0.520 | 0.387 | 0.039 | 0.064 |
| **Surface 14** | **August 4th** | 0.009 | 0.001 | 0.005 | 0.370 | 0.356 | 0.105 | 0.137 |

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