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MAJOR IONS IN URBAN STREAMS: A LOOK AT CONCENTRATIONS OVER TIME AND ACROSS LAND COVER

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THESIS APPROVAL PAGE

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Abstract

Major ions in urban streams remain understudied, despite the connections between ion concentrations and stream ecosystem health. The concentrations and variability of major ions were characterized for streams in the Maryland Piedmont with impervious surface cover (ISC) ranging from 0–21%. The five study watersheds have similar bedrock geology and thus would have similar major ion chemistry in the absence of ISC and urbanization. Water samples have been collected weekly since 1998 in the watersheds as part of the Baltimore Ecosystem Study (BES). Anion concentrations measured by BES for these weekly samples and cation concentrations from 100-200 samples per stream measured at TU were used to analyze the effects of ISC and temporal trends for major ions. Overall, ion concentrations become more elevated and more variable as the percentage of ISC in a watershed increases. Additionally, major ion concentrations for watersheds with $\geq 1\%$ ISC rose substantially from 1998–2014.

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CHAPTER 1: LITERATURE REVIEW

1.1 INTRODUCTION

The focus of this study is urban stream chemistry, and the three main research questions posed are: 1) What is the relationship between percent impervious surface cover and major ion chemistry, including concentrations, ratios, and fluxes? 2) Is there increased variability associated with ion chemistry in urban streams compared to forested streams? 3) Do major ion concentrations and ratios change as urban watersheds "age" (i.e., with duration of urban land use)?

These research questions will be answered using data from five small watersheds in the Baltimore area with similar bedrock geology in the Maryland Piedmont. These watersheds have been monitored by the Baltimore Ecosystem Study (BES) since 1998. The BES collected water samples weekly at these watersheds and archived all samples collected since 1998. Originally, the BES measured anion concentrations in all collected samples, referred to here as the BES dataset. Analysis of the BES dataset has generally been limited to nutrient studies, and this will be one of the few studies to focus on the non-nutrient data collected by the BES. In this study, BES weekly water sample archive was subsampled and a new dataset was generated, referred to as the TU dataset. The TU dataset includes 100-200 archived samples collected from 1998-2014 at each watershed that were analyzed for both cation and anion concentrations. By re-analyzing the archived samples, I will be able to better describe how urbanization impacts stream chemistry and add to the current understanding of the processes impacting urban streams.

In the current literature, a growing number of studies discuss the changes observed in urban stream chemistry, but often the watersheds that are used have variable bedrock geology, point sources of pollution, or lack a reference site to compare to urban streams. This study will be able to quantify the contributions of major ions from the addition of urban land cover, without contributions from variable bedrock or point sources altering urban stream chemistry. Further, the addition of cation concentrations to the discussion of urban stream chemistry will add to literature that focuses mainly on nutrients and chloride concentrations. The datasets used in this study are also unique, because they describe changes occurring on the decadal scale in watersheds with relatively little land cover change over the study period. Urban stream chemistry impacts sensitive biota, nutrient cycling, drinking water, and infrastructure. Understanding how urban stream chemistry changes with urban land cover intensity and time are critical to any efforts to restore or protect urban streams.

To contextualize the research and results presented in this study, a summary of current literature will be provided in Chapter 1. This chapter will include how natural stream chemistry is largely determined by underlying bedrock and precipitation in a region, current studies on urban stream chemistry, and impacts of urban stream chemistry to biota. Chapter 2 outlines how the research questions were answered by detailing the methods used in this thesis. The results of the research, along with the discussion, are provided in Chapter 3. Finally, Chapter 4 will summarize the main conclusions of this study. Figures and tables are presented at the end of the paper, as well as appendices that provide additional results from this study's analyses.

1.2 NATURAL STREAM CHEMISTRY

To understand how stream chemistry is altered in urban watersheds, the natural stream chemistry must first be determined. The major influences on stream chemistry in forested settings are precipitation and the chemical weathering of bedrock, which are relatively well understood since chemical weathering has been the subject of major study for decades (*e.g.*, White and Blum, 1995; Ohrui and Mitchell, 1998; Nelson et al., 2011; Berner and Berner, 2012; Shin et al., 2014).

The influence of precipitation on stream chemistry arises from the aerosols deposited by precipitation, which are dependent upon geographic setting (White and Blum, 1995; Berner and Berner, 2012). Generally, coastal environments have higher Cl⁻ and Na⁺ concentrations in precipitation, primarily due to ocean water aerosols, and continental interior environments have higher Ca²⁺ and SO4²⁻ concentrations in precipitation, primarily due to dust aerosols (White and Blum, 1995; Berner and Berner, 2012). Precipitation also influences stream chemistry because of its weakly acidic nature (pH 4-6), which contributes to mineral dissolution in soil and bedrock (White and Blum, 1995; Berner and Berner, 2012). Local precipitation inputs of major ions should be considered in order to quantitatively determine contributions to major ions in stream chemistry from

materials introduced anthropogenically or via chemical weathering of soils and bedrock (Table 1) (Berner and Berner, 2012).

Chemical weathering of bedrock has the biggest influence on major ion chemistry in streams by releasing ions from minerals within a watershed's bedrock and soils (White and Blum, 1995; Nelson et al., 2011; Berner and Berner, 2012; Shin et al., 2014). The weatherability of some common minerals and the ions the minerals contribute to streams are provided in Table 2 (Berner and Berner, 2012). In general, Ca²⁺, Na⁺, and Mg²⁺ are highly mobile, weather easily, and are released into streams, while Al^{3+} and Fe^{3+} are immobile, preferentially precipitating as clays and oxyhydroxides (Cleaves et al., 1970; Viers et al., 2004; Berner and Berner, 2012). Watersheds with evaporite, carbonate, and silicate bedrock have vastly different major ion compositions and concentrations in natural stream chemistry due to their different mineral compositions (Table 3) (Berner and Berner, 2012). Evaporites have the highest dissolution rates, followed by carbonates and silicates (White and Blum, 1995; Viers et al., 2004). Evaporite and carbonate minerals dissolve several orders of magnitude faster than silicate minerals (Tables 2-3). If present in a watershed, evaporites and carbonates contribute more total dissolved solids to water chemistry than silicates, even if silicates make up a majority of the watershed's geology (White and Blum, 1995; Lyons et al., 2005; Nelson et al., 2011; Berner and Berner, 2012; Moore et al., 2013a; Shin et al., 2014). Evaporites are the main source of Na⁺, Cl⁻, and SO₄²⁻ in stream water chemistry. Specifically, halite (evaporite) contributes Na⁺ and Cl⁻ to stream water chemistry (Table 2). Carbonates are the main sources for Ca^{2+} and HCO_3^{-} with calcite and dolomite contributing Ca^{2+} and Mg^{2+} (Table 2) (Viers et al., 2004; Berner and Berner, 2012; Wang et al., 2015).

Chemical weathering rates are also influenced by climate, physical erosion, topography and vegetation (Viers et al., 2004; Nédeltcheva et al., 2006; Berner and Berner, 2012; Beylich and Laute, 2012). By looking at watersheds with similar geology along a gradient, such as climate (White and Blum, 1995) or erosion (Moore et al., 2013a), differences in chemical weathering rates have been observed, which can impact stream chemistry. Further, studies have shown that higher physical weathering rates increase the mineral surface area that can be chemically weathered, thereby increasing major ion contributions to stream chemistry (White and Blum, 1995; Lyons et al., 2005). Biological processes can also change chemical weathering rates. Vegetation generates CO_2 and some organic acids that accelerate silicate hydrolysis (White and Blum, 1995). Some cations, like Ca^{2+} , Mg^{2+} , and K^+ , are dominant cations in exchange reactions and are influenced by vegetation uptake within a watershed (Cleaves et al., 1970; White and Blum, 1995; Rice and Price, 2014). During the plant growth season, the concentrations of Ca^{2+} , Mg^{2+} , and K^+ generally decrease by 50% or more (Rice and Price, 2014).

1.2.1 Natural Chemistry of Study Sites

The five watersheds focused on in this study are underlain by the same silicate bedrock making these watersheds ideal for quantitatively measuring stream chemistry changes along a gradient (e.g. land use). The watersheds are underlain by schist, which includes the minerals quartz, plagioclase, muscovite, and biotite (Table 2) (Cleaves et al., 1970, Crowley and Cleaves, 1974; Crowley et al., 1975; Crowley, 1977; Reinhardt and Crowley, 1979; Edwards Jr., 1993; Muller, 1994). The forested reference watershed in this study, Pond Branch (POBR) has relatively dilute stream chemistry (major ions ≤ 2 mg/L, Table 4) that is dominated by weathering of oligoclase (a type of plagioclase) and biotite (Cleaves et al., 1970). At POBR, oligoclase is the sole source of Ca²⁺ and Na⁺. biotite is a source of K^+ , and both oligoclase and biotite weather to clay minerals. The anions Cl⁻ and SO₄²⁻ come from precipitation inputs, as POBR has no mineral source present within the watershed (Cleaves et al., 1970). Since all study watersheds have the same silicate bedrock and are located in close proximity within the Piedmont physiographic province, which is characterized by slowly weathering bedrock(Cleaves et al., 1970; Morgan et al., 2012; Utz et al., 2016), then in the absence of disturbance, all the watersheds would be expected to have similar stream chemistry to POBR.

1.2.2 Acid Deposition

Streams in forested, undeveloped watersheds are still vulnerable to anthropogenic pollutants which alter stream chemistry. In this study, the primary anthropogenic pollutant of concern at POBR is SO₂. Elevated atmospheric emissions of SO₂ prior to the 1970s were correlated to increases in precipitation and surface water concentrations of SO₄²⁻ across developed areas of North America and Europe, especially the Northeastern and Mid-Western US (Driscoll et al., 2001; Böhlke and Michel, 2009; McDonnell et al.,

2014). Between the 1970s and 1990s, significant decreases in SO_4^{2-} in both precipitation and surface water were observed due to the passage of the Clean Air Act (Likens et al., 1996; Stoddard et al., 1999; Kahl et al., 2004). After 1990, the Clean Air Act was amended to further limit SO₂ emissions (Likens et al., 1996; Driscoll et al., 2001).

Acid deposition is of concern to streams within the Northeastern United States due to regional point sources, primarily along the Ohio River, of SO₂ emissions (*e.g.*, coal power plants) (Driscoll et al., 2001; McDonnell et al., 2014). Increased SO4²⁻ deposition from precipitation in forested streams has been correlated with decreased pH, reduced acid neutralizing capacity (ANC), reduced Ca²⁺ or other cations in soil, and increased cations in surface water (Likens et al., 1996; Lawrence et al., 1999; Cosby et al., 2006; Böhlke and Michel, 2009; USEPA, 2009; McDonnell et al., 2014). Further, lower pH changes equilibrium in aquatic systems, leading to the mobilization of potentially toxic metals or changing cation exchange interactions, via redox reactions, between elements (*e.g.*, Ca²⁺, Mg²⁺, Al³⁺) in impacted streams (McDonnell et al., 2014). In watersheds with bedrock that weathers slowly (i.e. watersheds in this study), the amounts of Ca²⁺, Mg²⁺, and K⁺ are important to acid-base processes within the stream that support biota (McDonnell et al., 2014). Often these changes in pH, ANC, metal ion availability, and cation concentration result in the reduced richness and fitness of stream biota (Cosby et al., 2006; USEPA, 2009).

1.3 URBAN STREAM SYNDROME

Urban streams typically display a number of consistent features, collectively termed "urban stream syndrome", linked to the increase of impervious surfaces within their watersheds (Paul and Meyer, 2001; Meyer et al., 2005; Walsh et al., 2005). These features include flashier hydrology, elevated nutrient and contaminant concentrations, reduced nutrient uptake, altered geomorphology, reduced richness of biota, increased species tolerant to contamination, and altered ecosystem function (Paul & Meyer, 2001; Meyer et al., 2005; Walsh et al., 2005). As part of alterations accompanying land use change, urban streams may be artificially straightened, which increases hydraulic efficiency (Walsh et al., 2005) or streams may be buried during the development process (Elmore and Kaushal, 2008; Napieralski and Carvalhaes, 2016). Burying streams usually impacts first and second order (smaller) streams first, and a lack of natural headwater stream ecosystems can impact water quality and quantity in the downstream portions of the watershed (Elmore and Kaushal, 2008). Physical alterations to urban streams and the presence of impervious surface cover impact all components of flow: magnitude, duration, frequency of flows, timing of flows, and rate of change between flow rates (Bhaskar and Welty, 2012; Fletcher et al., 2014). These physical changes to urban streams are intertwined with changes to urban stream chemistry, but the focus on this research will be the altered chemistry of urban streams.

1.4 URBAN STREAM CHEMISTRY

Altered flow regimes caused by urbanization leads to flashy hydrology in urban streams (Paul and Meyer, 2001; Meyer et al., 2005; Walsh et al., 2005; Bhaskar and Welty, 2012), but despite the flashy hydrology associated with urban streams, recent studies have documented that major ion concentrations in urban streams are elevated (Table 5) (Prowse, 1987; Barnes and Raymond, 2009; Connor et al., 2014; Halstead et al., 2014; Tippler et al., 2014). Several recent studies, particularly those in the last 10 years, indicate that major ion concentrations in urban streams are elevated due to increased chemical weathering or direct anthropogenic contributions (Prowse, 1987; Fitzpatrick et al., 2007; Lewis et al., 2007; Barnes and Raymond, 2009; Peters, 2009; Connor et al., 2014; Halstead et al., 2014). These concentration increases are somewhat counterintuitive because flashier hydrology creates higher runoff and discharge over shorter periods of time, which, if all else were equal, would cause urban streams to be diluted by the increased discharge. Further, shorter travel times due to paved surfaces increasing velocity creates less contact with weatherable materials as precipitation inputs quickly runoff impervious surfaces to urban streams which might be expected to decrease the concentrations of chemical weathering products. The specific effects of urban land cover on stream chemistry are still unclear given a wide range of climates, bedrock chemistries, historical land use patterns, and the ages of the urban development that may be impacting urban streams (Walsh et al., 2005; Cuffney et al., 2010; King et al., 2011; Utz et al., 2016). Further, urban stream degradation is often compounded because, in addition to anthropogenic sources of ions and contaminants, any retention or natural processing of

contaminants is drastically reduced in urban streams do to the altered hydrology of these systems (Walsh et al., 2005; Elmore and Kaushal, 2008).

Changes to stream chemistry occur at relatively low levels of urbanization (Walsh et al., 2005) with some authors suggesting that less than 5% impervious surface cover (ISC) can change the overall chemistry of an urban stream (Kaushal et al., 2005; Morgan et al., 2012; Halstead et al., 2014; Tippler et al., 2014; Corsi et al., 2015). A variety of anthropogenic sources are linked to the elevated concentrations of specific ions in urban streams. The application of road salts to highways contributes Cl⁻ and Na⁺ (Kaushal et al., 2005; Corsi et al., 2010; Kelly et al., 2012; Halstead et al., 2014; Corsi et al., 2015) and Na⁺ loading specifically plays a role in cation exchange (Löfgren, 2001; Norrström and Bergstedt, 2001; Bäckström et al., 2004). Some studies suggest that building materials, such as concrete, contribute Ca^{2+} , Mg^{2+} , and HCO_3^- to urban stream chemistry (Prowse, 1987; Barnes and Raymond, 2009; Peters, 2009; Bain et al., 2012; Tippler et al., 2014). Leaking sewers or septic systems may contribute Cl⁻, Na⁺, K⁺, and SO₄²⁻ (Williams et al., 2005; Rose, 2007), and the application of fertilizers to lawns and gardens can contribute K⁺ to urban streams (Prowse, 1987; Halstead et al., 2014). Since road salts and concrete weathering appear to be the main drivers of elevated major ions in the urban streams in this study, a review of previous work on these sources is provided in the next two sections.

1.4.1 Road Salt

The use of road salt in northern latitudes as a deicer for major roadways is perhaps the most studied anthropogenic activity altering major ion chemistry in streams (*e.g.* Kaushal et al., 2005; Kelly et al., 2012; Morgan et al., 2012; Moore, et al., 2013b; Perera et al., 2013; Cooper et al., 2014; Dailey et al., 2014; Price and Szymanski, 2014; Corsi et al., 2015). Regions that receive frozen precipitation in winter months rely on road salts to keep roadways safe for traffic, and annual application of road salt has increased drastically in the US from <5 million metric tons in the 1960s to >20 million metric tons in 2009 (Kelly et al., 2012). Generally, halite (NaCl) is the primary road salt used to deice roads. However, CaCl₂ or MgCl₂ may be used; Mg²⁺ has been measured in deicers in the Chicago area, and other impurities have been reported (Kaushal et al., 2005; Kelly et al., 2012). In the literature, Cl⁻ and conductivity have been the primary measures of road

salt impact on streams (Kaushal et al., 2005; Kelly et al., 2012; Corsi et al., 2015). Chloride has been the focus of road salt research due its chemically conservative nature: Cl⁻ is relatively unreactive, does not readily adsorb to mineral faces, and is minimally biologically cycled (Daley et al., 2009; Kelly et al., 2012; Dailey et al., 2014; Price and Szymanski, 2014). Sodium inputs from road salt use, which are not as well studied in the literature, also has watershed level implications. High concentrations of Na⁺ in soils can release cations (Ca²⁺, Mg²⁺, K⁺) into surface water through cation exchange, impacting both soil chemistry and stream chemistry within a watershed (Kelly et al., 2012; Moore, et al., 2013b; Halstead et al., 2014). Finally, both Cl⁻ and Na⁺ are of concern because they pose human health and infrastructure concerns, such as contaminating reservoirs or damaging bridges and other structures (Kaushal et al., 2005; Daley et al., 2009; Kelly et al., 2012; Kaushal et al., 2015).

Overwhelmingly, the current literature shows that Cl⁻ concentrations are increasingly elevated with higher ISC (Kaushal et al., 2005; Corsi et al., 2015), proximity to major highways (Cooper et al., 2014; Price and Szymanski, 2014), and proximity to up-gradient stormwater ponds (Casey et al., 2013; Moore, et al., 2013b; Snodgrass et al., 2017). Cl⁻ concentrations begin to increase at low levels of ISC (1%) (Kaushal et al., 2005; Corsi et al., 2015), and remain elevated throughout the year in urban streams. Baseline concentrations of Cl⁻ have been steadily increasing over the past 30-50 years (Godwin et al., 2003; Kaushal et al., 2005; Kelly et al., 2012; Dailey et al., 2014; Price and Szymanski, 2014; Corsi et al., 2015). Increased summer concentrations of Cl⁻ are caused by the contamination of groundwater by Cl⁻ and Na⁺, which slowly travels through the watershed before being released into urban streams (Kelly et al., 2012; Moore, et al., 2013b; Cooper et al., 2014; Price and Szymanski, 2014; Corsi et al., 2015). Proximity to highways also have clear impacts on water-bodies: elevated concentrations of Cl⁻ and Na⁺ in the Kampoosa Bog were observed 600 m from the Massachusetts Turnpike (Richburg et al., 2001). Stormwater ponds are also a long term source of Na^+ and Cl^- , with salt concentrations high enough to change water density and halt spring turnover infiltrating through groundwater into receiving surface waters (Casey et al., 2013; Sibert et al., 2015).

An understudied aspect of road salt usage is the impact that high concentrations of Na⁺ have on cation exchange in impacted watersheds. At high concentrations, sodium can displace Ca²⁺, Mg²⁺, K⁺, and trace metal cations into surface waters (Norrström and Bergstedt, 2001). Cation exchange is of concern because Na⁺ loading along highways after road salting can also mobilize metals associated with roadways *e.g.*, Zn²⁺ or Cd²⁺ (Löfgren, 2001; Norrström and Bergstedt, 2001; Bäckström et al., 2004). Studies of soils along highways have shown increases in Cd²⁺, Cu³⁺, Pb²⁺, and Zn²⁺ concentrations with the greatest impact occurring between 6 and 10 m of major roadways but limited to 50 m (Löfgren, 2001; Norrström and Bergstedt, 2001; Bäckström et al., 2004). Further, stormwater ponds, which are a sink for many anthropogenic pollutants, were found to have high amounts of available/exchangeable Cd²⁺ in porewater (above toxicity standards), which was linked to complexation from added Cl⁻ from road salts (Mayer et al., 2008; Nelson et al., 2009). This could potentially mean that Na⁺ and Cl⁻ work in tandem to create more toxic waters through cation exchange (Na⁺) and complexation (Cl⁻) to mobilize metal ions such as Cd²⁺ (Bäckström et al., 2004; Mayer et al., 2008).

Road salt usage also has negative impacts to infrastructure and human health. Chloride has corrosive properties, which threaten infrastructure such as bridges, roads, and pipes (Kelly et al., 2012). Elevated Na⁺ concentrations are a health concern to those on low salt diets (EPA recommended concentration: <20 mg/L), and public water sources are required to be treated to below 250 mg/L for consumption (Kaushal et al., 2005; Kelly et al., 2012; USEPA, 2014a). Local Baltimore reservoirs are at risk of exceeding Na⁺ drinking water recommendations due to increasing concentrations of Cl⁻ and Na⁺ in urban streams that flow into the reservoirs (Kaushal et al., 2005; Kaushal et al., 2015). Road way proximity has also been shown to have impacts on drinking water wells, with wells as close to 500 m to road ways having increased concentrations of Na⁺ and Cl⁻ (Daley et al., 2009; Kelly et al., 2012). In wells tested by Daley et al. (2009) in New Hampshire, average concentrations exceeded 20 mg/L Na⁺ in ~50%, 200 mg/L Cl⁻ in ~25% and 250 mg/L Na⁺ in <5% of wells.

1.4.2 Concrete Weathering

Some field studies and laboratory experiments suggest that concrete may be easily weatherable and thus may have a substantial impact on stream chemistry, but the impact of concrete on urban streams has not yet been conclusively shown. Studies investigating the potential impacts of urban infrastructure weathering on urban stream chemistry often take place in watersheds with variable geology, point source pollution, or no reference site, preventing authors from disentangling urban infrastructure contributions to urban stream chemistry.

Pavements, such as asphalt and concrete, make up most ISC in urban watersheds. Asphalt is made up of a petroleum-based binder, limestone aggregate, and stone or natural sand, while concrete is made up of Portland cement, aggregates (limestone or gravel), water, and chemical mixtures (Bernot et al., 2011; Stutzman, 2012). Portland cement is made up of various calcium silicates (e.g. Ca_3SiO_5 , Ca_2SiO_4), and gypsum ($CaSO_4 \cdot 2H_2O$) (Stutzman, 2012). Both asphalt and concrete have been shown experimentally to elevate pH to 8-12 <2 days after being submerged in water. The pH in these experiments remains elevated (>9) for the entire 30 day study period (Setunge et al., 2009). Further, concrete and asphalt submerged in water elevate Cl^{-} , SO_4^{2-} , and Mg^{2+} concentrations in the water (Bernot et al., 2011). Water cycled through concrete pipes elevate pH, as well as Ca^{2+} , HCO₃⁻, and SO₄²⁻ concentrations (Setunge et al., 2009; Davies et al., 2010; Bernot et al., 2011; Grella et al., 2014). Further, despite concentration and pH differences of water entering concrete pipes (e.g. rain water and stream water), concentrations and pH were comparable at the end of the study regardless of the water's origin (Davies et al., 2010). Studies have also shown that PVC pipes increased pH and the concentrations of Ca²⁺ and HCO₃⁻ at comparable or slightly lower amounts, suggesting multiple sources within urban infrastructure could be contributing to elevated ion concentrations (Davies et al., 2010). The use of epoxy resin coating, was the only scenario under which concrete did not increase pH or ion concentrations (Grella et al., 2014).

Increasing evidence suggests that concentrations of Ca^{2+} , Mg^{2+} , and HCO_3^- are elevated as urbanization increases, and are often attributed to concrete weathering (Lewis et al., 2007; Peters, 2009; Bain et al., 2012; Kaushal et al., 2013; Connor et al., 2014; Halstead et al., 2014; Tippler et al., 2014). Despite the presence of gypsum in Portland cement and experiments showing increased SO_4^{2-} concentrations in water exposed to concrete (Davies et al., 2010; Bernot et al., 2011; Stutzman, 2012; Grella et al., 2014), SO_4^{2-} is often not discussed as a weathering product of concrete or urban infrastructure. Interestingly, SO₄²⁻ production and cycling has not been focused on in any previous studies of urban streams.

1.5 MAJOR ION IMPACTS ON BIOTA AND ECOSYSTEMS

While disentangling the effects of the multiple stressors posed by urban stream syndrome, it is clear that urban stream biota are negatively impacted (Paul and Meyer, 2001; Walsh et al., 2005; Wallace and Biastoch, 2016). In general, urban streams have degraded biotic communities and score lower on biotic metrics (*e.g.*, species richness, tolerant species present) (Stepenuck et al., 2002; Madden et al., 2007; Morgan et al., 2007; Cuffney et al., 2010; King et al., 2011). Many studies focus on ISC as the main factor of decline. Studies have found various thresholds of urban land cover that lead to deteriorated biota, usually around 10% ISC (Stepenuck et al., 2002; Madden et al., 2007). Some recent studies suggested thresholds may ignore the impacts of low ISC, using macroinvertebrate biotic indices and assemblages (measures of stream biota health) to show even at 2-5% ISC, these biotic metrics changed by 13-23% or taxa shifts occurred (Cuffney et al., 2010; King et al., 2011).

The natural chemistry of a watershed may influence the severity of a community's response to urbanization (Cuffney et al., 2010; King et al., 2011; Utz et al., 2016). One national-scale study found that in streams with lower background concentrations of conductivity, Cl^- , and SO_4^{2-} , macroinvertebrate communities are altered to a greater degree by urbanization (Cuffney et al., 2010). Utz et al. (2016) suggests that pre-adaptation to higher ionic concentrations may mute urbanization impacts in urban streams, citing the Maryland Piedmont as an example of low natural ionic water chemistry leading to more pronounced responses to urbanization in these streams. In King et al. (2011), Maryland streams were impacted a very low levels (0-2%) of urbanization.

The community structure within streams are often altered or degraded as urbanization increases. For instance, in macroinvertebrate communities scrapers may be replaced by gatherers or collectors due to food source availability in urban streams (Stepenuck et al., 2002) and fish assemblages may contain more pioneer species (species that initially

colonize an ecosystem) in urban watersheds, compared to their rural counterparts (Lewis et al., 2007; Morgan et al., 2012). While these communities respond to higher conductivity levels (linked to road salt usage), other urban stressors may impact community composition (Morgan et al., 2012). In general, urbanization has been linked to degraded biologic conditions in urban streams, and responses to specific sources of major ions in urban streams are detailed in the following subsections.

1.5.1 Road Salt Impact on Biota

Many studies have described or quantified the impacts of road salts on urban biota as a function of conductivity or Cl⁻ concentrations (Table 6). Often these streams are also impacted by other symptoms of urban stream syndrome, which makes quantifying the source of any degradation difficult. Further, the different organisms focused on in each study have wide ranges of tolerance to salty conditions. In general, organisms with mechanisms to avoid episodes of road salt run off have higher tolerance, and organisms that are sedentary or unable to avoid episodes of road salt runoff have lower tolerance (Morgan et al., 2012; Wallace and Biastoch, 2016). The specific impacts of road salts on organisms are often measured by monitoring stream chemistry to determine specific biotic thresholds, reporting changes biotic indices or metrics, measuring changes in nutrient cycling in high Cl⁻ concentrations, or direct toxicity testing. Table 6 summarizes results from various studies quantifying the impacts of road salt has on biotic communities, nutrient cycling, or specific organisms at different concentrations, some of which will be discussed in this section.

The EPA has set both chronic (230 mg/L) and acute (860 mg/L) toxic thresholds for Cl⁻ in US streams (US EPA, 2014), as an attempt to protect aquatic life. Unfortunately, urban streams exceed Cl⁻ toxic thresholds for aquatic life often in the Midwest and Northeast: Chicago, St. Louis, Milwaukee, and Detroit exceed chronic thresholds in >70% of streams during winter months and in >30% of streams during summer months (Corsi et al., 2010). Concentrations producing no young or causing complete mortality to daphnia were exceeded in ~40% of samples collected in Milwaukee, WI (Corsi et al., 2010). Regular exceedances of the EPA criteria may hamper any ability for biota within urban streams to recover after salt loading occurs. Biotic thresholds are quantified by monitoring several streams with varying levels of conductivity or Cl⁻ concentration, and calculating a limit at which biotic communities (usually fish or benthic macroinvertebrates) begin to shift or become degraded. Generally, these thresholds occur at much lower concentrations than the EPA chronic guidelines for aquatic life. For example, in the Maryland Piedmont, streams had a threshold of 33-108 mg/L Cl⁻ in fish communities. In this study, biotic indices from the Maryland Biologic Stream Survey (MBSS) were compared to Cl⁻ concentrations in streams across the state of Maryland (Morgan et al., 2012). In Toronto, using benthic macroinvertebrate biotic indices, a similar community threshold was calculated at 50-90 mg/L Cl⁻ (Wallace and Biastoch, 2016). Studies have also shown that more subtle changes may be occurring at low ISC (<5%) and Cl⁻ concentrations (<33-50 mg/L), such as shifts in taxonomy or reduced activity not registered by biotic indices or biotic threshold calculations (Madden et al., 2007; Tyree et al., 2016).

Nutrient cycling in urban streams is also impacted by higher Cl⁻ loads. Hale and Groffman (2006) found that nutrient cycling in streams with lower ISC is more negatively impacted by Cl⁻ loads than higher ISC watersheds, where nutrient cyclers may have adapted to high Cl⁻ conditions. Further, in streams where Cl⁻ concentrations have historically been low, debris dams may become sources of N loading when Cl⁻ concentrations were suddenly spiked during experimentation (Hale and Groffman, 2006). Microbial activity is also impacted by increased Cl⁻ concentrations. In a study where soil was treated with 100 mg/L Cl⁻ treatment, soil microbial activity was 50% that of control samples and nitrification was <10% of the control sample (Groffman et al., 1995).

Due to the complexity of measuring community level effects in the field, single species toxicity tests are often used to assess the specific impacts of Cl⁻ on individual organisms. Toxicity effects of road salts vary from organism to organism and are usually measured as an LC50 (lethal concentration of 50%). Table 6 documents some LC50 concentrations for daphnia, frogs, and salamanders, ranging from 1812 mg/L Cl⁻ to 5161 mg/L road salt (Gardner and Royer, 2010; Jones et al., 2015). The type of salt that organisms are exposed to moderately impacts toxicity, with pure NaCl having slightly higher LC50 values than local road salt obtained from the Towson University Police Department

(Jones et al., 2015). Studies also show sub-lethal impacts, such as freshwater mussels being unable to clamp onto host fish (EC50 1500 mg/L NaCl), which may make organisms inviable without directly killing them (Roy et al., 2015). Organisms may change their behavior by preferentially seeking out lower concentrations of Cl⁻ in their habitat, such as free swimming frog embryos preferentially swimming higher in the water column or frog species laying their clutches higher in the water column to avoid higher Cl⁻ concentrations (Brand et al., 2010; Dobbs et al., 2012).

1.5.2 Cation Concentration Impact on Biota

The concentrations and ratios of cations in urban streams have been understudied compared to road salt and Cl⁻ toxicity (Peters, 2009; Connor et al., 2014), despite the impact of cation concentrations and ratios on the toxicity of Cl⁻ (Mount et al., 1997; Gardner and Royer, 2010; Roy et al., 2015; Mount et al., 2016), the toxicity of heavy metals (Paquin et al., 2000; Lock et al., 2007; Luo et al., 2008; He et al., 2014), and the composition of biota assemblages (Potapova and Charles, 2002; Potapova and Charles, 2003).

Elevated mixed cation concentrations have been shown to reduce the toxicity of road salts. In a series of experiments testing the toxicity of major ion salts, Ca²⁺ was found to have a large impact on NaCl toxicity, with LC50 calculated at 1168 mg/L Cl⁻ in 2 mg/L Ca²⁺ and 2,920 mg/L Cl⁻ in 40 mg/L Ca²⁺ (Mount et al., 2016). Further, in a previous study the same authors found that Cl⁻ toxicity was reduced when in a solution containing two or more cations (Mount et al., 1997). Elevated Ca²⁺ and Mg²⁺ concentrations (or increased hardness) resulted in a lower Cl⁻ LC50 for freshwater mussels (Roy et al., 2015). They found that Cl⁻ concentrations that resulted in 50-100% mortality in low hardness water, only caused 20% mortality in water with increased hardness. One study reviewed appeared to show filtered stream water had a lower LC50 for Cl⁻, but cation concentrations were not presented in this study and other contaminants may have been present in the filtered stream water (Gardner and Royer, 2010).

Elevated cation concentrations in streams also reduce metal toxicity. The biotic ligand model (BLM) is a metal toxicity model used by the EPA, and it determines water quality standards in different aquatic environments by taking pH and concentrations of organic

matter and hardness into account when calculating metal toxicity (Paquin et al., 2000). The main concept behind the BLM is that cations such as Ca^{2+} , Mg^{2+} , Na^+ and H^+ can compete for biotic ligand binding sites, thereby reducing the toxicity of metals in water and soils (Paquin et al., 2000; Luo et al., 2008; He et al., 2014). Metals like nickel, zinc, copper, and cobalt have been shown to have reduced toxicity when organisms are exposed to both the metal and cations (Paquin et al., 2000; Luo et al., 2000; Luck et al., 2007; Luo et al., 2008; He et al., 2014).

Aquatic communities in unaffected watersheds are often adapted to a specific set of geochemical conditions, and cation chemistry controls diatom assemblage in the US (Potapova and Charles, 2003, Potapova and Charles, 2002). Further, in urban streams, major ion chemistry also plays a factor in diatom assemblage, along with physical habitat parameters (Potapova et al., 2005). Understanding how stream chemistry changes with urbanization will better identify how lower order organisms may be changing the overall structure of urban biotic communities.

1.6 GAPS IN KNOWLEDGE

Changes in stream chemistry as a result of urbanization have been reported in the current literature (Peters, 2009; Connor et al., 2014), but often links between the sources of specific ion concentrations and anthropogenic activities are unclear. One example is $SO_4^{2^-}$ in urban streams. It is assumed that most $SO_4^{2^-}$ in urban stream chemistry has an anthropogenic source, but the source of elevated sulfate in urban streams has not been discussed. Another example is concrete weathering, which may increase Ca^{2^+} , Mg^{2^+} , and HCO_3^- in streams, but other sources (fertilizers or septic sewage) or processes (ion exchange due to increased salinity) may also contribute to these elevated concentrations (Connor et al., 2014; Halstead et al., 2014; Tippler et al., 2014). This study will remove some uncertainty by studying watersheds with no point sources of major ions (e.g. waste water treatment plants), that lack geology with a similar geochemical signature to concrete (*e.g.*, carbonate bedrock), and a reference site within an unaltered watershed for direct comparisons.

Geochemical processes occurring within urban streams, such as cation exchange, are also poorly understood, despite thorough documentation of road salting in the US. Elevated Cl⁻ concentrations have been well documented in streams across the US in connection to road salt, but Na⁺ concentrations in these same streams are not nearly as well documented (Kaushal et al., 2005; Corsi et al., 2010; Morgan et al., 2012; Corsi et al., 2015). Both anion and cation data are analyzed in this study, and Na⁺ data can be used to better understand the cation exchange processes taking place after road salt enters streams. A 15-year time series of major ion chemistry in watersheds with varying levels of development will allow for a better understanding of how altered ion chemistry changes long-term chemical processes in urban streams, which is sparsely documented in the current literature. While studies have documented the differences between natural stream and urban stream chemistry (Fitzpatrick et al., 2007; Halstead et al., 2014), few have looked at changes in ion concentrations over time. Often these studies lack reference sites to compare urban concentrations to, so while they observe increasing concentrations, the contributions from urban processes is unknown. This thesis will analyze data over a 15year time scale to better contextualize the temporal impact of urbanization urbanizations impact temporally.

The three main questions posed by this study are: 1) What is the relationship between percent impervious surface cover and major ion chemistry, including concentrations, ratios, and fluxes? 2) Is there increased variability associated with ion chemistry in urban streams compared to forested streams? 3) Do major ion concentrations and ratios change as urban watersheds "age" (i.e., with duration of urban land use)? Using a forested watershed (POBR) as a reference site and choosing watersheds along a forested-urban gradient underlain by the same schist bedrock allows for direct comparisons of major ion chemistry between watersheds. With the varying levels of impervious surfaces in each watershed, the impact of road salt application, concrete weathering, and other sources of major ions can begin to be quantified. Variability can also be quantified using the large BES and TU datasets in this study. While some studies have documented the differences in concentrations between land cover types, few have quantified the variability of these concentrations with increasing ISC. Finally, the watersheds in this study have remained relatively unchanged since at least early 2000 (Table 7), allowing for a long-term analysis of concentrations in watersheds as urban land cover ages but does not increase.

CHAPTER 2: METHODS AND MATERIALS

2.1 SITE DESCRIPTION

Five watersheds are analyzed from the Baltimore Ecosystem Study (BES) archived dataset with the same underlying bedrock chemistry in the Maryland Piedmont (Figure 1). These sites have relatively stable land cover between 2001-2011 (<1% change, Table 7). Four of the watersheds lie along a forested to urban gradient and a fifth watershed serves as an agricultural land use comparison. Each of the sites are located within a 10-mile radius in Baltimore County, Maryland.

For each watershed, geology, impervious surface cover (ISC), tree canopy, and land cover data were compiled (Table 8). Bedrock geology was determined by using US Geologic Survey (USGS) 1:24,000 geologic quadrangles (Crowley and Cleaves, 1974; Crowley et al., 1975; Crowley, 1977; Reinhardt and Crowley, 1979; Edwards Jr., 1993; Muller, 1994) and digitizing these maps within ArcGIS. While Baltimore County provided ISC data (Figure 2), the data was only available for 2002. Therefore, data from Baltimore County and the National Land Cover Database (NLCD) were compared, and were within 1-2% for 2001 (NLCD) and 2002 (Baltimore County) data. For this study, ISC (Figure 3) and land cover (Figure 4) were determined using the more current National Land Cover Database (NLCD) data for 2011 (Homer et al., 2015). Each watershed's land use or ISC percentage was calculated within ArcGIS using a raster tool (zonal geometry as table) that counts each pixel within the watershed's boundary and sums the pixels by category. The following equations were used to calculate the percent of land cover, ISC, and tree canopy cover, where L_C in Equation 1 is land cover category and L_P in Equation 2 is each percentage category (0-100%).

$$\frac{L_c \ pixels}{total \ pixels} * 100 = Percentage \ Land \ Cover$$
 Eq. 1

$$\frac{\sum_{0}^{100} L_P * pixels}{Total Pixel} * 100 = Total Cover$$
 Eq. 2

2.2 BES DATA SET

The BES collected weekly water samples from 1998-2014 across a wide range of flow conditions at POBR, MCDN, BARN, GFGL, and GFGB (defined in Table 8). Water

samples were filtered in the field using a 0.47 μ m glass microfiber and 0.45 μ m poresized nylon filter. Anion concentrations were measured using a Dionex LC20 series ion chromatograph and archived on the web (Groffman et al., 2004). Weekly anion concentration data for these samples were obtained from the BES data archive (referred to as "BES dataset") from 10/15/1998 – 11/5/2014. After analysis by the BES, samples were archived and kept refrigerated at the Cary Institute in Millbrook, NY until the present.

2.3 SUBSAMPLING PROCEDURE

A subsample of archived BES stream water samples was collected from the Cary Institute in summer 2016. These samples were then reanalyzed for anions and analyzed for cations at Towson University. The original BES anion results are referred to as the "BES dataset" with >800 samples per watershed. Subsampled water samples analyzed for both anion and cation concentrations at Towson University are referred to as the "TU dataset", and includes 100 to >200 samples per watershed.

The subsampling procedure for the TU dataset was designed to avoid discharge and small sample related biases. To reduce potential discharge biases in the subsamples, stratifiedrandom sampling was used. The stratified-random sampling followed the recommendations of Hirsch (2014), by focusing sampling efforts on the highest 20% of discharge values to avoid discharge related biases in the Weighted Regressions on Time, Discharge, and Season (WRTDS) model (explained more fully in Section 2.6). At each site, daily average USGS discharge values for sample collection days were sorted into "Quartiles". Quartile 1 represents the lowest 25% of the data points, while Quartile 4 represents the highest 25%. Following the recommendations of Hirsch (2014), the 4th quartile and any high discharge outliers were sampled 1.5 times more frequently (66 samples at BARN, GFGL, GFGB and 33 samples at POBR, MCDN) than each of the other quartiles (44 samples each at BARN, GFGL, GFGB and 22 samples at POBR, MCDN). Within each quartile, sample dates were randomly selected, and then vetted to ensure no long-time gaps occurred and all seasons were represented by the sub-sampling. The only samples not randomly sampled were the first and last dates of the study period. Not all streams had discharge data for the entire study period, so the start dates were

10/15/1998 for POBR, GFGB, and GFGL, 10/5/1999 for BARN, and 12/9/1999 for MCDN, and the study period ends on 11/5/2014 for all streams.

Small sample related bias was reduced by following the recommendation of Hirsch (2014). Hirsch (2014) recommends that the minimum sample size for WRTDS be 100 sample points, but suggests larger sample sizes (200+) to reduce small sample bias. Due to the relative stable anion concentrations for POBR and MCDN, we concluded a smaller sample size would adequately capture the trends for these watersheds ($n \approx 100$). BES anion data for BARN, GFGB, and GFGL showed higher variability in anion concentrations and were more extensively sampled ($n \approx 200$).

2.4 BOTTLE CLEANING/SAMPLE FILTERING

After the subsampling procedure was executed and BES samples were selected, archived samples were collected in August 2016. Before collecting the samples, LDPE bottles, transfer pipettes, and syringes were soaked for a minimum of 6 hours in deionized (DI) water. After being allowed to soak, the bottles were rinsed three times with DI water and stored in a clean lab environment until dry. 0.45 µm poly-pro filters had 5 mL of DI water filtered through them before being allowed to dry overnight in the clean lab environment. During sample collection, samples that appeared to need filtering were filtered (marked F on the bottle) at the archive bunker. 1 mL of sample water was filtered through the clean filters before water was added to the sample bottles. Two years of archived samples were unfiltered by the BES and later filtered at Towson University using a 0.45 µm polypropylene filter. Extra samples from the 2008-2009 period were taken from the filtered archive samples to ensure that the unfiltered and filtered archived samples yielded similar results. Concentrations for the filtered and unfiltered samples were within 1 mg/L when compared. Several samples that were originally selected could not be located within the BES sample archive, and were replaced with samples within the same year, usually within one week of the original date or within the same month in a different year, when possible. After sample collection, samples were transported on ice from Millbrook, NY to Towson, MD and then refrigerated.

2.5 TOWSON DATA ANALYSIS

Water samples for the TU dataset were analyzed for cations (K⁺, Na⁺, NH₄⁺, Mg²⁺, and Ca²⁺) and anions (Cl⁻, SO₄²⁻, NO₃⁻, and PO₄⁻) using a Dionex ICS-500 series ion chromatograph (IC). The IC was calibrated before each run and each run included check standards and blanks. Check standards were run every \leq 20 samples. If calibration curves were <0.995 R² or average check standard concentrations differed by >10% from expected, samples were rerun. The range for the IC was 0.315 mg/L - 225 mg/L. Samples that fell above the upper limit were diluted and reanalyzed, while samples that fell below this limit were reported as NA for the respective ion. Both PO₄⁻ and NH₄⁺ fell below the detection limits of the IC for all samples, and therefore are not reported in the results.

After IC analysis was completed, charge balance errors (CBE) were calculated using concentration data from the IC analysis (Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, K⁺, Mg²⁺, Ca²⁺) and estimated alkalinity (as HCO₃⁻) concentrations from data collected by the Moore Lab. The Moore lab analyzed ion concentrations and alkalinity for 22 sample dates from May 2014- July 2016 at POBR, BARN, GFGB, and Beaver Run (an agriculture stream not included in this study). From the 2014 – 2016 samples, calcium-alkalinity ratios were calculated (Table 9) to estimate HCO₃⁻ for each stream. The Moore Lab does not monitor GFGL or MCDN, so end members that best represented watershed land use were used instead (GFGB for urban and Beaver Run for agricultural). Using Equation 3, Ca²⁺ data measured during the TU analysis (Ca_{TU}) was multiplied by the reciprocal of the ratios from the Moore Lab (Ca_{ML}/Alkalinity_{ML}) to estimate HCO₃⁻ concentration for each sample.

$$Ca_{TU} * \frac{1}{\frac{Ca_{ML}}{Alkalinity_{ML}}} = Estimated HCO_3^-$$
 Eq. 3

The CBEs and a comparison of BES to TU concentrations of Cl⁻ and SO₄²⁻ were used to create criteria that checked the quality of the TU dataset (Table 10). Samples that fell outside a $\pm 15\%$ CBE range were removed from the dataset, except for POBR. At POBR the range was extended to $\pm 25\%$ due to the low ionic concentrations observed at this stream, and current monitoring reporting an average CBE of -16%. TU Cl⁻ and SO₄²⁻ data were then compared to the BES dataset. If the Cl⁻ and SO₄²⁻ data were within 15% of the

TU dataset for samples >10 mg/L, 1.5 mg/L Cl⁻ for samples <10 mg/L, or 2 mg/L SO₄²⁻ for samples <10 mg/L , the data were considered acceptable for further consideration. The only caveat to these criteria occurred when Cl⁻ concentrations were both >250 mg/L and >10x SO₄²⁻ concentrations, which triggered an "AND" clause. In this situation, data were dropped only if both Cl⁻ and SO₄²⁻ data were >15% different from the BES dataset. Data that failed any of these criteria were removed from final boxplot and WRTDS analyses. Table 10 details the total number of samples that failed each (or both) criteria. Figures D1- D3 plot the BES and TU datasets against a 1:1 plot and symbolize the data by samples that passed the criteria and samples that failed the criteria.

2.6 R ANALYSIS

The R statistical package was used to analyze concentration data at each stream, quantify variability, and quantify temporal trends seen at each stream. Non-parametric statistics, such as median concentrations and inter-quartile ranges, were analyzed using R, mainly by utilizing boxplots. Flow-normalized concentrations and temporal trends were analyzed by the WRTDS model. Both boxplots and WRTDS were used to analyze major ion concentrations seasonally.

Using the statistical program R, non-parametric statistics were used to analyze concentration data, variability, and seasonality. To reduce small sample biases and improve the meaningfulness of comparisons, the TU dataset was split into three 5-year periods (N for each 5-year period is equal to \approx 33 samples for POBR and MCDN and \approx 66 samples for BARN, GFGB, and GFGL) and medians are reported from these boxplots, unless otherwise noted, to quantify concentrations. Boxplots were also used to quantify the Inter-Quartile Range (IQR), which was used as the primary measure of variability in this study. The boxplots were also used to analyze seasonal differences in concentrations, specifically winter versus non-winter concentrations. Winter, for the purposes of analysis, was defined locally using National Oceanic and Atmospheric Administration (NOAA) snowfall data from BWI. Months with average snowfall greater than 1 inch (December - March) from 1985-2014 were considered "winter" months, with all other months considered "non-winter" (NOAA, 2017). To determine if the two groupings (year and season) were statistically significant from one another within each watershed, and to

determine if watershed chemistries were statistically different, the R "Wilcox" Test was used. This test uses Wilcoxon Signed Ranks to determine statistical significance. Wilcoxon Signed Ranks Test compares two samples and looks for distinct clustering of the two samples to determine if they are different, or overlap to determine if they are similar (Corder and Foreman, 2011). Results for the R "Wilcox" test within each watershed (by 5-year period and season) are indicated by asterisks above each boxplot if p values <0.05 (95% statistically significant). Watersheds were also tested against one another to determine if they were statistically different, and all watersheds had p values <0.05 for all major ions.

Annual flow-normalized concentrations, temporal trends, and seasonal variation in each watershed were analyzed using the WRTDS model. WRTDS is part of the Exploration and Graphics of RivEr Trends (EGRETS) statistical package published by the USGS (Hirsch et al., 2010; Hirsch and De Cicco, 2015). The goal of the WTRDS model was to create a descriptive statistical approach, as the author's term it, to analyzing ion concentrations in streams and rivers, that is driven by data rather than a fit to linear or quadratic functions, is internally consistent, accounts for concentration changes caused by fluctuations in discharge, and has no *a priori* assumptions about constant flow, concentration-discharge relationships, or seasonal patterns. The model accomplishes these goals by using a flow-normalized 3-dimensional weighted regression model of concentrations based on time, discharge, and season. Flow-normalized concentrations calculated by the model reduce the variability seen in annual averages of raw concentrations, better allowing long term trends to be determined. Due to the temporal patterns of discharge, average concentrations are often driven by flow rather than concentration. In datasets where flow-normalized concentrations are not used, often short term changes in climate (e.g. droughts) will indicate temporal signals that do not reflect actual change in concentration within a stream or river (Hirsch et al., 2010).

WRTDS is ideal for analyzing a large number of concentration and discharge data collected on decadal time scales (Hirsch et al., 2010; Hirsch and De Cicco, 2015). The WRTDS model is the least biased of the concentration and flux analysis packages released by the USGS (*e.g.* LOADSET), due to its use of weighted regressions on time,

discharge, and season. The accuracy of the WRTDS model is influenced by the size of the dataset and the amount of sampling among different discharge magnitudes. Datasets with 100 to >200 samples have lower bias, and sample pools that either equally sample all discharge magnitudes or oversample higher discharges reduce bias (Hirsch, 2014).

The WRTDS package also contains an added uncertainty package, WRTDS Bootstrap Test (WBT). WBT allows users to analyze the uncertainty of their datasets in two ways. First, the package allows users to produce graphics that show an uncertainty band along the flow normalized trend lines. Second, the WBT package also provides users with a magnitude of change over the study period and a confidence rating for this trend. Runs of the BES data through the WBT used a replicate number of 100 and a 95% confidence interval for all runs, following recommendations from the WBT manual (Hirsch et al., 2015).

CHAPTER 3: RESULTS & DISCUSSION

3.1 BES V TU DATASETS

The data will be presented as raw concentrations (medians and inter-quartile ranges) and flow-normalized concentrations with two sets of analyses reported for Cl⁻ and for SO₄²⁻, one for the larger Baltimore Ecosystem Study (BES) dataset and a second for the TU dataset. Comparisons of annual boxplot statistics between the two datasets are provided in Appendix E (Tables E1-11, Figures E1-4). The average difference between the two datasets for annual Cl⁻ medians are <8.28% or <1 mg/L for each watershed, and the average difference for annual SO_4^{2-} medians are <10.87% or <1 mg/L (Table E1). The flow-normalized concentrations are <15% different for all average and flow normalized concentrations except for MCDN 2001-2004 SO4²⁻, and GFGB Cl⁻ in 2014 (Figure 9, Tables B1-4 and C1). The greatest differences generally occur during the first and last years of the sample period. Increased variability in the first and last years is expected because those years are the most uncertain in the Weighted Regressions on Time, Discharge, and Season (WRTDS) model. In WRTDS, the weighted regression utilizes time as one of the factors, and when no data is available in the years before or after a sample, the regression becomes more uncertain. The flow-normalized Cl⁻ concentration trends calculated using the WRTDS model (Figure 9, Table 11) are quite similar between the BES and TU datasets for the low impervious surface cover (ISC) streams (POBR, MCDN, BARN) while the trends diverge by 20–25 mg/L for the high ISC streams (GFGB, GFGL). While the difference in slopes between the two datasets is not statistically significant given the overlap in 95% confidence intervals, some difference is not surprising given the episodic nature of road salt inputs in urban watersheds (Figure 9A, Table 11). These comparisons demonstrate that the TU dataset captures the overall trends in the watershed chemistry. To analyze the most complete dataset for each ion, chloride and sulfate results from the BES dataset, and sodium, potassium, calcium, magnesium, and ion ratio results from the TU dataset will be discussed for the rest of this section.

3.2 CHLORIDE AND SODIUM

Cl⁻ and Na⁺ concentrations are elevated and increase over the study period in watersheds with higher ISC. Additionally, Cl⁻ and Na⁺ concentrations are more variable and seasonally distinct in watersheds with higher ISC. The lowest median concentrations of Cl⁻ occur in the forested POBR and agricultural MCDN watersheds (2.57 and 4.53mg/L, respectively), which have no ISC (Figure 5A, Table A1). Median Cl⁻ increases to 33.7 mg/L in BARN, a watershed with only 1% ISC (Figure 5A, Table A1). The highest median concentrations of Cl⁻ (86.8 and 121 mg/L) occur in the most urbanized watersheds, GFGB and GFGL (Figure 5A, Table A1). Similarly, Na⁺ concentrations increase with ISC (Figure 6A, Table A1). POBR has the lowest median concentration of Na⁺ (2.11 mg/L, Figure 6A). As was the case for Cl⁻, MCDN has slightly higher median Na⁺ concentrations (8.06 mg/L, Table A1). Median Na⁺ concentrations are 14.0, 29.7, and 34.7 mg/L, respectively, for the BARN, GFGB, GFGL watersheds, where ISC increases from 1% to 17% to21%, respectively (Figure 6A, Table A1).

Using inter-quartile ranges (IQRs), POBR shows the least variability for Cl⁻ (<0.43 mg/L) and Na⁺ (<0.36 mg/L). The urban watersheds are the most variable, with GFGB at 23.0 mg/L Cl⁻ and 15.9 mg/L Na⁺, and GFGL at 39.1 mg/L Cl⁻ and 30.0 mg/L Na⁺ (Figures 5A, 6A, Table A1). In POBR, Cl⁻ is slightly lower and decreases slightly in the winter months (-0.07 mg/L), while Na⁺ is not statistically distinct during the winter months (Figures 7A 8A, Table A2). Winter median Cl⁻ and Na⁺ concentrations are elevated compared to non-winter months in all watersheds containing ISC (Figures 7A and 8A, Table A2). BARN increases modestly (5.6 mg/L Cl⁻, 2.5 mg/L Na⁺) during the winter months, and both urbanized watersheds increase much more during the winter months (Figures 7A 8A, Table A2). While GFGB has less ISC (17%) than GFGL (21%), GFGB increases more during the winter (33.9 mg/L Cl⁻, 20.9 mg/L Na⁺ than GFGL (17.5 mg/L Cl⁻, 15.5 mg/L Na⁺) (Figures 7A and 8A, Table A2). In addition, Cl⁻ and Na⁺ variability during winter months is much higher in watersheds with ISC. At POBR Cl⁻ variability remains relatively unchanged during winter months (0.39 mg/L Cl⁻) compared to non-winter months (0.36 mg/L Cl⁻, 0.26 mg/L Na⁺), but in BARN winter variability (11.4 mg/L Cl⁻, 7.37 mg/L Na⁺) is slightly higher than non-winter variability (9.07 mg/L Cl^{-} , 3.63 mg/L Na⁺) (Figure 7A, Table A2). In the urban watersheds, winter variability is

substantially higher (89.7-96.4 mg/L Cl⁻, 46.0-51.6 mg/L Na⁺) than non-winter variability (39.2-40.1 mg/L Cl⁻, 12.9-15.8 mg/L Na⁺) (Figure 7A, Table A2).

The WRTDS results show that Cl⁻ and Na⁺ increase over the study period (Figures 9A 10A, Table 11) and are elevated during winter months in higher ISC watersheds (Figures 11-14). From 1999-2014, Cl⁻ and Na⁺ concentrations show no significant increase in the forested or agricultural watershed, a 17.3 and 8.17 mg/L increase in BARN, 88.7, and 24.3 mg/L increase in GFGB, and a 56.4 and 39.9 mg/L increase in GFGL (Figures 9A and 10A, Table 11). Cl⁻ and Na⁺ concentrations are increasing fastest in the two watersheds with higher ISC but also show significant and steady increases in BARN (Figures 9A and 10A, Table 11). The watersheds with no ISC, POBR and MCDN, do not experience higher concentrations of Cl⁻ or Na⁺ during the winter. Instead, at POBR the highest Cl⁻ and Na⁺ concentrations occur during the summer months (Figures 11-14). Conversely, in watersheds with ISC, Cl⁻ and Na⁺ concentrations have strong seasonal signals. In addition, winter concentrations are increasing faster than summer concentrations, with differences noted at the beginning of the study period 2-5x lower than those noted at the end of the study period. In BARN, concentrations increased 5-20 mg/L Cl⁻ and 2-10 mg/L Na⁺ during winter months, and at GFGB and GFGL winter concentrations were $\approx 60-100 \text{ mg/L Cl}^-$ and $\approx 20-100 \text{ mg/L Na}^+$ higher during winter months (Figures 11-14).

Most literature discussing road salt impacts on urban stream chemistry focuses on Cl⁻ concentrations (Kaushal et al., 2005; Cooper et al., 2014; Price and Szymanski, 2014; Corsi et al., 2015) rather than Na⁺ concentrations (Daley et al., 2009). One of the main additions this thesis makes to the current road salt literature is the analysis of long term trends of Na⁺ concentrations in urban streams. Few studies have reported Na⁺ concentrations due to its propensity to interact with the environment, unlike Cl⁻. Cl⁻ is conservative in nature, does not adsorb, and is not usually biologically cycled, thereby moving through a watershed relatively unimpeded (Daley et al., 2009; Kelly et al., 2012; Dailey et al., 2014; Price and Szymanski, 2014). In contrast, sodium interacts with Ca²⁺ and Mg²⁺ in watersheds during cation exchange, and this process has been poorly documented in the current literature. This section will discuss the results of the analyses

performed in this thesis, focusing on ISC, variability, seasonality, and temporal trends of both Cl⁻ and Na⁺ and comparing these results to the current literature.

The elevated Cl⁻ concentrations reported in this study agree with studies in the current literature. Increased ISC has been linked to elevated Cl⁻ concentrations in multiple studies (Kaushal et al., 2005; Daley et al., 2009; Morgan et al., 2012; Corsi et al., 2015). The elevated Cl⁻ and Na⁺ concentrations reported at 1% ISC in BARN agree with other studies in the current literature, which find that streams begin to have elevated concentrations of Cl⁻ when there is any ISC in a watershed (Kaushal et al., 2005; Morgan et al., 2012; Corsi et al., 2015). GFGL (21% ISC) has a median Cl⁻ concentration of 101 m/L for 2005-2009 (Table A1), which is consistent with average concentrations for watersheds with 20% ISC in the Northern US (Corsi et al., 2015). The Na⁺ flownormalized concentrations, which were slightly higher than the median concentrations reported in this study, at BARN (18.2 mg/L in 2014) and GFGL (71.1 mg/L in 2014) are comparable to those reported in Daley et al. (2009), where Na^+ becomes elevated at 1% ISC and at 10-20% ISC Na⁺ concentrations ranged from 50-60 mg/L. Increased variability in both Cl⁻ and Na⁺ concentrations associated with ISC increase and season are not surprising, due to the episodic nature of road salting during winter months, which create sudden peaks, increasing variability. Variability of Cl⁻ over both ISC and season have been reported in Baltimore (Kaushal et al., 2005), and over seasons alone in Milwaukee, WI (Corsi et al., 2010).

Using the WRTDS trend results, GFGB Cl⁻ is increasing 5.91 mg/L per year, and GFGL is increasing 3.76 mg/L per year. Assuming constant annual increase, flow normalized concentrations of Cl⁻ will exceed the EPA's chronic limit for biotic life by 2030 at GFGB and 2034 at GFGL, in an area only receiving 20 inches of snow in an average winter (NOAA, 2017). The Cl⁻ concentration increases of 88.7 mg/L and 56.4 mg/L (Table 11) observed at GFGL and GFGB, respectively, are similar to increases seen in Toronto from a two time point series (2002 and 2012), where median Cl⁻ concentrations in 17 urban streams increased 67 mg/L (Wallace and Biastoch, 2016). Godwin et al. (2003) showed that in upstate NY, concentrations of Cl⁻ increased by 243% and concentrations of Na⁺ increased by 130% from 1952-1998, and another study using historic US Geologic

Survey (USGS) specific conductivity data (related to both Na and Cl) at a single site found that from 1978-2008 specific conductivity increased in New Hampshire by approximately 3.5x (Daley et al., 2009). While these studies have looked at long term trends, they have used limited years of data, limited sites, or a small number of discrete sampling events (Godwin et al., 2003; Daley et al., 2009; Kelly et al., 2012; Corsi et al., 2015). The data presented in this thesis represents 15 years of weekly sampling in Baltimore streams, a more detailed and robust look at the changing concentrations of Na⁺ and Cl⁻ over time.

While these annual trends are startling, they do not consider the winter peaks occurring due to increased road salt use. To further understand Cl⁻ concentrations in urban streams, an analysis was conducted to determine how often Cl⁻ concentrations exceeded the EPA's aquatic life limits of 230 mg/L and 860 mg/L (Table 12). At POBR and MCDN the aquatic life limit for Cl⁻ was never exceeded, at BARN the chronic limit was exceeded once and the acute limit was never exceeded, and in GFGB and GFGL both the chronic and acute limits were exceeded during most winters (Table 12). Over the 5-year periods, the number of times the chronic limit was exceeded do not appear to be increasing or decreasing, at least based on a weekly sampling regime, but on a year to year basis the winter of 2014 had the most instances of exceedance (8 chronic/2 acute for GFGB and 9 chronic/2 acute for GFGL). There was only one year and one site where exceedances occurred outside of winter months. Summer Cl⁻ concentrations exceeded chronic limit in 2007 3 times at GFGL, suggesting a temporary point source discharge in the watershed (Table 12). The frequency of the acute and chronic limit exceedances for GFGB and GFGL fail to meet the EPA's requirements: chronic limits should not be exceeded more than once every 3 years and acute limits should not be exceeded more than once every 5 years due to the stress placed on organisms under the acute and chronic conditions (Stephen et al., 2010). Other studies have also looked at the number of times streams with ISC have exceeded the chronic and acute EPA limits. During a Maryland stream survey that reported Cl⁻ concentrations during spring baseflow, 0.26% of streams exceeded the acute limits and 1.5% of streams exceeded the chronic limits (n > 3,000) (Morgan et al., 2012). Other studies collecting data throughout the year found average Cl⁻ concentrations tend to exceed the chronic aquatic life limit in watersheds with 20% (Daley et al., 2009),

35% (Kaushal et al., 2005), and 40% ISC (Corsi et al., 2015). Differing amounts of ISC leading to the same average concentration of Cl⁻ are most likely due to differences in road salting practices based on the climates of the watersheds used in each study.

Seasonal Cl⁻ and Na⁺ concentrations are statistically different in watersheds, but watersheds with no ISC have little change in concentrations between seasons compared to the 3 watersheds with $\geq 1\%$ ISC (Figures 9A 10A, Table A2). In POBR, non-winter concentrations were higher than winter concentrations, which may be due to water evaporating in the watershed and leaving behind a slightly elevated concentration of Cl⁻ during summer months, as Cl⁻ has no other natural source within the watershed (Figure 9A, Table A2). For all watersheds with ISC, winter concentrations of Cl⁻ and Na⁺ were significantly higher than non-winter concentrations (Figure 9A 10A, Table A2) The WRTDS seasonal analysis also demonstrates seasonal differences and elevated winter concentrations of Cl^{-} and Na^{+} across the study period in watersheds with >1% ISC (Figures 11-14). The elevated winter concentrations of 60-100 mg/L Cl⁻ and 20-100 mg/L Na⁺ observed in this study (Figure 12) were similar to the seasonal signals measured in a less developed (6% ISC, \approx 50 mg/L) and an urban watershed (28% ISC, \approx 100 mg/L) (Corsi et al., 2015). This change from relatively stable chemistries year-round (<1 mg/L change) in the reference site to elevated chemistries in urban watersheds based on season can be harmful to biota. Increased summer concentrations may impact different development stages of biota in urban streams. For example, increased summer concentrations impact amphibian embryo and larvae stages, as has been shown by experiments using measured June concentrations of Cl- in stormwater ponds(Brand et al., 2010; Corsi et al., 2010; Dobbs et al., 2012).

3.3 SULFATE

Sulfate concentrations are elevated in watersheds with ISC and decreased over time in all watersheds. Additionally, SO₄²⁻ concentrations are more variable and seasonally distinct in watersheds with higher ISC. Sulfate concentrations become elevated along the forested to urban gradient (Figure 5C, Table A1); POBR has the lowest median SO₄²⁻ concentration (1.26 mg/L), followed by BARN (3.02 mg/L) and GFGB (7.13 mg/L). MCDN has a higher median concentration of SO₄²⁻ (17.1 mg/L) despite having 0% ISC.
GFGL has the highest median concentration of SO_4^{2-} (26.9 mg/L), \approx 4x the concentration at GFGB. Sulfate is the least variable at POBR (1.21 mg/L) and most variable at GFGL (7.0 mg/L) (Figure 5C, Table A1). Winter SO_4^{2-} concentrations are 0.8-1.7 mg/L higher than non-winter month concentrations in all watersheds (Figure 7C, Table A2). Overall, SO_4^{2-} concentrations slightly decrease with time at all the sites (Figure 9C, Table 11). This trend ranges from 0.58 mg/L to 2.97 mg/L decrease over the 15-year period (Figure 9C, Table 11). Generally, the more ISC within a watershed, the larger the decrease in SO_4^{2-} concentration (except at MCDN which has the greatest decrease, Table 11).

Other studies focusing on urban streams have also reported elevated concentrations of SO_4^{2-} in urban streams at $\approx 20-30$ mg/L, comparable to the results presented in this study (Williams et al., 2005; Rose, 2007; Barnes and Raymond, 2009; Peters, 2009; Tippler et al., 2014). Other studies focusing on urban streams have seen increased variability with increased urbanization, and in this study the highest variability in SO_4^{2-} concentration is at GFGL (7.0 mg/L). In a study reporting minimum and maximum SO_4^{2-} concentrations, low and moderate ISC (0-8%) had a range of 0.5-19 mg/L SO_4^{2-} , comparable to this study, while the high ISC (9-66%) had a range of 0.5-190 mg/L SO_4^{2-} (Tippler 2014). While these ranges are not directly comparable to this study due to the grouping of all ISC >9%, the sheer number of watersheds sampled, and the variability of bedrock geology in the previous study, the ranges reported do show that variability increases with ISC. Previous studies have attributed elevated SO_4^{2-} , along with K⁺, to sewer leaks (Rose, 2007), snow melt releasing atmospheric deposits of SO_4^{2-} (Williams et al., 2005), or have not discussed observed elevated concentrations of SO_4^{2-} in urban streams. While a small difference in seasonality was observed between winter and non-winter months (<2 mg/L, Table A2) that could be attributed to snow melt releasing atmospheric deposits of SO_4^{2-} or SO₄²⁻ contamination from road salt (i.e. Williams et al., 2005), the differences observed between watersheds with higher ISC cannot be solely attributed to snow melt releasing atmospheric deposits of SO_4^{2-} (≈ 25 mg/L, Figure 5C).

Another potential source of elevated SO_4^{2-} concentrations, concrete, is discussed in a few studies from the urban stream chemistry literature, but generally in the context of increased Ca²⁺ or HCO₃⁻ concentrations (Peters, 2009; Tippler et al., 2014). In lab

experiments, increased concentrations of SO_4^{2-} are reported in water cycled through concrete pipes (Davies et al., 2010; Bernot et al., 2011), suggesting that the increase in urban land cover could explain the increase in SO_4^{2-} concentrations between watersheds along the forested-urban gradient. Concrete is made up of Portland cement containing gypsum (CaSO₄ ·2H₂O) (Stutzman, 2012), which could be the main source of elevated SO_4^{2-} from concrete weathering in urban streams.

Specific land cover also appears to impact $SO4^{2-}$ concentrations in streams. MCDN, a watershed dominated by agricultural land cover, had much higher concentrations of $SO4^{2-}$ than GFGB, which is dominated by urban land cover. But, the results from GFGL seem to suggest that while agricultural streams are elevated, highly urbanized streams may exceed the concentrations observed in these agricultural settings. Barnes and Raymond (2009) observed higher $SO4^{2-}$ concentrations in agricultural streams relative to urban streams, which was not seen in this study at GFGL. Further, the variability in $SO4^{2-}$ concentration observed at MCDN was only 1.2 mg/L, suggesting that variability is associated with the sources contributing $SO4^{2-}$: urban land cover and agricultural land cover have different sources of $SO4^{2-}$, which are less variable in agricultural watersheds. In watersheds such as MCDN, where there is no ISC, but agriculture is the main land cover type, horse farming and other agricultural practices might bring sources of ammonium sulfate or elemental sulfur to the watershed, most likely through direct application as fertilizer (Wayland et al., 2003).

The decreasing SO_4^{2-} concentrations over time shown through the WRTDS analysis (Table 11) are consistent with findings from other studies in both forested and urban watersheds (Stoddard et al., 1999; Driscoll et al., 2001; Godwin et al., 2003; Kahl et al., 2004; Kelly et al., 2012). Out of the 42 stream sites sampled in Kelly et al. (2012), 23 had significant decreasing SO_4^{2-} trends between 1975 and 2008, and in forested streams, Godwin et al. (2003) found that SO_4^{2-} concentrations decreased by 23% in New York from the 1950s-1990s. The ≈ 0.5 -3 mg/L decreases in all sampled watersheds between 1999 and 2014 are expected based on the general downward trend of SO_4^{2-} in precipitation regionally (Table 1). This has primarily been attributed to both the original Clean Air Act and the 1990 amendments (Stoddard et al., 1999; Driscoll et al., 2001;

Kahl et al., 2004; McDonnell et al., 2014). In Maryland, specifically, SO_4^{2-} concentrations in precipitation have decreased $\approx 1 \text{ mg/L}$ since 1998 (Table 1).

The decreasing trend of $SO_4^{2^-}$ is also interesting in context with the other ion concentrations measured in this study. Sulfate is the only ion that decreases with time in watersheds with any ISC, but $SO_4^{2^-}$ is elevated as a function of ISC: at GFGL, $SO_4^{2^-}$ concentration is drastically higher than at GFGB. This may suggest that urban contributions from $SO_4^{2^-}$ may be elevated and increasing over time, but the decreasing contribution from atmospheric deposition is greater in magnitude. Therefore, urban streams may be experiencing fewer benefits from decreased atmospheric deposition than forested streams, because a part of the decrease is masked by the addition of $SO_4^{2^-}$ from concrete and other sources in the urban environment.

3.4 CALCIUM, MAGNESIUM, AND BICARBONATE

Calcium, magnesium, and bicarbonate concentrations are elevated, and increased over the study period for all streams in high ISC watersheds. Additionally, Ca²⁺, Mg²⁺, and HCO₃⁻ are more variable in higher ISC watersheds but are not seasonally distinct in the watersheds studied, except for GFGB. Calcium is elevated in higher ISC watersheds: the lowest median concentrations are observed at POBR (0.73 mg/L) and the highest at GFGL (62.1 mg/L) (Figure 6C, Table A1). Magnesium is also elevated in higher ISC watersheds: the lowest median concentration was observed at POBR (0.63 mg/L) and the highest at GFGL (27.9 mg/L) (Figure 6B, Table A1). Finally, HCO₃⁻ is elevated along the forest-urban gradient, from 9.91 mg/L at POBR to 141 mg/L at GFGL (Figure 6D, Table A1). Variability in concentrations increase with ISC: POBR had the lowest variability for Ca^{2+} (0.33 mg/L), Mg²⁺ (0.20 mg/L), and estimated HCO₃⁻ (4.53 mg/L), and GFGL has the highest variability for Ca^{2+} (25.8 mg/L), Mg²⁺ (15.9 mg/L) and HCO₃⁻ (58.5 mg/L) (Figure 6B-D, Table A). Statistically, Ca^{2+} , Mg^{2+} , and HCO_3^{-} do not show seasonally distinct concentrations, except at GFGB where concentrations are 5-15 mg/L lower during winter months (Figure 8B-D, Table A2). Over the study period Ca²⁺, Mg²⁺, and estimated HCO₃⁻ increase over time in all watersheds, but the changes are not as large in magnitude as the Cl⁻ or Na⁺ results and at GFGL Mg²⁺ did not steadily increase over the study period as all other cations in this study have in this watershed. Calcium did not

increase significantly at POBR (0.35 mg/L), and was highest at GFGL (13.4 mg/L) (Figure 10D, Table 11). Magnesium remains relatively unchanged at POBR (0.16 mg/L), and increases for the entire study period in watersheds with ISC, except at GFGL (Figure 10B, Table 11). At GFGB a steady increase in Mg²⁺ is observed from 1999-2014 (5.53 mg/L) (Figure 10B, Table 11). Magnesium is the only ion besides SO_4^{2-} to decrease, but only at GFGL and only from 1999-2006 (-2.86 mg/L). After 2006, Mg²⁺ increases 4.45 mg/L at GFGL, similar to the increase at GFGB for the whole study period (5.53 mg/L). In total, Mg²⁺ at GFGL only total increases 1.59 mg/L from 1999-2014 (Figure 10B, Table 11). Bicarbonate increases at approximately the same magnitude for POBR, MCDN, and BARN (\approx 4 mg/L), but has greater increases in GFGB (19.6 mg/L) and GFGL (30.3 mg/L) over the study period (Figure 10C, Table 11).

Calcium, magnesium, and bicarbonate are observed at elevated concentrations in urban settings by other authors (Fitzpatrick et al., 2007; Rose, 2007; Peters, 2009; Connor et al., 2014; Tippler et al., 2014). Direct comparisons with other studies are complicated by differences in natural stream chemistry between studies, so this discussion will focus on how elevated Ca^{2+} , Mg^{2+} , and HCO_3^{-} were in urban streams compared to reference sites in this study and studies in the current literature. GFGL median concentrations with respect to POBR are 74x higher for Ca²⁺, 40x higher for Mg²⁺, and 12x higher for HCO₃⁻ (Figure 6B-D, Table A1). In Peters (2009), Ca²⁺ is 8x higher, Mg²⁺ is 4x higher, and HCO_3^- is 10x higher in urban streams (Table 5). Rose (2007) also notes a smaller increase in ionic concentrations between rural streams and urban streams, with $Ca^{2+} 4x$ higher, Mg^{2+} 2.5x higher and HCO_3^- 3x higher (Table 5). In these two studies from Georgia, the reference streams had some developed land cover, suggesting that the increases observed may be muted compared to those observed in this study due to the pristine nature of POBR. Fitzpatrick et al. (2007) reported the lowest increases from urban land use compared to reference sites, with 1.5x Ca²⁺, 1x Mg²⁺, and 1x HCO₃⁻, most likely due to the concentrated nature of the baseline stream chemistry in this study being so concentrated (Table 5). Conversely, Tippler et al. (2014) reports more drastic increases between reference and urban streams for $Ca^{2+}(20x)$, but not $Mg^{2+}(3x)$, or $HCO_3^{-}(4x)$ (Table 5). In many of these studies, the added complication of variable or carbonate bedrock chemistry contributing to natural stream chemistry may mute or alter the

geochemical signature of urban infrastructure weathering. The consistent bedrock chemistry throughout all watersheds in this study better defines the chemical signature observed for the chemical weathering of urban infrastructure, compared to many of these studies. Further, the variable being tested in each watershed was different, often using land use (Fitzpatrick et al., 2007) or population density data (Rose, 2007) rather than ISC (Peters, 2009; Tippler et al., 2014). Variability of major ion concentrations have also been shown to increase along land use gradients (Williams et al., 2005; Tippler et al., 2014). While other studies have not used IQR as a measurement of variability, Tippler et al. (2014) reported minimum and maximum concentration values at multiple watersheds within Sydney, Australia, which can be used to calculate a range. The range of the reference site in Tippler et al. (2014) was much lower for Ca²⁺ (11.5 mg/L), Mg²⁺ (5.5 mg/L), and HCO_{3⁻} (28.7 mg/L), compared to the urban site's much higher ranges of Ca^{2+} (96 mg/L), Mg^{2+} (57 mg/L), and HCO_3^- (395 mg/L).. While these ranges are not directly comparable to this study due to the presence of variable bedrock, the number of watersheds tested, the range of ISC used, and the lack of IQR calculations, Tippler et al. (2014) does show that urban streams are usually more variable than rural sites.

Concrete weathering is the most often suggested source for increased Ca^{2+} , Mg^{2+} , and HCO_3^- concentrations in urban streams. Cation exchange from road salting during winter months (Norrström and Bergstedt, 2001; Bäckström et al., 2004), accelerated concrete weathering from road salts (Shi et al., 2010), and atmospheric deposition of SO_4^{2-} increasing chemical weathering (Likens et al., 1996; Lawrence et al., 1999; Cosby et al., 2006; Böhlke and Michel, 2009; USEPA, 2009; McDonnell et al., 2014) have all also been suggested as mechanisms for increased cation concentrations. Concrete contains Portland cement, made up of numerous calcium silicates (Bernot et al., 2011; Stutzman, 2012), which are a potential source of elevated cations in urban watersheds. In experiments, increases in Ca^{2+} and HCO_3^- in water cycled through concrete pipes have been reported (Setunge et al., 2009; Davies et al., 2010; Bernot et al., 2011; Grella et al., 2014). The addition of road salts to urban watersheds, especially Na⁺, may increase cation exchange in impacted watersheds. As Na⁺ concentrations are elevated, Ca^{2+} is preferentially released to surface waters while Na⁺ sorbs to clay surfaces, do to the increased molecular weight and charge of Ca^{2+} (Norrström and Bergstedt, 2001). Road

salts may have a further impact on the release of Ca²⁺ to streams: in a set of laboratory experiments, concrete weathering was shown to be accelerated by NaCl and NaCl-based deicers (Shi et al., 2010). Elevated SO4²⁻ in urban watersheds may also increase cation concentrations, as observed in forested streams impacted by atmospheric deposition (Likens et al., 1996; Lawrence et al., 1999; Cosby et al., 2006; Böhlke and Michel, 2009; USEPA, 2009; McDonnell et al., 2014). Overall, concrete weathering, assisted by road salts and sulfate accelerating chemical weathering, are the most likely contributors to elevated cation concentrations in urban stream, especially due to the muted seasonal responses of these ions in urban streams.

Few studies have looked at the change in Ca²⁺, Mg²⁺, and HCO₃⁻ over time, as they generally collect samples over the course of three years or less (Fitzpatrick et al., 2007; Rose, 2007; Peters, 2009; Connor et al., 2014; Tippler et al., 2014). One study documented HCO₃⁻ concentrations in 97 streams across the eastern US, and found HCO₃⁻ to be increasing in 62 of those streams (Kaushal et al., 2013). Kaushal et al. (2013) suggested that increased atmospheric deposition of SO₄²⁻ increased weathering of carbonate lithologies in the Northeastern US, but in the Baltimore and Washington D.C. area the dissolution of concrete was cited as the probable source of increased alkalinity (as HCO₃⁻) in streams. In Bowie, MD, the annual increase of HCO₃⁻ was ≈1.3 mg/L and in Washington D.C. the annual increase was ≈0.5 mg/L (Kaushal et al., 2013), comparable to GFGB (≈1.3 mg/L per year) but less than GFGL (≈2.02 mg/L per year). Overall, this increase over time of Ca²⁺, Mg²⁺, and HCO₃⁻ seems to suggest that as infrastructure ages, more easily weatherable material may be exposed for chemical weathering, driving elevated concentrations in urban streams, and causing these concentrations to increase over time.

3.5 POTASSIUM

Potassium concentrations are only slightly elevated, and show much smaller changes through time in watersheds with higher ISC than other ions in this study. Additionally, K^+ was less variable in all watersheds and minimally seasonally distinct in all watersheds except GFGL. The median concentration of K^+ is lowest at POBR (0.72 mg/L) and highest at GFGL (2.45 mg/L), only \approx 3.5 times greater along the forested-urban gradient

(Figure 6E, Table A1). Variability is lowest at POBR (0.24 mg/L) and highest at GFGL (0.62 mg/L), a much smaller distribution of variability compared to the other ions discussed. Potassium shows minimal seasonal distinction (0.14-0.32 mg/L) at all watersheds except GFGL where K⁺ is not seasonally distinct. Further, K⁺ increased between 0.18 mg/L (POBR) and 0.95 mg/L (GFGL) during the study period, a much smaller increase compared to other cations in this study (Figure 10E).

Potassium is an example of a cation that is not readily weathered from the urban environment in the watersheds focused on in this study, and therefore has less dramatic elevated concentrations in urban stream chemistry (only 3.5x higher than forested site). These results are somewhat counter to other studies that have reported elevated K⁺ in urban steams (Prowse, 1987; Williams et al., 2005; Rose, 2007; Peters, 2009). Potassium has even been suggested as the best indicator of human disturbance because of septic sources leaking into groundwater within urban watersheds (Williams et al., 2005; Rose, 2007). Potassium may be seen in higher concentrations due to dispersed fertilizer inputs (Prowse, 1987), or point sources (*e.g.*, golf courses, sewer leaks) (Peters, 2009), which do not seem to be drastically impacting the urban streams in this study, compared to other sources of elevated ion concentrations. Low K⁺ concentrations may be evidence of a lack of leaking septic sewers contributing major ions to urban stream chemistry in the watersheds in this study, further supporting conclusions from the sulfate and chloride sections that suggest concrete weathering and road salting as respective sources of those ions rather than septic sources.

3.6 ION RATIOS

Ion ratios in this study compare Na:Cl, Ca:Na, Ca:Cl, and CaMg:Cl ratios across the forested-urban gradient (Figures 15-16). POBR, with no ISC, has Na:Cl ratios just above 1, while the three watersheds with >1% ISC have Na:Cl ratios between 0.49 and 0.68 (Figure 15A). Na:Cl remains relatively constant between winter and non-winter months at POBR but shows increases in the winter at BARN (0.07 Na:Cl), GFGB (0.22 Na:Cl), and GFGL (0.21 Na:Cl) (Figure 16A). Along the forested-urban gradient, Ca:Na ratios increase from 0.21 Ca:Na at POBR to 1.10 Ca:Na at GFGL (Figure 15B, Table A3). Ca:Na ratios decrease in the winter in all watersheds (Figure 16B Table A4). In POBR

this decrease is much less (-0.04 Ca:Na) than at GFGL (-0.15 Ca:Na) (Figure 16B, Table A4). Both Ca:Cl and Ca+Mg:Cl ratios increase along the forested to urban gradient (Figure 15C-D, Table A3). Compared to POBR, GFGL has 2x the Ca:Cl ratio, and 1.5x the Ca+Mg:Cl ratio (Figure 15C-D, Table A3). Ca:Cl and Ca+Mg:Cl decrease at all watersheds in the study during the winter (Figure 16 C-D, Table A4).

As shown in Figures 15 and 16 (Tables A4-5), ion ratios change along the forested-urban gradient, and with season. Ion ratios in urban streams seem to be driven mostly by road salt inputs, especially due to the seasonal distinctions in watersheds with >1% ISC. Ion ratios are an important part of lower-order organism assemblages: in the US, ion composition of stream water was found to be a controlling factor in diatom assemblages in unaltered streams and rivers (Potapova and Charles, 2002; Potapova and Charles, 2003). Further, changes in ion composition in urban streams have also lead to altered biota assemblages, along with physical alterations to habitat (Potapova et al., 2005).

In the context of road salting, Ca^{2+} has been suggested as a product of increased cation exchange due to Na⁺ loading. Generally, Na:Cl ratios <1 have been used to show that Na⁺ moves slowly through watersheds, participating in cation exchange (Daley et al., 2009). Ca:Na ratios calculated through this study show Ca^{2+} concentrations increase in relation to Na⁺ along the forested-urban gradient. A combination of concrete weathering and cation exchange likely drives the increase in the Ca:Na ratios in watersheds with higher ISC.

CHAPTER 4: CONCLUSIONS

Concentrations of Cl⁻, Na⁺, Mg²⁺, Ca²⁺, HCO₃⁻, and SO₄²⁻ are elevated and all but SO₄²⁻ are increasing in watersheds with high impervious surface cover (ISC) in this five watershed study in Baltimore, MD. In addition, urban stream chemistry is highly variable, and Cl⁻, Na⁺, and SO₄²⁻ concentrations vary seasonally. With no major point sources of Cl⁻ or Na⁺ within the studied watersheds, road salts are the obvious source of increased Cl⁻ and Na⁺. Further, the low concentration of Cl⁻ observed in watersheds with no ISC (POBR and MCDN) and the seasonality of Cl⁻ concentrations in the watersheds with higher ISC indicate road salts are the major source of elevated Cl⁻ and Na⁺

>1% ISC, indicating that Na⁺ moves slowly through urban watersheds relative to Cl⁻ after road salting events. The remaining ions, Mg²⁺, Ca²⁺, HCO₃⁻, and SO₄²⁻ are all chemical constituents of concrete, suggesting that concrete weathering is another important contributor to elevated ion concentrations in urban streams. Over the 15-year period, ion concentrations increased in all watersheds with >1% ISC, and the rate of concentration increase was higher in watersheds with greater ISC. These increases occurred despite no major changes in land use within the watersheds across the study period. The most likely reason for increasing concentrations is loading of road salt and concrete weathering products into soils and groundwater. However, the transit time of groundwater results in a lag between application of road salt and weathering of concrete and the delivery of the dissolved products to urban streams.

The culmination of the ion data presented in this study describes the evolution of previously dilute streams becoming increasingly less dilute with higher ISC within watersheds and over time. Due to the naturally dilute conditions of the streams in this study, the biotic communities in these streams are likely be relatively vulnerable to these chemical changes (Cuffney et al., 2010; King et al., 2011; Utz et al., 2016). Urbanization is changing the major ion compositions of stream and river water across the globe, with real implications to both biota and humans. As Table 6 summarizes, biotic communities are often impacted at low levels of anthropogenically-added road salts and other studies have found that diatom community composition is dependent on Ca^{2+} and HCO_3^{-} concentrations and composition of major ions in US rivers (Potapova and Charles, 2002; Potapova and Charles, 2003). Drinking water sources in proximity to watersheds with elevated ISC, such as wells and reservoirs, are often contaminated by elevated concentrations of salts in urban streams and groundwater (Kaushal et al., 2005; Daley et al., 2009; Kelly et al., 2012). The results from this study demonstrate the need to more carefully study major ion chemistry in urban watersheds across a range of geological and climatic settings to understand the impact on stream biota. Additionally, efforts to understand or restore ecosystem function in urban streams need to account for the altered major ion chemistry in those streams.

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	Ca ²⁺	Mg ²⁺	\mathbf{K}^+	Na ⁺	$\mathrm{NH_4^+}$	NO ₃ -	Cl	SO42-	pН
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	
Median ^a	0.0885	0.02	0.0255	0.1	0.2375	1.015	0.239	1.537	4.495
1998 (White Rock, MD)	0.09	0.021	0.017	0.104	0.234	1.717	0.248	2.187	4.28
2014 (Beltsville, MD)	0.063	0.018	0.064	0.09	0.196	0.68	0.167	0.589	4.99

Table 1: Major Ion Concentrations in Precipitation (Maryland)

Data from the National Atmospheric Deposition Program (NADP, 2017).

^a Annual data from 1998-2002 are from the station at White Rock, MD (west of study sites) and annual data from 2003-2014 are from Beltsville, MD (south of study sites). These datasets did not overlap. Calculated median from all annual medians provided between the two datasets.

Mineral	General composition	Ions added to stream chemistry	Dissolution Rate
Halite	NaCl	Na ⁺ , Cl ⁻	Fastest
Calcite	CaCO ₃	Ca^{2+}	
Dolomite	CaMg(CO ₃) ₂	Ca^{2+}, Mg^{2+}	
Oligoclase	NaAlSi ₃ O ₈ (albite)	Na ⁺ , Ca ²⁺	
Plagioclase Feldspar	CaAl ₂ Si ₂ O ₈ (anorthite)	Na ⁺ , Ca ²⁺	
Biotite	$K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$	K ⁺ , Mg ²⁺	
K-Feldspar	KAISi ₃ O ₈	\mathbf{K}^+	
Muscovite	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂	\mathbf{K}^+	
Quartz	SiO ₂		Slowest

Table 2: Relative Mineral Weatherability

Replicated from Berner and Berner (2012) and Cleaves et al. (1970).

Minerals listed from highest weatherability/dissolution rate to lowest, and grouped by rock type the minerals usually compose. Evaporites (Halite), Carbonates (Calcite and Dolomite), and Silicates (Oligoclase, Plagioclase Feldspar, Biotite, K-Feldspar, Muscovite, Quartz).

Table 3: Major Ion Contributions	to Streams	Dominated	by Evaporite,	Carbonate, a	and
Silicate Bedrock					

Major Ion	Evaporite	Carbonate	Carbonate	Silicate
	Salt & gypsum marl	Limestone	Dolomite	Granite/gneiss/ schists
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Ca ²⁺	187.4	85.67	63.85	0.39
HCO3 ⁻	335.6	267.7	329.4	6.74
Na^+	208.6	0.62	0.14	1.94
Cl	351.0	0.00	0.00	0.00
SO4 ²⁻	574.8	5.34	23.82	0.93
Mg^{2+}	107.0	1.64	32.99	0.24
K+	8.602	0.70	0.23	0.25

Data partially replicated from Meybeck (1987) and Meybeck (2003).

Reported water chemistry in unaltered watersheds dominated by evaporite, carbonate, and silicate bedrock.

Tuble II I one Di		i ater enen	mon y (1900	, 1,00)		
	Cl ⁻	SO_4^{2-}	Na ⁺	\mathbf{K}^{+}	Ca ²⁺	Mg^{2+}
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Precipitation	0.6	1.7	0.2	0.2	0.3	0.1
Base Flow	2.1	1.3	1.7	0.9	1.4	0.8
Flood flow	2.2	6.3	1.4	1.3	1.9	1.3

 Table 4: Pond Branch Stream Water Chemistry (1966-1968)

Data partially replicated from Cleaves et al. (1970).

Table 5: Ma	ior ion	concentrations 1	reported in	the	literature
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Location	Ca ²⁺	Mg^{2+}	Na^+	K^+	Cl	SO4 ²⁻	HCO32-
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
US EPA Drinking water standard ^a US EPA recommended			<20mg/L low sodium diet <30-60 mg/L recommended		<250 *secondary	<250 *secondary	
aquatic life quality ^b					>860 acute >230 chronic		Alkalinity >20
North America Natural ^c	20.1	4.9	6.5	1.5	7	14.9	71.4
Urban Anacostia River, D.C. ^d Forested	26.63	7.78	32.98	4.14			
Michigan, US ^e	40	12	4	2	6	20	184
Agriculture Michigan, US ^e	64	22	9	0.5	20	8	279
Urban Michigan, US ^e	60	14	43	3	92	30	187
Reference Sydney, AUS ^f	1.0	3.0	16.5	0.5	30.5	4.7	4.0
Peri-urban Sydney, AUS ^f	6.5	3.0	16.5	2.0	42.5	8.5	22.0
Urban Sydney, AUS ^f	21.9	10.0	66	4.0	109	29	87.0
Rural Atlanta, GA ^g	2.00	0.852	3.31	1.44	4.57	2.11	13.0
Urban Atlanta, GA ^g	8.88	2.04	7.20	2.54	10.33	4.90	38.2
Urban- Reference comparison							
Atlanta, GA ^h	8x	4x	4x	4x		30x	10x

^aUS EPA (2014a) ^bUS EPA (2014b)

^eBerner and Berner (2012), average of all major rivers in North America

^d Connor et al. (2014), downstream of Washington, D.C., no impervious surface data given

°Fitzpatrick et al. (2007), 50-77% Urban land use, 58-82% Forested land use

^fTippler et al. (2014), Reference <0.1 directly connected impervious area (DCIA), Peri-Urban 0.1-8% DCIA, Urban 9-66% DCIA

^g Rose (2007), reference watersheds <50 people/km², urban watersheds 2000-4000 people/km²

^hPeters (2009), 69-96% urban land cover

Concentration (Cl ⁻ unless otherwise noted)	Organism	Impact	Author
10 mg/L	Benthic Invertebrates	Taxonomy shifts	Madden et al. (2007)
54 mg/L	Fen species	Decreased species richness, evenness, and abundance	Richburg et al. (2001)
81 mg/L	Benthic Invertebrates	Community Threshold	Wallace and Biastoch (2016)
33-108 mg/L	Fish	Community Threshold	Morgan et al. (2012)
100 mg/L	Soil microbes	Soil Respiration reduced, nitrification reduced	Groffman et al. (1995)
112 mg/L Na ⁺	Fen species (vegetation)	Decreased species richness, evenness, and abundance	Richburg et al. (2001)
600 mg/L NaCl	Daphnia	Decreased time integrated population densities	Searle et al. (2015)
1500 mg/L NaCl	Freshwater mussels	EC50	Roy et al. (2015)
1770	Daphnia	No young produced	Corsi et al. (2010)
1812 mg/L Cl (filtered stream water) 2042 mg/L Cl (lab water) 2421 mg/L NaCl	Daphnia Frogs	LC50 LC50	Gardner and Royer (2010) Jones et al. (2015)
2384 mg/L Road Salt			
2420 mg/L	Daphnia	Complete mortality	Corsi et al. (2010)
2505 mg/L	Fresh water mussels	EC50- clamping ability (clamping onto host fish required in order for mussels to be viable)	Beggel and Geist (2015)
5505 mg/L NaCl 5161 mg/L Road Salt	Salamanders	LC50	Jones et al. (2015)
Conductivity (uS/cm)			
968-3694	Frogs	Embryo survival decreased with increasing conductivity	Brand et al. (2010)
500-5000	Frogs	Low survival at high conductivity, free swimming embryos avoided higher concentrations	Dobbs et al. (2012)

Table 6. Road	Salt Impacts to	Riota with	Increasing	Concentrations
	San minuació n	\mathbf{D}	moreasme	

Land Cover/Land Use Type	POBR	MCDN	BARN	GFGB	GFGL
ISC (NLCD)					
2001	0%	0%	1%	16%	20%
2006	0%	0%	1%	17%	21%
2011	0%	0%	1%	17%	21%
Developed LC* (NLCD) ^a					
2001	0%	0%	25%	81%	79%
2006	0%	0%	25%	82%	79%
2011	0%	0%	25%	82%	79%
Forested LC* (NLCD) ^b					
2001	100%	20%	74%	18%	21%
2006	100%	20%	74%	17%	21%
2011	100%	20%	74%	17%	21%
Agricultural LC* (NLCD) ^c					
2001	0%	80%	1%	0.50%	0%
2006	0%	80%	1%	0%	0%
2011	0%	80%	1%	0%	0%
Tree Canopy Cover (NLCD) ^d					
2001	94%	17%	68%	26%	22%
2011	84%	23%	68%	30%	33%

Table 7: Land Cover Over Time in Study Watersheds

2001 Data: Homer et al. (2007) 2006 Data: Fry et al. (2011)

2011 Data: Homer et al. (2015) *LC = Land Cover

^a Developed land cover includes open space, low intensity, medium intensity, and high intensity development ^b Forested land cover includes deciduous forest, evergreen forest, mixed forest, and shrub/scrub

° Agricultural land cover includes pasture/hay and cultivated crops. Woody wetlands were not included in total percentages, but usually made up <1%. ^d Tree canopy cover was not analyzed for 2006.

Table 8: Site Information

					Tree	Developed	Impervious
Stream and			Watershed		Cover	Cover	Surfaces
Abbreviation	Abbreviation	Location ^a	Area ^a	Geology ^b	(2011) ^c	(2011) ^c	(2011) ^c
Pond Branch	POBR	N 39°28'49.1"	0.12 mi ²	100%	84%	0%	0%
		W 76°41'15.0"		Schist			
McDonogh Trib.	MCDN	N 39°24'01.6"	0.03 mi ²	100%	23%	0%	0%
		W 76°46'13.6"		Gneiss			
Baisman Run	BARN	N 39°28'46.1"	1.47 mi ²	100%	68%	25%	1%
		W 76°40'40.9"		Schist			
Gwynns Falls-	GFGB	N 39°26'34.6"	4.23 mi ²	100%	30%	82%	17%
Delight		W 76°47'00.3"		Schist			
Gwynns Falls-	GFGL	N 39°28'18.1"	0.32 mi ²	100%	33%	79%	21%
Glyndon		W 76°49'00.8"		Schist			
Beaver Run		N 39°29'22.0"	14.0 mi ²	100%	30%	20%	3%
		W 76°54'10.6		Schist			

Five watersheds in study and Beaver Run, a watershed monitored by the Moore Lab.

Beaver Run was used as an agricultural (46% Agricultural Land Cover) end point to calculate HCO₃⁻ concentrations to calculate charge balance error (Table 9).

^aNWIS (National Water Information System) (USGS, 2016).

^bCrowley and Cleaves (1974); Crowley et al. (1975); Crowley (1977); Reinhardt and Crowley (1979); Edwards Jr. (1993); Muller (1994)

Reported in Table 7, summarized in this table for 2011

Table 9: Calcium:Alkalinity (as HCO₃⁻) ratios

Site	Median Ca:Alk Ratio ^a	Inter-Quartile Range (IQR)
POBR	0.112	0.027
BARN	0.669	0.086
GFGB [♭]	0.671	0.060
Beaver Run ^c	0.655	0.076

^a Ca: Alk ratios measured as (umol/L)/(umol/L) by the Moore Lab (n=22).

^b Ca:Alk ratio for GFGB was also used for GFGL

^c Ca:Alk value for Beaver Run was used for MCDN (both have agricultural land cover)

10010 10										
	Total					Total Kept				
Stream	Samples	#2 Fail	#3 Fail	#4 Fail	Total Fail	(n)	% Kept			
POBR	109	2	2	2	6	103	94.4			
BARN	210	6	9	1	16	194	92.3			
MCDN	115	0	8	1	9	106	91			
GFGB	210	5	14	1	24	186	93.3			
GFGL	211	5	13	0	19	192	93.8			

Table 10: Failure criteria for quality control of the TU dataset

The quality control standards for the TU dataset had two criteria: Charge Balance Error (CBE) (#2), and BES v TU difference (#3). If a data point failed both criteria it was considered a #4 fail.

#2) CBE >15% (or 25% POBR) constituted a failure

#3) BES-TU data comparisons: >15% difference, or >1.5 ppm Cl⁻ and >2ppm SO₄²⁻ for data points <10ppm constituted a failure. The only caveat to these criteria were data with >250 ppm Cl⁻, which triggered an "AND" clause. When Cl⁻ data was >250ppm and >10x SO₄²⁻, Cl⁻ data was weighted more heavily, causing data to only be discarded if both Cl⁻ and SO₄²⁻ failed the BES v TU difference (Criteria #3).

Table 11: WRTDS WBT Results 1999-2014

Site	POBR	MCDN	BARN	GFGB	GFGL
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Cl ⁻ BES	0.49*1 (+0.21/-0.25)	1.69* (+0.42/-0.46)	17.3* (+4.8/-7.3)	88.7* (+23.9/-35.4)	56.4* (+33.2/-40.6)
Cl ⁻ TU	0.41*1 (+0.29/-0.37)	1.25* (+0.46/-0.44)	18.6* (+6.7/-8.1)	67.2*1 (+26.5/-65.0)	81.7*1 (+58.1/-68.0)
SO42- BES	-0.58* (+0.44/-0.25)	-2.97* (+1.21/-0.85)	-0.433 (+0.68/-0.54)	-0.831 (+1.11/-0.80)	-1.05 ³ (+2.03/-1.98)
SO42- TU	-0.68* (+0.63/-0.51)	-5.43* (+1.81/-1.27)	-0.51 (+0.73/-0.43)	-1.05*1 (+1.04/-1.14)	-1.71 ³ (+2.96/-2.89)
HCO3 ⁻ TU	4.74* (+3.42/-2.80)	3.95* (+2.08/-2.58)	3.68* (+1.31/-1.53)	19.6* (+4.00/-4.80)	30.3* (+29.3/-12.8)
Na ⁺ TU	0.13 (+0.13/-0.23)	-0.001*4 (+0.48/-0.6)	8.17* (+3.53/-3.73)	24.31 (+17.3/-27.0)	39.9 ¹ (+32.0/-40.5)
$K^+ TU$	0.181 (+0.21/-0.19)	0.311 (+0.23/-0.35)	0.68* (+0.29/-0.26)	0.95* (+0.36/-0.44)	0.29 ² (+0.24/-0.46)
$Mg^{2+} TU$	0.16*1 (+0.16/-0.14)	0.57* (+0.22/-0.36)	1.02* (+0.39/-0.70)	5.33* (+0.76/-0.83)	1.59 ² (+3.91/-2.23)
Ca ²⁺ TU	0.35* (+0.25/-0.24)	1.7* (+0.83/-1.22)	1.62* (+0.59/-0.76)	8.62* (+1.48/-2.23)	13.4* (+10.4/-6.67)

Trends are based on the WRTDS Bootstrap Tests (WBTs) conducted from 1999-2014. Annual flow-normalized concentrations are provided in Appendix B.

BARN (2000-2014) and MCDN (2001-2014) have different start dates from the rest of the watersheds in the dataset.

+/- indicate the size of the 95% confidence interval, based on the trend given by the WBT model.

Dataset indicated by BES (BES dataset) and TU (TU dataset)

*double sided p value <0.05, likelihood of trend direction >99.5% unless otherwise noted

¹ 95.5-98.5% likelihood of trend direction (highly likely)

² 90.6-91.6% likelihood of trend direction (very likely)

³ 69.8-90% likelihood of trend direction (likely)

⁴ 61.9% likelihood of trend direction (about as likely as not)

Table 12: Winter Exceedances of EPA Aquatic Life Criteria

Seasons	POBR		MCDN		BARN		GFGB		GFGL	
	chronic	acute								
Winters 1999-2004	0	0	0	0	0	0	12	4	17	3
Winters 2005-2009	0	0	0	0	1	0	14	5	11	2
Winters 2010-2014	0	0	0	0	0	0	14	3	15	2
Summer 2007 ^a	0	0	0	0	0	0	0	0	3	0

Number of times samples exceeded the chronic (230 mg/L) or acute (860 mg/L) Cl⁻concentrations set by the EPA (USEPA, 2014b). The time limits (4 days and 1 hour, respectively) are not reflected in these numbers, as samples were only collected once every 7 days. A winter (Winter X) is defined as Nov Year X – April Year Y.

^a Summer 2007 was an anomaly, no other seasons outside of winter experienced exceedances of the EPA biotic life limits.



Reference map for locations of study watersheds boundaries (yellow)(USGS, 2016). County line (black), and interstate (red) layers are from the Maryland GIS Database, (iMAP, 2016a; iMAP, 2016b). All watersheds are within Baltimore County, Maryland. Gwynns Falls watersheds are near I-795 in Owings Mills, MD, and Pond Branch and Baisman Run are near I-83 in Cockeysville, MD.



Impervious surfaces defined by polygon area in Baltimore County, MD (Baltimore County, 2002). Impervious surface data only available for 2002. ISC calculation: POBR 0%, MCDN 0%, BARN 3%, GFGB 19%, GFGL 20%.

Figure 3: NLCD Impervious Surface Cover



Impervious surface cover (ISC) data (raster) from the National Land Cover Database (NLCD) for 2011 (Homer et al., 2015). ISC changed <1% in all watersheds from 2001-2011 (Table 7).

Figure 4: NLCD Land Cover Map



Land cover data from the National Land Cover Database (NLCD) for 2011 (Homer et al., 2015). Land Cover changed <1% in all watersheds from 2001-2011 (Table 7).



Figure 5: 5-Year Boxplot Results BES and TU (Cl and SO₄²⁻)

BES and TU boxplots for chloride and sulfate along a forested-urban gradient (left to right). Median indicated by middle line, 25th-75th percentile of data within box (Inter quartile range- IQR), whiskers set at 4x IQR, outliers plotted as dots.

*Asterisks above boxplots for specific year groups indicates that the boxplot is statistically different (p<0.05) from the next group of years. Statistics provided in Table A1.



Figure 6: 5-Year Boxplot Results TU (Na⁺, Mg²⁺, Ca²⁺, HCO₃⁻, K⁺)

TU boxplots for cations and bicarbonate along a forested-urban gradient (left to right). Median indicated by middle line, 25th-75th percentile of data within box (Inter quartile range- IQR), whiskers set at 4x IQR, outliers plotted as dots.

*Asterisks above boxplots for specific year groups indicates that the boxplot is statistically different (p<0.05) from the next group of years. Statistics provided in Table A1.



Figure 7: Seasonal Boxplot Results BES and TU (Cl⁻ and SO₄²⁻)

BES and TU boxplots for chloride and sulfate along a forested-urban gradient (left to right) by season. Median indicated by middle line, 25th-75th percentile of data within box (Inter quartile range- IQR), whiskers set at 4x IQR, outliers plotted as dots. *Asterisks above boxplots for specific year groups indicates that the boxplot is statistically different (p<0.05) from the next group of years. Statistics provided in Table A2.



Figure 8: Seasonal Boxplot Results TU (Na⁺, Mg²⁺, HCO₃⁻, Ca²⁺, K⁺)

TU boxplots for cations and bicarbonate along a forested-urban gradient (left to right) by season. Median indicated by middle line, $25^{th}-75^{th}$ percentile of data within box (Inter quartile range- IQR), whiskers set at 4x IQR, outliers plotted as dots. *Asterisks above boxplots for specific year groups indicates that the boxplot is statistically different (p<0.05) from the next group of years. Statistics provided in Table A2.



Figure 9: WRTDS Results BES and TU (Cl⁻ and SO4²⁻)

BES and TU WRTDS analysis for chloride and sulfate, showing concentration change over the study period. Line represents flownormalized annual concentrations, dots represent annual mean concentrations, dotted lines represent a 95% confidence interval calculated by the WBT model (replicates = 100, block = 200). Both the BES and TU datasets were run for chloride and sulfate to note any biases from the smaller (TU) dataset.

Annual flow-normalized concentrations provided in Tables D1-4.



Figure 10: WRTDS Results TU (Na⁺, Mg²⁺, HCO₃⁻, Ca²⁺, K⁺)

TU WRTDS analysis for cations and bicarbonate, showing concentration change over the study period. Line represents flownormalized annual cooncentrations, dots represent annual mean concentrations, dotted lines represent a 95% confidence interval calculated by the WBT model (replicates = 100, block = 200). Annual flow-normalized concentrations provided in Tables D5-8.



Figure 11: Seasonal WRTDS Results (Cl⁻-POBR, MCDN, BARN)

WRTDS Seasonal Analysis for winter and summer seasons. Winter centered on February 15th, summer centered on August 15th. Discharge represents the median, 25th percentile, and 75th percentile of all daily discharge observed by the USGS during the study period. BES dataset used for analysis.



Figure 12: Seasonal WRTDS Results (Cl⁻-GFGB, GFGL)

WRTDS Seasonal Analysis for winter and summer seasons. Winter centered on February 15th, summer centered on August 15th. Discharge represents the median, 25th percentile, and 75th percentile of all daily discharge observed by the USGS during the study period. BES dataset used for analysis.



Figure 13: Seasonal WRTDS Results (Na⁺- POBR, BARN)

WRTDS Seasonal Analysis for winter and summer seasons. Winter centered on February 15th, summer centered on August 15th. Discharge represents the median, 25th percentile, and 75th percentile of all daily discharge observed by the USGS during the study period. TU dataset used for analysis.

MCDN not used in this analysis, there were not enough samples to satisfy the model parameters.



Figure 14: Seasonal WRTDS Results (Na⁺- POBR, BARN)

WRTDS Seasonal Analysis for winter and summer seasons. Winter centered on February 15th, summer centered on August 15th. Discharge represents the median, 25th percentile, and 75th percentile of all daily discharge observed by the USGS during the study period. TU dataset used for analysis.



Figure 15: 5-Year Boxplots (Ion Ratios)

TU boxplots for ion ratios along a forested-urban gradient (left to right) by season. Median indicated by middle line, 25th-75th percentile of data within box (Inter quartile range- IQR), whiskers set at 4x IQR, outliers plotted as dots.

*Asterisks above boxplots for specific year groups indicates that the boxplot is statistically different (p<0.05) from the next group of years. Statistics provided in Table A3.



Figure 16: Seasonal Boxplot Results (Ion Ratios)

TU boxplots for ion ratios along a forested-urban gradient (left to right) by season. Median indicated by middle line, 25th-75th percentile of data within box (Inter quartile range- IQR), whiskers set at 4x IQR, outliers plotted as dots.

*Asterisks above boxplots for specific year groups indicates that the boxplot is statistically different (p<0.05) from the next group of years. Statistics provided in Table A4.

Appendix A: Boxplot Results

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Ion	POBR		MCDN	5	BARN	/	GFGB		GFGL	
	Median	IQR								
BES Dataset										
Cl										
1999-2004	2.57*	0.43	4.53*	0.47	24.2*	4.48	36.7*	21.2	87.3*	30.8
2005-2009	2.76	0.37	4.99*	0.55	28.9*	9.70	60.8*	23	101*	35.8
2010-2014	2.75	0.33	5.60*	0.40	33.7*	6.85	86.8*	20.4	121*	39.1
SO4										
1999-2004	1.47*	1.21	17.1*	1.26	2.97	1.75	7.13	2.88	26.9	4.79
2005-2009	1.49*	0.94	15.3*	1.10	3.02	1.22	6.94	2.35	26.2	6.60
2010-2014	1.26*	0.92	14.4*	0.75	3.02	1.36	6.21*	2.18	26.3	7.00
TU Dataset										
Cl										
1999-2004	2.67*	0.66	4.68*	0.39	24.4*	3.49	37.1*	28.7	84.0	24.9
2005-2009	2.99	0.43	4.97*	0.53	27.4*	8.57	60.3*	22.6	97.8	51.4
2010-2014	3.12	0.58	5.92*	0.64	33.6*	9.13	83.9*	24.6	114*	41.7
SO4										
1999-2004	1.80	0.86	19.5*	1.89	3.18	1.79	7.94*	3.05	28.3*	3.63
2005-2009	1.60	1.01	16.0*	1.29	3.13	1.42	7.29*	2.53	27.0	5.41
2010-2014	1.90	1.07	15.1*	0.85	3.16	1.13	6.22*	1.72	27.0	6.71
НСО3										
1999-2004	9.91*	4.91	22.5*	2.54	12.8	2.63	45.0*	6.89	114	42.2
2005-2009	12.5	5.55	26.5	2.52	13.2	3.15	50.8*	9.53	115	58.5
2010-2014	11.3	4.53	25.8	1.40	13.8	2.91	59.6*	7.13	141*	51.9
Na										
1999-2004	2.11	0.31	7.97	0.83	10.1*	2.32	16.2*	15.9	25.7	10.9
2005-2009	2.00	0.36	8.15	0.46	12.2*	4.32	22.3*	9.75	28.0	19.7
2010-2014	2.06	0.23	8.06	1.00	14.0*	2.85	29.7*	10.4	34.7	30.0
K										
1999-2004	0.72*	0.29	1.46*	0.34	1.17*	0.52	1.86*	0.48	1.89*	0.62
2005-2009	0.84	0.24	1.91	0.54	1.60	0.58	2.61	0.53	2.45*	0.62
2010-2014	0.78	0.28	1.73	0.25	1.54	0.46	2.64	0.74	1.93*	0.58
Mg										
1999-2004	0.63*	0.20	4.17*	0.42	3.68	0.61	7.90*	1.26	25.3*	9.93
2005-2009	0.73	0.23	4.83	0.37	3.57	1.07	9.47*	1.73	21.5*	13.2
2010-2014	0.70	0.23	4.70	0.32	4.03*	0.70	11.9*	2.65	27.9*	15.9
Ca										
1999-2004	0.73*	0.36	9.69*	1.09	5.63	1.16	19.8*	3.04	50.5	18.6
2005-2009	0.92	0.41	11.4	1.08	5.82	1.38	22.4*	4.20	50.8	25.8
2010-2014	0.84	0.33	11.1	0.60	6.05	1.28	26.3*	3.14	62.1*	22.9

 Table A1: 5-Year Boxplot Statistics- Major Ions (Figures 5-6)

*Statistically different values (p <0.05)

Ratio	POBR		BARN	BARN			GFGL	
	Median	IQR	Median	IQR	Medain	IQR	Median	IQR
BES Dataset	(mg/L)							
Cl								
Non-Winter	2.72*	0.36	26.8*	9.07	54.0*	39.2	95.5*	40.1
Winter	2.65*	0.39	32.4*	11.4	87.9*	96.4	113*	89.7
SO4 ²⁻								
Non-Winter	1.09*	0.81	2.61*	1.13	6.03*	1.91	26.1*	6.70
Winter	1.87*	0.69	3.57*	0.97	8.37*	2.31	27.8*	5.00
TU Dataset	(mg/L)							
Cl								
Non-Winter	3.00	0.67	27.4*	8.86	56.0*	42.8	96.1*	45.9
Winter	2.92	0.63	30.8*	13.5	85.6*	63.9	103*	81.2
SO ₄ ²⁻								
Non-Winter	1.53*	1.10	2.85*	1.11	6.24*	1.61	27.3*	5.47
Winter	2.00*	0.62	3.75*	1.04	8.74*	2.61	29.0*	5.01
HCO3 ⁻								
Non-Winter	12.3*	5.83	13.5	2.93	50.2	14.5	131*	58.7
Winter	10.3*	4.26	12.9	2.85	50.9	14.7	115*	38.0
Na ⁺								
Non-Winter	2.11	0.26	11.8*	3.63	20.3*	12.9	25.3*	15.8
Winter	1.99	0.33	14.3*	7.37	41.2*	46.0	40.8*	51.6
\mathbf{K}^{+}								
Non-Winter	0.85*	0.32	1.54*	0.52	2.47*	0.75	2.08	0.75
Winter	0.71*	0.20	1.30*	0.59	2.15*	0.88	1.97	0.70
Mg^{2+}								
Non-Winter	0.7	0.21	3.85	0.83	9.22	3.83	26.8*	14.8
Winter	0.6	0.22	3.79	0.84	9.43	3.96	21.6*	11.1
Ca ²⁺								
Non-Winter	0.91	0.43	5.95	1.29	22.1	6.39	57.7*	25.9
Winter	0.76	0.31	5.68	1.25	22.4	6.47	50.7*	16.8

 Table A2: Seasonal Boxplot Statistics- Major Ions (Figures 7-8)

*Statistically different values (p <0.05)

Ratio	POBR		MCDN		BARN	BARN		GFGB		GFGL	
	Median	IQR									
Na:Cl											
1999-2004	1.20*	0.27	2.58	0.33	0.66	0.12	0.65	0.20	0.49	0.33	
2005-2009	1.03	0.17	2.50	0.31	0.67	0.10	0.57	0.16	0.57	0.31	
2010-2014	1.03	0.17	2.07*	0.39	0.68	0.09	0.57	0.13	0.56	0.39	
Ca:Cl											
1999-2004	0.25	0.14	1.78*	0.32	0.20	0.03	0.49	0.21	0.55	0.18	
2005-2009	0.29	0.10	2.04*	0.24	0.19	0.03	0.32	0.09	0.52	0.21	
2010-2014	0.25	0.10	1.68*	0.22	0.16	0.04	0.28	0.06	0.50	0.20	
Ca+Mg:Cl											
1999-2004	0.60	0.27	3.05*	0.44	0.42	0.06	0.81	0.36	0.97	0.24	
2005-2009	0.65	0.15	3.44*	0.36	0.37	0.06	0.55	0.13	0.87	0.38	
2010-2014	0.57	0.24	2.85*	0.38	0.34	0.08	0.49	0.09	0.87	0.38	
Ca:Na											
1999-2004	0.21*	0.10	0.71*	0.08	0.30	0.08	0.77	0.49	1.10	0.59	
2005-2009	0.27	0.12	0.80	0.03	0.29	0.07	0.59	0.24	0.95	0.82	
2010-2014	0.23	0.10	0.80	0.07	0.25	0.05	0.52	0.10	0.91	0.79	

Table A3: 5-Year Boxplot Statistics- Ion Ratios (Figure 15)

*Statistically different values (p < 0.05)

Table A4: Seasonal Boxplot Statistics- Ion Ratios (Figure 16)

Ratio	POBR		MCDN		BARN		GFGB		GFGL	
	Median	IQR	Median	IQR	Median	IQR	Medain	IQR	Median	IQR
Na:Cl										
Non-Winter	1.05	0.21	2.44	0.48	0.65*	0.09	0.56*	0.08	0.48*	0.31
Winter	1.07	0.24	2.40	0.39	0.72*	0.1	0.78*	0.33	0.69*	0.35
Ca:Cl										
Non-Winter	0.29*	0.12	1.88	0.35	0.19*	0.03	0.35*	0.19	0.55*	0.15
Winter	0.25*	0.1	1.80	0.39	0.16*	0.05	0.23*	0.14	0.4*	0.25
Ca+Mg:Cl										
Non-Winter	0.64	0.2	3.21	0.52	0.38*	0.07	0.58*	0.27	0.95*	0.22
Winter	0.56	0.19	3.08	0.58	0.34*	0.11	0.39*	0.26	0.71*	0.46
Ca:Na										
Non-Winter	0.24*	0.12	0.79	0.1	0.29*	0.06	0.61*	0.25	1.13*	0.73
Winter	0.20*	0.08	0.79	0.06	0.23*	0.1	0.29*	0.37	0.64*	0.63

*Statistically different values (p <0.05)

Appendix B: WRTDS Annual Flow-Normalized Concentrations

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Year	BES Flow- Normalized Concentraiton	TU Flow Normalized Concentration	BES Flow Normalized Concentration	TU Flow Normalized Concentration	Flow Normalized Concentration Difference	Flow Normalized Concentration Differnce
	Cl ⁻ (mg/L)	Cl ⁻ (mg/L)	SO4 ²⁻ (mg/L)	SO4 ²⁻ (mg/L)	% Cl-	% SO4 ²⁻
1999	2.4	2.7	1.9	2.1	-11.9%	-9.8%
2000	2.5	2.8	1.9	2.1	-11.3%	-8.9%
2001	2.5	2.8	1.9	2.0	-10.7%	-7.4%
2002	2.6	2.8	1.9	2.0	-10.2%	-6.5%
2003	2.6	2.9	1.8	1.9	-10.0%	-4.9%
2004	2.7	2.9	1.8	1.9	-9.1%	-4.4%
2005	2.7	2.9	1.8	1.8	-8.5%	-4.0%
2006	2.7	3.0	1.7	1.8	-8.0%	-3.5%
2007	2.8	3.0	1.7	1.8	-7.6%	-5.4%
2008	2.8	3.0	1.6	1.7	-7.9%	-6.2%
2009	2.8	3.0	1.6	1.7	-9.0%	-7.1%
2010	2.8	3.1	1.5	1.6	-9.7%	-7.9%
2011	2.8	3.1	1.5	1.6	-10.8%	-8.8%
2012	2.8	3.1	1.4	1.6	-11.5%	-9.1%
2013	2.8	3.1	1.4	1.5	-12.2%	-9.3%
2014	2.8	3.2	1.4	1.5	-13.7%	-10.3%

Table B1: BES and TU WRTDS Annual Flow Normalized Concentrations (Cl⁻ & SO₄²⁻, POBR)

Flow-normalized concentrations presented in Figure 9.

Table B2: BES and TU WRTDS Annual Flow Normalized Concentrations (Cl ⁻ & SO4 ²⁻ , B	ARN)
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Year	BES Flow- Normalized Concentraiton	TU Flow Normalized Concentration	BES Flow Normalized Concentration	TU Flow Normalized Concentration	Flow Normalized Concentration Difference	Flow Normalized Concentration Differnce
	Cl ⁻ (mg/L)	Cl ⁻ (mg/L)	SO4 ²⁻ (mg/L)	SO4 ²⁻ (mg/L)	% Cl-	% SO4 ²⁻
2000	23.1	22.9	3.3	3.4	0.9%	-3.0%
2001	24.0	23.6	3.3	3.4	1.7%	-2.7%
2002	24.9	24.4	3.3	3.4	2.0%	-2.4%
2003	26.0	25.3	3.3	3.4	2.7%	-1.8%
2004	27.1	26.2	3.3	3.4	3.3%	-1.8%
2005	28.3	27.3	3.3	3.4	3.5%	-1.5%
2006	29.6	28.6	3.3	3.4	3.4%	-1.5%
2007	30.8	29.9	3.3	3.3	2.9%	-2.2%
2008	31.8	31.1	3.2	3.3	2.2%	-2.8%
2009	33.1	32.6	3.1	3.2	1.5%	-2.6%
2010	34.4	34.2	3.1	3.2	0.6%	-2.3%
2011	35.9	35.9	3.0	3.1	0.0%	-1.6%
2012	37.3	37.7	3.0	3.0	-1.1%	-1.3%
2013	38.9	39.6	3.0	3.0	-1.8%	-1.4%
2014	40.4	41.5	2.9	2.9	-2.7%	-1.0%

Flow-normalized concentrations presented in Figure 9.
Year	BES Flow- Normalized Concentraiton	TU Flow Normalized Concentration	BES Flow Normalized Concentration	TU Flow Normalized Concentration	Flow Normalized Concentration Difference	Flow Normalized Concentration Differnce
	Cl ⁻ (mg/L)	Cl ⁻ (mg/L)	SO4 ²⁻ (mg/L)	SO4 ²⁻ (mg/L)	% Cl ⁻	% SO4 ²⁻
1999	43.0	44.4	7.6	7.8	-3.3%	-2.1%
2000	47.0	47.9	7.6	7.8	-1.9%	-2.6%
2001	51.3	51.7	7.5	7.8	-0.8%	-3.3%
2002	55.9	55.8	7.5	7.8	0.2%	-3.7%
2003	60.9	60.2	7.4	7.7	1.1%	-4.2%
2004	66.2	64.7	7.4	7.7	2.3%	-4.8%
2005	72.0	69.4	7.3	7.7	3.6%	-5.3%
2006	78.9	73.9	7.3	7.7	6.3%	-5.5%
2007	85.2	78.7	7.2	7.6	7.6%	-5.4%
2008	90.2	83.2	7.1	7.4	7.8%	-5.1%
2009	95.6	86.6	7.0	7.3	9.4%	-4.0%
2010	102.0	90.6	7.0	7.2	11.2%	-2.9%
2011	108.9	95.3	6.9	7.0	12.5%	-1.9%
2012	116.1	100.5	6.9	6.9	13.4%	-1.0%
2013	123.8	106.0	6.8	6.8	14.4%	-0.3%
2014	131.7	111.6	6.8	6.7	15.3%	0.6%

Table B3: BES and TU WRTDS Annual Flow Normalized Concentrations (Cl⁻ & SO₄²⁻, GFGB)

Flow-normalized concentrations presented in Figure 9.

Table B4: BES and TU WRTDS Annual Flow Normalized Concentrations (Cl⁻ & SO4²⁻, GFGL)

Year	BES Flow- Normalized Concentraiton	TU Flow Normalized Concentration	BES Flow Normalized Concentration	TU Flow Normalized Concentration	Flow Normalized Concentration Difference	Flow Normalized Concentration Differnce
	Cl ⁻ (mg/L)	Cl ⁻ (mg/L)	SO4 ²⁻ (mg/L)	SO4 ²⁻ (mg/L)	% Cl-	% SO4 ²⁻
1999	98.7	88.2	25.4	28.1	10.6%	-10.6%
2000	102.0	91.3	25.4	27.9	10.5%	-9.8%
2001	105.3	94.5	25.5	27.7	10.3%	-8.6%
2002	108.5	97.8	25.5	27.5	9.9%	-7.8%
2003	111.8	101.2	25.5	27.3	9.5%	-7.1%
2004	115.4	105.2	25.5	27.1	8.8%	-6.3%
2005	119.9	110.2	25.6	26.9	8.1%	-5.1%
2006	124.2	115.8	25.6	26.7	6.8%	-4.3%
2007	125.4	120.6	25.4	26.4	3.8%	-3.9%
2008	125.4	125.2	25.2	26.2	0.2%	-4.0%
2009	128.1	131.5	25.0	26.2	-2.7%	-4.8%
2010	132.2	138.1	24.8	26.2	-4.5%	-5.6%
2011	137.2	145.2	24.7	26.3	-5.8%	-6.5%
2012	142.6	152.8	24.5	26.3	-7.2%	-7.3%
2013	148.6	161.0	24.4	26.3	-8.3%	-7.8%
2014	155.1	169.9	24.3	26.4	-9.5%	-8.6%

Flow-normalized concentrations presented in Figure 9.

Year	TU Flow Normalized Concentration	TU Flow Normalized Concentration	TU Flow Normalized Concentration	TU Flow Normalized Concentration	TU Flow Normalized Concentration
	Na ⁺ (mg/L)	Mg ²⁺ (mg/L)	HCO ₃ ⁻ (mg/L)	Ca ²⁺ (mg/L)	K ⁺ (mg/L)
1999	2.02	0.621	9.85	0.727	0.764
2000	2.03	0.634	10.15	0.749	0.774
2001	2.04	0.646	10.45	0.771	0.786
2002	2.04	0.657	10.76	0.794	0.798
2003	2.05	0.669	11.09	0.818	0.808
2004	2.06	0.678	11.45	0.844	0.822
2005	2.06	0.689	11.78	0.869	0.836
2006	2.07	0.701	12.15	0.897	0.853
2007	2.07	0.707	12.58	0.928	0.869
2008	2.08	0.715	12.89	0.951	0.879
2009	2.09	0.723	13.14	0.97	0.891
2010	2.09	0.734	13.42	0.99	0.902
2011	2.1	0.744	13.71	1.011	0.914
2012	2.11	0.755	14	1.033	0.925
2013	2.12	0.766	14.29	1.054	0.937
2014	2.13	0.778	14.59	1.077	0.948

 Table B5: TU WRTDS Annual Flow Normalized Concentrations (POBR)

Flow-normalized concentrations presented in Figure 10.

Table B6: IU WRIDS Annual Flow Normalized Concent	trations	(BARN))
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Year	TU Flow Normalized Concentration	TU Flow Normalized Concentration	TU Flow Normalized	TU Flow Normalized Concentration	TU Flow Normalized Concentration
	Na ⁺ (mg/L)	Mg^{2+} (mg/L)	HCO ₃ ⁻ (mg/L)	Ca^{2+} (mg/L)	K ⁺ (mg/L)
2000	10	3.39	11.8	5.18	1.02
2001	10.3	3.42	12	5.27	1.07
2002	10.6	3.47	12.2	5.36	1.13
2003	11	3.51	12.4	5.46	1.2
2004	11.4	3.57	12.7	5.58	1.27
2005	11.9	3.64	13	5.71	1.34
2006	12.4	3.71	13.3	5.84	1.42
2007	13	3.77	13.5	5.95	1.5
2008	13.6	3.84	13.8	6.05	1.57
2009	14.2	3.92	14	6.16	1.61
2010	14.9	4.01	14.3	6.29	1.64
2011	15.7	4.11	14.6	6.42	1.66
2012	16.5	4.21	14.9	6.55	1.68
2013	17.3	4.31	15.2	6.68	1.69
2014	18.2	4.4	15.5	6.8	1.7

Flow-normalized concentrations presented in Figure 10.

Year	TU Flow Normalized Concentration				
	Na ⁺ (mg/L)	Mg^{2+} (mg/L)	HCO_3^- (mg/L)	Ca^{2+} (mg/L)	K ⁺ (mg/L)
1999	22.4	6.89	41.3	18.2	1.79
2000	24	7.17	42.3	18.6	1.86
2001	25.8	7.45	43.3	19.1	1.93
2002	27.6	7.75	44.2	19.5	2.01
2003	29.6	8.05	45.2	19.9	2.09
2004	31.6	8.36	46.2	20.4	2.17
2005	33.6	8.68	47.2	20.8	2.25
2006	35.1	9.01	48.4	21.3	2.34
2007	36.5	9.36	49.6	21.9	2.43
2008	37.8	9.71	51	22.5	2.5
2009	38.6	10.08	52.4	23.1	2.54
2010	39.7	10.47	53.9	23.8	2.58
2011	41.3	10.88	55.5	24.5	2.62
2012	43	11.3	57.2	25.2	2.66
2013	44.9	11.75	59	26	2.7
2014	46.7	12.22	60.9	26.8	2.74

 Table B7: TU WRTDS Annual Flow Normalized Concentrations (GFGB)

Flow-normalized concentrations presented in Figure 10.

Table B8: TU WRTDS Annual Flow Normalized Concentrations (GFGL)

Year	TU Flow Normalized Concentration	TU Flow Normalized Concentration	TU Flow Normalized Concentration	TU Flow Normalized Concentration	TU Flow Normalized Concentration
	Na ⁺ (mg/L)	Mg^{2+} (mg/L)	HCO ₃ ⁻ (mg/L)	Ca ²⁺ (mg/L)	K ⁺ (mg/L)
1999	31.2	25.5	113	49.8	1.83
2000	32.7	24.9	114	50.2	1.9
2001	34.2	24.4	115	50.6	1.98
2002	35.9	23.9	116	51	2.06
2003	37.6	23.4	117	51.5	2.14
2004	39.7	23	118	52.1	2.23
2005	42.4	22.8	120	53	2.32
2006	45.3	22.6	122	53.7	2.41
2007	47.9	22.7	122	54	2.46
2008	50.3	23	123	54.4	2.44
2009	53.2	23.5	126	55.6	2.38
2010	56.4	24.1	129	56.8	2.33
2011	59.8	24.8	132	58.2	2.28
2012	63.3	25.4	135	59.7	2.23
2013	67.1	26.2	139	61.4	2.17
2014	71.1	27.1	143	63.2	2.12

Flow-normalized concentrations presented in Figure 10.

Appendix C: McDonogh Tributary (MCDN) Results

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Figure C1: McDonogh Tributary (MCDN) Major Ion Concentrations 2001-2014

BES (Cl and SO4) and TU (Na, K, Ca, Mg, HCO3) WRTDS analysis for MCDN, showing concentration change over study period. Line represents flow-normalized annual concentrations, dots represent annual mean concentrations, dotted lines represent a 95% confidence interval calculated by the WBT model (replicates = 100, block = 200).

Year	BES Flow- Normalized Concentraiton	TU Flow Normalized Concentration	BES Flow Normalized Concentration	TU Flow Normalized Concentration	Flow Normalized Concentration Difference	Flow Normalized Concentration Differnce
	Cl ⁻ (mg/L)	Cl ⁻ (mg/L)	SO4 ²⁻ (mg/L)	SO4 ²⁻ (mg/L)	% Cl-	% SO4 ²⁻
2001	4.5	4.7	16.9	20.0	-5.2%	-18.3%
2002	4.6	4.8	16.6	19.4	-4.8%	-16.9%
2003	4.6	4.9	16.4	18.9	-5.0%	-15.2%
2004	4.7	4.9	16.1	18.4	-4.4%	-14.3%
2005	4.8	5.0	15.8	18.0	-4.1%	-13.9%
2006	4.9	5.1	15.6	17.5	-3.4%	-12.2%
2007	5.1	5.2	15.3	17.0	-2.6%	-11.1%
2008	5.2	5.3	15.1	16.6	-1.7%	-9.9%
2009	5.4	5.4	14.9	16.2	-0.7%	-8.7%
2010	5.5	5.5	14.7	15.9	0.4%	-8.2%
2011	5.7	5.6	14.5	15.5	1.2%	-6.9%
2012	5.8	5.7	14.3	15.2	2.1%	-6.3%
2013	6.0	5.8	14.1	14.8	2.8%	-5.0%
2014	6.2	6.0	13.9	14.5	3.4%	-4.3%

Table C1: BES and TU WRTDS Annual Flow Normalized Concentrations (Cl⁻ and SO₄²⁻)

Flow-normalized concentrations presented in Figure 9.

Year	TU Flow Normalized Concentration	TU Flow Normalized Concentration	TU Flow Normalized Concentration	TU Flow Normalized Concentration	TU Flow Normalized Concentration
	Na+ (mg/L)	Mg ²⁺ (mg/L)	HCO ₃ ⁻ (mg/L)	Ca ²⁺ (mg/L)	K ⁺ (mg/L)
2001	7.93	4.3	23.2	10	1.58
2002	7.94	4.36	23.6	10.2	1.61
2003	7.95	4.42	24	10.3	1.64
2004	7.96	4.48	24.5	10.5	1.66
2005	7.97	4.54	24.9	10.7	1.69
2006	7.99	4.6	25.3	10.9	1.72
2007	8	4.66	25.7	11.1	1.75
2008	7.99	4.69	26	11.2	1.77
2009	7.98	4.72	26.1	11.2	1.78
2010	7.97	4.74	26.3	11.3	1.8
2011	7.96	4.77	26.5	11.4	1.82
2012	7.94	4.8	26.7	11.5	1.84
2013	7.94	4.84	27	11.6	1.86
2014	7.93	4.87	27.2	11.7	1.88

Table C2: TU Annual Flow Normalized Concentrations (Na⁺, Mg²⁺, HCO₃⁻, Ca²⁺, K⁺)

Flow-normalized concentrations presented in Figure 10.

 Table C3: Annual Boxplot Statistics (Na⁺, MCDN)

		-		
	Lower		Upper	Inter-Quartile
Year	Quartile	Median	Quartile	Range (IQR)
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
2000	7.3	7.7	7.9	0.6
2001	7.8	8.3	8.4	0.6
2002	8.1	8.2	8.5	0.4
2003	7.1	7.1	7.1	0.0
2004	7.5	8.0	8.1	0.6
2005	7.3	7.5	8.0	0.7
2006	8.0	8.2	8.5	0.5
2007	8.2	8.4	8.7	0.5
2008	8.0	8.3	8.4	0.5
2009	7.5	7.9	8.0	0.5
2010	7.1	7.9	8.2	1.1
2011	8.4	8.5	8.6	0.2
2012	8.2	8.3	8.4	0.2
2013	7.8	7.9	8.2	0.3
2014	7.1	7.2	7.3	0.2

Boxplots summarized by 5-Year Groups, Table A1.

	Lower		Upper	Inter-Quartile
Year	Quartile	Median	Quartile	Range (IQR)
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
2000	3.9	3.9	4.1	0.2
2001	3.9	4.0	4.1	0.2
2002	4.2	4.7	5.0	0.8
2003	4.9	4.9	4.9	0.0
2004	4.2	4.3	4.4	0.2
2005	4.3	4.5	4.7	0.3
2006	4.7	4.9	5.0	0.2
2007	4.9	5.0	5.2	0.4
2008	4.7	4.7	4.8	0.1
2009	4.7	4.8	4.9	0.3
2010	4.7	4.8	4.9	0.2
2011	5.0	5.0	5.1	0.1
2012	4.7	4.7	4.8	0.1
2013	4.5	4.5	4.6	0.1
2014	4.5	4.6	4.6	0.1
D 1	11 5 11	G T 11		

 Table C4: Annual Boxplot Statistics (Mg²⁺, MCDN)

Boxplots summarized by 5-Year Groups, Table A1.

Table C5: Annual Boxplot Statistics (HCO3⁻, MCDN)

	Lower		Upper	Inter-Quartile
Year	Quartile	Median	Quartile	Range (IQR)
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
2000	20.8	21.4	21.7	0.9
2001	20.9	21.0	21.7	0.8
2002	22.5	24.6	25.9	3.3
2003	28.9	28.9	28.9	0.0
2004	23.4	23.4	24.1	0.7
2005	23.5	24.3	25.2	1.7
2006	25.6	26.0	27.0	1.5
2007	26.6	27.8	29.3	2.7
2008	27.1	27.5	28.1	1.0
2009	26.6	27.2	28.0	1.4
2010	26.0	26.0	26.8	0.9
2011	27.6	27.8	29.1	1.5
2012	25.4	25.7	26.4	1.0
2013	25.5	25.5	25.6	0.1
2014	24.5	25.0	25.8	1.3

201424.525.025.8Boxplots summarized by 5-Year Groups, Table A1.

Table C6: Annual Boxplot Statistics (Ca²⁺, MCDN)

	Lower		Upper	Inter-Quartile
Year	Quartile	Median	Quartile	Range (IQR)
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
2000	8.9	9.2	9.4	0.4
2001	9.0	9.0	9.3	0.3
2002	9.7	10.6	11.1	1.4
2003	12.4	12.4	12.4	0.0
2004	10.0	10.1	10.3	0.3
2005	10.1	10.5	10.8	0.7
2006	11.0	11.2	11.6	0.6
2007	11.4	11.9	12.6	1.2
2008	11.7	11.8	12.1	0.4
2009	11.4	11.7	12.0	0.6
2010	11.2	11.2	11.5	0.4
2011	11.9	12.0	12.5	0.6
2012	10.9	11.0	11.3	0.4
2013	10.9	11.0	11.0	0.1
2014	10.5	10.8	11.1	0.6

Boxplots summarized by 5-Year Groups, Table A1.

	Lower		Upper	Inter-Quartile
Year	Quartile	Median	Quartile	Range (IQR)
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
2000	1.5	1.7	1.8	0.3
2001	1.3	1.3	1.4	0.2
2002	0.8	1.6	1.7	0.9
2003	1.9	1.9	1.9	0.0
2004	1.4	1.4	1.5	0.2
2005	1.5	1.5	1.8	0.3
2006	1.9	2.0	2.2	0.2
2007	1.1	1.3	1.6	0.4
2008	1.9	1.9	2.0	0.1
2009	2.1	2.2	2.3	0.2
2010	1.7	1.8	1.9	0.2
2011	2.0	2.1	2.1	0.1
2012	1.5	1.5	1.6	0.1
2013	1.6	1.7	1.7	0.1
2014	1.7	1.7	1.8	0.1

 Table C7: Annual Boxplot Statistics (K⁺, MCDN)

Boxplots summarized by 5-Year Groups, Table A1.

Appendix D: BES v TU Concentrations (Cl⁻ & SO₄²⁻)

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Figure D1: BES Dataset v TU Dataset Chloride Plots

Each plot contains a 1:1 line, and +/- 15% or +/- 1.5 mg/L (<10 mg/L). Plot symbols based on TU data quality criteria, described in Section 2.5 and Table 10. Zoomed in plots are provided in Figure A6.



Figure D2: BES Dataset v TU Dataset Chloride Plots (Alternate Axes)

Each plot contains a 1:1 line, and +/- 15% or +/- 1.5 mg/L (<10 mg/L). Plot symbols based on TU data quality criteria, described in Section 2.5 and Table 10.



Figure D3: BES Dataset v TU Dataset Sulfate Plots

Each plot contains a 1:1 line, and +/- 15% or +/- 1.5 mg/L (<10 mg/L). Plot symbols based on TU data quality criteria, described in Section 2.5 and Table 10.

Appendix E: Comparisons of Boxplots Statistics for BES and TU (Cl⁻ & SO₄²⁻)

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	POBR	MCDN	BARN	GFGB	GFGL	
Cl						
Average Difference BES v TU Boxplot Medians	-8.28%	-3.04%	-0.96%	-5.02%	-0.87%	
SO ₄ ²⁻						
Average Difference BES v TU Boxplot Medians	-25.16% ^a (-0.3 mg/L)	-10.87% ^b	-7.59%	-7.93%	-4.81%	

Table E1: Average differences between BES and TU annual boxplot medians

Figures E 1-4 have all Cl⁻ and SO₄²⁻ boxplots for TU and BES Negative percentage indicates that TU dataset median concentrations were greater than BES dataset median concentrations. ^aAll medians within 1 mg/L, average -0.3 mg/L (Table A-7) ^b2000-2004 medians within 7.3 mg/L, average -3.8 mg/L; 2005-2014 medians within 2 mg/L, average -0.8 mg/L

Year	BES Lower Quartile	BES median	BES Upper Quartile	TU Lower Quartile	TU median	TU Upper Quartile	BES and TU Median Difference	BES and TU Median Difference
	Cl ⁻ (mg/L)	%						
1998	2.32	2.39	2.46	2.56	2.56	2.56	-0.17	-6.95%
1999	2.24	2.46	2.68	3.00	3.10	3.20	-0.64	-26.01%
2000	2.33	2.46	2.63	2.31	2.88	2.98	-0.42	-16.90%
2001	2.40	2.59	2.88	2.53	2.64	2.86	-0.05	-2.06%
2002	2.13	2.49	2.83	2.26	2.60	3.02	-0.11	-4.52%
2003	2.36	2.58	2.78	2.41	3.15	3.88	-0.57	-22.28%
2004	2.67	2.76	2.85	2.12	2.55	3.15	0.21	7.54%
2005	2.45	2.52	2.65	2.62	2.73	3.09	-0.21	-8.45%
2006	2.54	2.60	2.71	3.10	3.26	3.48	-0.66	-25.25%
2007	2.69	2.82	2.96	2.97	3.02	3.30	-0.20	-7.09%
2008	2.72	2.85	3.00	2.85	2.96	3.08	-0.11	-3.96%
2009	2.89	2.98	3.12	2.58	2.70	2.85	0.28	9.38%
2010	2.79	2.95	3.07	3.12	3.25	3.41	-0.30	-10.28%
2011	2.67	2.77	2.91	2.53	2.71	2.89	0.06	2.12%
2012	2.59	2.77	2.89	2.82	3.08	3.41	-0.31	-11.28%
2013	2.48	2.62	2.75	2.47	2.71	2.73	-0.09	-3.63%
2014	2.49	2.66	2.76	2.73	2.96	3.41	-0.30	-11.21%

Table E2: BES and TU Annual Boxplot Statistics (Chloride, POBR)

Figure E1 has all Cl⁻ boxplots for TU and BES at POBR

Negative values indicates that TU dataset median concentrations were greater than BES dataset median concentrations.

			1	· · · · · · · · · · · · · · · · · · ·	,	/		
Year	BES Lower Quartile	BES median	BES Upper Quartile	TU Lower Quartile	TU median	TU Upper Quartile	BES and TU Median Difference	BES and TU Median Difference
	Cl ⁻ (mg/L)	Cl ⁻ (mg/L)	Cl ⁻ (mg/L)	Cl ⁻ (mg/L)	Cl ⁻ (mg/L)	Cl ⁻ (mg/L)	Cl ⁻ (mg/L)	%
1999	4.38	4.47	4.62	NA	NA	NA	NA	NA
2000	4.30	4.49	4.75	4.43	4.74	4.78	-0.25	-5.65%
2001	4.34	4.50	4.62	4.61	4.85	5.13	-0.36	-7.96%
2002	3.98	4.44	4.84	4.68	4.75	5.81	-0.31	-7.02%
2003	4.29	4.54	4.95	5.49	5.49	5.49	-0.95	-21.03%
2004	4.52	4.68	4.80	4.33	4.62	4.66	0.06	1.31%
2005	4.47	4.67	4.79	4.52	4.64	4.68	0.03	0.67%
2006	4.69	4.82	5.07	5.21	5.29	5.69	-0.47	-9.72%
2007	4.97	5.09	5.38	4.58	4.88	5.16	0.21	4.07%
2008	4.93	5.12	5.27	4.70	4.91	5.17	0.21	4.10%
2009	5.32	5.50	5.67	5.04	5.09	5.15	0.41	7.42%
2010	5.41	5.53	5.68	6.05	6.24	6.44	-0.71	-12.78%
2011	5.34	5.49	5.80	5.35	5.41	5.42	0.07	1.32%
2012	5.42	5.58	5.78	5.30	5.40	5.71	0.18	3.21%
2013	5.46	5.66	5.83	5.55	5.65	5.95	0.01	0.10%
2014	5.60	5.80	6.14	5.93	6.06	6.17	-0.26	-4.49%

Table E3: BES and TU Annual Boxplot Statistics (Chloride, MCDN)

Figure E1 has all Cl⁻ boxplots for TU and BES at MCDN Negative values indicates that TU dataset median concentrations were greater than BES dataset median concentrations.

Year	BES Lower Quartile	BES median	BES Upper Quartile	TU Lower Quartile	TU median	TU Upper Quartile	BES and TU Median Difference	BES and TU Median Difference
	Cl ⁻ (mg/L)	%						
1998	19.27	19.38	19.68	NA	NA	NA	NA	NA
1999	22.12	23.68	26.01	26.92	30.26	30.29	-6.58	-27.79%
2000	18.68	20.43	22.59	18.18	21.71	23.16	-1.28	-6.27%
2001	23.60	24.11	26.04	23.68	24.41	26.27	-0.30	-1.25%
2002	23.93	25.21	25.99	24.85	26.39	29.06	-1.18	-4.69%
2003	25.35	27.90	29.72	23.95	26.34	29.24	1.56	5.60%
2004	22.35	24.40	25.40	21.93	24.26	24.50	0.14	0.56%
2005	22.70	24.20	27.30	22.38	23.73	25.22	0.47	1.92%
2006	26.20	27.80	29.00	24.13	25.70	27.65	2.10	7.55%
2007	24.90	26.20	29.70	26.44	27.27	29.81	-1.07	-4.07%
2008	33.15	36.20	38.45	30.52	34.05	35.77	2.15	5.93%
2009	31.20	35.40	40.45	32.76	34.49	44.91	0.91	2.57%
2010	29.50	32.70	35.10	30.10	33.76	35.23	-1.06	-3.26%
2011	36.70	41.20	43.00	41.08	44.65	52.97	-3.45	-8.38%
2012	31.60	33.15	34.20	29.37	30.74	32.90	2.41	7.27%
2013	29.50	31.40	34.00	27.56	29.89	32.48	1.51	4.82%
2014	32.70	38.00	46.40	33.97	36.46	45.93	1.54	4.06%

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Figure E1 has all Cl⁻ boxplots for TU and BES at BARN

Negative values indicates that TU dataset median concentrations were greater than BES dataset median concentrations.

Year	BES Lower Quartile	BES median	BES Upper Quartile	TU Lower Quartile	TU median	TU Upper Quartile	BES and TU Median Difference	BES and TU Median Difference
	Cl ⁻ (mg/L)	%						
1998	24.14	24.53	24.58	22.94	24.36	25.78	0.17	0.70%
1999	25.04	28.86	37.76	28.53	30.97	37.10	-2.11	-7.30%
2000	26.35	29.54	33.80	29.63	32.21	36.98	-2.67	-9.03%
2001	30.79	33.88	46.01	31.48	56.29	111.5	-22.41	-66.16%
2002	31.96	35.90	42.01	34.47	37.24	56.06	-1.34	-3.73%
2003	44.40	48.40	54.47	36.00	44.72	84.28	3.68	7.60%
2004	47.45	49.95	55.00	46.07	49.93	53.92	0.02	0.04%
2005	51.15	54.95	71.55	45.48	58.01	80.56	-3.06	-5.56%
2006	53.00	55.90	59.20	46.70	55.84	57.10	0.06	0.11%
2007	56.35	59.95	74.05	54.58	82.42	225.8	-22.47	-37.49%
2008	60.50	68.40	79.20	55.64	62.14	69.05	6.26	9.15%
2009	68.35	76.20	94.65	69.64	71.88	77.88	4.32	5.67%
2010	73.00	81.10	90.80	62.29	71.46	83.89	9.64	11.88%
2011	77.60	89.00	94.80	83.62	89.39	121.3	-0.39	-0.44%
2012	73.30	83.55	87.50	76.82	82.58	86.65	0.97	1.16%
2013	85.20	88.70	94.10	79.78	83.60	86.52	5.10	5.75%
2014	74.70	103.0	139.0	83.09	100.6	111.6	2.43	2.36%

Table E5: BES and TU Annual Boxplot Statistics (Chloride, GFGB)

Figure E2 has all Cl⁻ boxplots for TU and BES at GFGB Negative values indicates that TU dataset median concentrations were greater than BES dataset median concentrations.

TADIE F.O. BES and IU Annual Boxplot Statistics (Unioride, GFU	Table	le E6: 1	BES	and TU	Annual	Boxplot	Statistics	(Chloride.	GFGI
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			1	<pre></pre>	,	,		
Year	BES Lower Quartile	BES median	BES Upper Quartile	TU Lower Quartile	TU median	TU Upper Quartile	BES and TU Median Difference	BES and TU Median Difference
	Cl ⁻ (mg/L)	%						
1998	105.7	109.3	115.3	117.3	121.3	125.2	-11.97	-10.95%
1999	62.52	73.29	91.00	67.12	77.47	93.43	-4.18	-5.70%
2000	62.32	72.54	79.45	75.35	80.98	93.13	-8.44	-11.64%
2001	82.61	88.94	97.71	78.32	83.14	89.15	5.80	6.52%
2002	69.89	78.59	92.73	72.15	88.52	98.24	-9.94	-12.65%
2003	77.86	99.83	117.0	63.80	115.0	133.4	-15.20	-15.22%
2004	88.15	99.80	105.5	82.86	97.44	103.8	2.36	2.36%
2005	92.60	107.5	136.5	81.70	98.90	134.1	8.60	8.00%
2006	52.85	70.00	92.90	49.68	63.51	82.14	6.49	9.27%
2007	83.85	109.0	134.5	67.08	108.8	129.1	0.24	0.22%
2008	88.90	107.0	117.0	97.17	106.2	120.2	0.79	0.74%
2009	98.90	106.0	118.0	97.45	104.4	111.9	1.58	1.49%
2010	101.0	123.0	136.0	104.7	120.2	131.8	2.81	2.28%
2011	89.15	113.0	137.0	82.99	115.7	182.9	-2.71	-2.40%
2012	96.30	110.0	118.0	72.59	105.8	116.5	4.22	3.84%
2013	111.0	125.5	138.0	96.11	106.0	125.6	19.47	15.51%
2014	108.3	140.0	184.5	117.5	149.0	182.7	-9.01	-6.43%

Figure E2 has all Cl⁻ boxplots for TU and BES at GFGL Negative values indicates that TU dataset median concentrations were greater than BES dataset median concentrations.

Year	BES Lower Quartile	BES median	BES Upper Quartile	TU Lower Quartile	TU median	TU Upper Quartile	BES and TU Median Difference	BES and TU Median Difference
	SO4 ²⁻ (mg/L)	%						
1998	0.86	0.91	1.03	1.00	1.00	1.00	-0.10	-10.67%
1999	0.98	1.60	2.33	2.00	2.56	3.27	-0.96	-60.41%
2000	0.99	1.44	1.96	1.66	2.22	2.35	-0.78	-54.00%
2001	0.86	1.15	1.70	1.41	1.58	2.00	-0.43	-37.72%
2002	1.25	1.62	2.97	1.61	1.80	2.07	-0.18	-11.21%
2003	1.37	2.37	3.40	2.28	2.28	2.28	0.09	3.63%
2004	1.15	1.54	2.11	1.09	1.23	1.75	0.31	20.22%
2005	0.99	1.45	1.98	0.98	1.54	1.71	-0.09	-6.48%
2006	1.00	1.49	1.74	1.23	1.80	2.26	-0.31	-20.81%
2007	0.80	1.44	1.76	1.18	1.57	1.86	-0.13	-8.84%
2008	0.88	1.50	1.89	1.40	2.10	2.25	-0.60	-39.77%
2009	0.85	1.68	2.10	1.53	1.87	2.15	-0.19	-11.43%
2010	0.78	1.11	2.04	1.11	1.94	2.21	-0.83	-74.86%
2011	0.88	1.16	1.76	1.00	1.50	2.00	-0.34	-29.37%
2012	0.89	1.21	1.59	1.13	1.48	1.90	-0.27	-22.06%
2013	0.85	1.24	1.75	1.13	1.67	1.89	-0.43	-34.73%
2014	1.00	1.65	2.05	1.90	2.13	2.52	-0.48	-29.22%

Table E7: BES and TU Annual Boxplot Statistics (Sulfate, POBR)

Figure E3 has all SO_4^{2-} boxplots for TU and BES at POBR

Jegative values indicates that TU dataset median concentrations were greater than BES dataset median concentrations

Year	BES Lower Quartile	BES median	BES Upper Quartile	TU Lower Quartile	TU median	TU Upper Quartile	BES and TU Median Difference	BES and TU Median Difference
	SO4 ²⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	SO4 ²⁻ (mg/L)	SO4 ²⁻ (mg/L)	SO4 ²⁻ (mg/L)	%
1999	17.68	17.79	17.86	NA	NA	NA	NA	NA
2000	16.34	16.91	17.51	18.78	18.92	19.41	-2.01	-11.89%
2001	17.18	17.46	17.68	19.87	20.32	20.76	-2.87	-16.42%
2002	17.44	18.38	20.61	20.85	22.59	23.67	-4.21	-22.88%
2003	15.10	16.48	17.52	23.79	23.79	23.79	-7.31	-44.36%
2004	16.00	16.40	16.75	16.62	18.87	19.38	-2.47	-15.06%
2005	15.45	16.00	16.70	16.51	16.76	17.72	-0.76	-4.74%
2006	15.40	16.00	16.70	15.49	16.28	16.52	-0.28	-1.73%
2007	14.60	14.90	15.30	14.42	15.22	15.71	-0.32	-2.15%
2008	14.80	15.30	15.80	14.96	15.45	16.88	-0.15	-1.01%
2009	14.50	14.75	14.90	15.77	15.86	16.30	-1.11	-7.51%
2010	13.90	14.70	15.45	15.13	16.72	16.97	-2.02	-13.72%
2011	14.30	14.60	15.00	15.13	15.20	15.82	-0.60	-4.10%
2012	14.20	14.40	14.80	14.65	14.98	15.52	-0.58	-4.03%
2013	14.20	14.40	14.60	14.86	15.06	15.16	-0.66	-4.57%
2014	13.40	13.70	14.00	14.51	14.91	15.02	-1.21	-8.85%

Figure E3 has all $SO_4^{2^\circ}$ boxplots for TU and BES at MCDN Negative values indicates that TU dataset median concentrations were greater than BES dataset median concentrations.

Year	BES Lower Quartile	BES median	BES Upper Quartile	TU Lower Quartile	TU median	TU Upper Quartile	BES and TU Median Difference	BES and TU Median Difference
	SO4 ²⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	SO4 ²⁻ (mg/L)	%				
1998	1.82	1.88	2.08	NA	NA	NA	NA	NA
1999	2.47	3.17	3.84	3.41	3.51	4.13	-0.34	-10.87%
2000	2.10	2.72	3.47	2.85	3.45	4.33	-0.73	-26.89%
2001	1.94	2.36	3.02	2.17	2.46	2.97	-0.10	-4.34%
2002	2.10	2.38	3.59	2.22	2.50	4.47	-0.12	-4.94%
2003	4.24	4.90	5.59	3.87	4.42	5.57	0.48	9.78%
2004	2.54	3.13	3.90	2.53	2.71	3.60	0.42	13.31%
2005	2.42	3.03	3.68	2.41	2.96	3.98	0.07	2.24%
2006	2.67	3.09	3.76	2.72	3.54	4.21	-0.45	-14.58%
2007	1.96	2.55	3.58	2.27	3.49	4.10	-0.94	-37.10%
2008	2.34	2.67	3.35	2.34	2.83	3.22	-0.16	-5.90%
2009	2.49	3.31	3.96	2.95	3.28	3.82	0.03	0.96%
2010	2.08	2.62	3.79	2.53	3.56	4.64	-0.94	-35.89%
2011	2.49	3.11	3.69	3.01	3.26	3.79	-0.15	-4.89%
2012	2.44	3.00	3.30	2.74	3.08	3.38	-0.08	-2.81%
2013	2.18	2.81	3.61	2.34	2.96	3.68	-0.15	-5.24%
2014	2.61	3.36	4.02	2.73	3.17	3.75	0.19	5.68%

Table E9: BES and TU Annual Boxplot Statistics (Sulfate, BARN)

Figure E3 has all SO4²⁵ boxplots for TU and BES at BARN

Figure E3 has all SO_4^{2-} boxplots for TU and BES at BARN
Negative values indicates that TU dataset median concentrations were greater than BES dataset median concentrations.
Table E10: BES and TU Annual Boxplot Statistics (Sulfate, GFGB)

Year	BES Lower Quartile	BES median	BES Upper Quartile	TU Lower Quartile	TU median	TU Upper Quartile	BES and TU Median Difference	BES and TU Median Difference
	SO ₄ ²⁻ (mg/L)	SO4 ²⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	SO4 ²⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	%
1998	4.77	4.91	5.23	4.66	4.95	5.25	-4.91	-0.99%
1999	6.19	7.96	9.68	6.48	8.71	10.03	-7.96	-9.47%
2000	5.85	6.86	7.78	6.10	6.53	7.89	-6.86	4.78%
2001	4.91	6.44	8.64	5.85	8.22	10.12	-6.44	-27.73%
2002	5.73	6.82	8.68	8.29	8.56	9.71	-6.82	-25.49%
2003	6.87	8.16	10.10	6.87	9.50	11.76	-8.16	-16.38%
2004	6.18	7.12	8.09	6.47	7.60	8.14	-7.12	-6.75%
2005	5.89	7.26	9.39	6.58	7.75	8.70	-7.26	-6.87%
2006	6.01	7.03	8.05	6.16	6.85	8.66	-7.03	2.55%
2007	4.71	6.17	8.00	6.86	8.75	11.09	-6.17	-41.87%
2008	5.56	6.88	7.62	5.27	6.83	7.41	-6.88	0.73%
2009	6.27	7.19	8.02	5.74	7.62	7.96	-7.19	-6.01%
2010	5.13	6.14	7.73	5.45	5.83	6.42	-6.14	5.00%
2011	5.73	6.64	7.59	6.16	6.89	9.07	-6.64	-3.77%
2012	5.49	5.98	6.88	6.05	6.46	7.38	-5.98	-8.15%
2013	5.43	6.17	7.83	5.55	5.88	7.18	-6.17	4.61%
2014	5.05	6.21	8.86	5.48	6.15	7.41	-6.21	1.02%

Figure E4 has SO₄²⁻ boxplots for TU and BES at GFGB. Negative values indicates that TU dataset median concentrations were greater than BES dataset median concentrations.

Year	BES Lower Quartile	BES median	BES Upper Quartile	TU Lower Quartile	TU median	TU Upper Quartile	BES and TU Median Difference	BES and TU Median Difference
	SO4 ²⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	%					
1998	28.75	30.03	30.43	30.63	30.84	31.04	-30.03	-2.69%
1999	23.08	24.93	27.56	27.44	28.66	30.13	-24.93	-14.96%
2000	24.05	26.14	28.57	27.32	28.58	30.91	-26.14	-9.35%
2001	25.11	26.84	28.46	26.13	27.99	29.04	-26.84	-4.29%
2002	23.05	27.00	29.50	25.39	28.47	29.81	-27.00	-5.43%
2003	18.32	27.40	29.20	22.88	28.14	31.45	-27.40	-2.70%
2004	26.20	28.40	30.40	26.83	28.51	30.45	-28.40	-0.40%
2005	26.35	28.75	30.70	22.12	28.29	32.16	-28.75	1.61%
2006	18.60	22.50	26.65	20.90	25.11	26.86	-22.50	-11.60%
2007	23.25	25.30	31.05	24.09	25.58	29.88	-25.30	-1.10%
2008	23.80	26.65	29.10	26.37	27.22	29.25	-26.65	-2.13%
2009	22.95	26.10	28.40	23.96	27.61	29.01	-26.10	-5.79%
2010	21.60	26.65	28.60	20.46	26.89	29.03	-26.65	-0.90%
2011	19.90	24.80	27.60	21.07	26.56	27.57	-24.80	-7.08%
2012	22.60	25.10	27.30	22.40	26.35	28.66	-25.10	-4.98%
2013	24.90	27.40	28.70	24.07	27.52	28.59	-27.40	-0.45%
2014	18.05	26.30	29.60	24.47	28.79	34.71	-26.30	-9.47%

Table E11: BES and TU Annual Boxplot Statistics (Sulfate, GFGL)

Figure E4 has SO_4^{2-} boxplots for TU and BES at GFGL Negative values indicates that TU dataset median concentrations were greater than BES dataset median concentrations.



Figure E1: BES and TU Annual Boxplots (Chloride- POBR, BARN, MCDN)

BES and TU dataset chloride boxplots for POBR, BARN, and MCDN. Statistics are provided in Tables E2-4.



Figure E2: BES and TU Annual Boxplots (Chloride- GFGB, GFGL)

BES and TU dataset chloride boxplots for GFGB and GFGL. Statistics are provided in Tables E5-6.



Figure E3: BES and TU Annual Boxplots (Sulfate- POBR, BARN, MCDN)

BES and TU dataset sulfate boxplots for POBR, BARN, and MCDN. Statistics are provided in Tables E7-9.



Figure E4: BES and TU Annual Boxplots (Sulfate- GFGB, GFGL)

BES and TU dataset sulfate boxplots for GFGB and GFGL. Statistics are provided in Tables E10-11.

Appendix F: Annual Boxplot Statistics (TU Dataset)

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Year	LQ	median	UQ	IQR
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
1998	2.2	2.2	2.2	0.0
1999	2.2	2.3	2.3	0.1
2000	1.7	1.9	2.0	0.3
2001	1.9	2.1	2.1	0.2
2002	2.0	2.2	2.4	0.4
2003	2.0	2.1	2.1	0.2
2004	2.0	2.1	2.2	0.3
2005	1.8	1.8	1.9	0.1
2006	2.0	2.2	2.3	0.3
2007	2.2	2.3	2.4	0.2
2008	1.7	1.9	2.0	0.2
2009	1.8	1.9	2.0	0.2
2010	2.0	2.0	2.1	0.2
2011	2.1	2.1	2.1	0.1
2012	2.0	2.2	2.4	0.4
2013	2.1	2.2	2.3	0.2
2014	1.8	1.9	2.1	0.3

Table F1: Annual Boxplot Statistics (Na⁺, POBR)

Boxplots summarized by 5-Year Groups, Figure 7A

Table F2: Annual Boxplot Statistics (Na⁺, BARN)

Year	LQ	median	UQ	IQR
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
1999	10.7	11.5	11.6	0.9
2000	7.8	8.4	9.8	2.0
2001	9.8	10.4	11.0	1.2
2002	9.0	9.9	12.1	3.2
2003	11.3	11.5	14.2	2.8
2004	9.2	9.8	10.1	0.9
2005	9.3	9.7	10.4	1.1
2006	10.1	12.0	12.4	2.3
2007	10.7	11.0	13.3	2.5
2008	13.7	14.9	15.1	1.4
2009	13.8	15.6	20.3	6.6
2010	13.0	13.5	14.1	1.1
2011	18.2	21.7	27.9	9.7
2012	13.5	14.0	14.5	1.0
2013	13.0	13.5	14.2	1.2
2014	12.8	14.4	17.4	4.6

Boxplots summarized by 5-Year Groups, Figure 7A

Year	LQ	median	UQ	IQR
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
1998	7.6	8.1	8.6	1.0
1999	10.0	12.0	16.5	6.4
2000	10.7	12.2	15.4	4.7
2001	12.5	34.2	72.4	60.0
2002	13.3	15.3	28.2	14.9
2003	16.2	19.3	49.2	33.0
2004	17.0	18.9	21.6	4.6
2005	17.2	19.0	36.6	19.4
2006	16.6	17.2	18.4	1.7
2007	20.5	39.2	115.4	95.0
2008	20.4	23.4	26.1	5.7
2009	23.7	26.6	29.5	5.9
2010	21.3	25.5	31.6	10.4
2011	31.2	32.2	57.4	26.2
2012	25.3	27.5	28.4	3.1
2013	28.6	29.4	31.0	2.4
2014	32.0	35.1	41.9	9.9

Table F3: Annual Boxplot Statistics (Na⁺, GFGB)

Boxplots summarized by 5-Year Groups, Figure 7A

Tabl	e F4: Ann	ual Boxplo	t Statist	ics (Na+, GFG	L)
'ear	LQ	median	UQ	IQR	

Year	LQ	median	UQ	IQR
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
1998	23.6	24.6	25.7	2.1
1999	20.4	21.6	24.0	3.6
2000	18.1	22.5	31.7	13.6
2001	22.7	25.8	31.1	8.4
2002	18.3	22.5	26.1	7.8
2003	30.0	51.8	62.0	31.9
2004	26.2	32.1	38.9	12.8
2005	21.9	33.8	54.6	32.8
2006	16.1	17.9	23.3	7.3
2007	22.4	27.8	42.1	19.7
2008	25.2	32.6	54.9	29.7
2009	24.2	32.1	39.5	15.3
2010	25.4	28.9	57.6	32.2
2011	28.0	39.8	87.0	58.9
2012	21.0	26.2	38.3	17.3
2013	22.5	29.1	43.1	20.7
2014	37.2	59.9	87.1	50.0

Boxplots summarized by 5-Year Groups, Figure 7A

Year	LQ	median	UQ	IQR
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
1998	0.6	0.6	0.6	0.0
1999	0.7	0.7	0.8	0.1
2000	0.4	0.5	0.6	0.1
2001	0.5	0.5	0.5	0.0
2002	0.7	0.7	0.9	0.2
2003	1.0	1.0	1.0	0.0
2004	0.6	0.6	0.6	0.1
2005	0.6	0.6	0.6	0.1
2006	0.8	0.9	1.0	0.2
2007	0.8	0.8	0.9	0.1
2008	0.5	0.5	0.7	0.2
2009	0.8	0.8	0.9	0.1
2010	0.5	0.6	0.6	0.1
2011	0.7	0.8	0.8	0.1
2012	0.5	0.6	0.8	0.3
2013	0.8	0.8	0.8	0.0
2014	0.8	0.8	0.9	0.1

Table F5: Annual Boxplot Statistics (Mg²⁺, POBR)

Boxplots summarized by 5-Year Groups, Figure 7B

Table F6: Annual Boxplot Statistics (Mg²⁺, BARN)

Year	LQ	median	UQ	IQR
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
1999	3.8	4.1	4.1	0.4
2000	2.7	3.4	3.6	0.8
2001	3.5	3.6	3.8	0.3
2002	3.9	4.0	4.0	0.1
2003	3.9	4.2	4.4	0.5
2004	2.9	3.3	3.4	0.5
2005	3.0	3.1	3.5	0.5
2006	3.5	3.6	4.2	0.7
2007	3.1	3.3	3.8	0.8
2008	3.7	4.7	5.1	1.4
2009	4.0	4.3	4.3	0.3
2010	3.3	3.7	4.1	0.9
2011	4.4	4.7	5.3	0.9
2012	3.9	4.0	4.3	0.4
2013	3.6	3.8	4.2	0.6
2014	3.6	4.0	4.2	0.6

Boxplots summarized by 5-Year Groups, Figure 7B

Year	LQ	median	UQ	IQR
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
1998	5.7	6.2	6.6	0.9
1999	5.7	7.1	7.5	1.8
2000	7.5	7.9	8.2	0.7
2001	6.5	7.7	8.0	1.6
2002	7.7	8.0	8.6	0.9
2003	8.4	8.7	9.8	1.4
2004	8.6	9.0	9.5	0.9
2005	7.8	9.5	10.0	2.2
2006	8.8	9.0	9.2	0.4
2007	9.9	10.3	10.5	0.6
2008	9.0	9.3	10.6	1.7
2009	10.9	11.1	12.0	1.1
2010	8.7	10.1	11.4	2.7
2011	11.9	12.5	12.8	0.9
2012	11.1	12.0	12.3	1.2
2013	11.8	12.5	13.7	1.9
2014	10.7	12.5	13.2	2.5
-		~		

Table F7: Annual Boxplot Statistics (Mg²⁺, GFGB)

Boxplots summarized by 5-Year Groups, Figure 7B

Table	e F8: Annu	al Boxplo	t Statisti	ics (Mg ²⁺ ,	GFGL)
ear	IO	median	UO	IOR	

Year	LQ	median	UQ	IQR
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
1998	36.5	39.1	41.8	5.3
1999	25.3	31.4	34.6	9.3
2000	19.7	24.2	28.5	8.8
2001	19.8	25.3	29.1	9.3
2002	19.7	23.9	28.0	8.4
2003	15.3	18.2	24.8	9.5
2004	19.0	23.9	28.3	9.3
2005	16.8	23.1	29.9	13.0
2006	9.2	12.4	16.9	7.7
2007	13.3	20.0	26.6	13.3
2008	17.6	22.2	27.3	9.7
2009	24.0	25.7	31.3	7.3
2010	16.9	29.5	32.1	15.3
2011	15.4	25.8	28.0	12.6
2012	18.4	28.6	30.3	11.9
2013	16.8	29.9	34.3	17.5
2014	16.3	24.1	32.2	16.0

Boxplots summarized by 5-Year Groups, Figure 7B

$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	Year	LQ	median	UQ	IQR
19989.99.99.90.0199913.214.114.91.82000 6.7 7.5 9.4 2.7 2001 6.7 7.4 8.4 1.7 200212.013.415.9 3.8 200314.915.716.51.62004 8.1 9.0 10.01.82005 7.2 7.8 8.8 1.5200614.816.718.13.3200712.212.715.12.9200812.312.416.33.9200913.214.615.52.32010 7.9 9.6 12.24.3201111.211.712.20.92012 8.3 9.1 13.24.9201311.211.211.70.5201412.313.513.61.3		(mg/L)	(mg/L)	(mg/L)	(mg/L)
1999 13.2 14.1 14.9 1.8 2000 6.7 7.5 9.4 2.7 2001 6.7 7.4 8.4 1.7 2002 12.0 13.4 15.9 3.8 2003 14.9 15.7 16.5 1.6 2004 8.1 9.0 10.0 1.8 2005 7.2 7.8 8.8 1.5 2006 14.8 16.7 18.1 3.3 2007 12.2 12.7 15.1 2.9 2008 12.3 12.4 16.3 3.9 2009 13.2 14.6 15.5 2.3 2010 7.9 9.6 12.2 4.3 2011 11.2 11.7 12.2 0.9 2012 8.3 9.1 13.2 4.9 2013 11.2 11.2 11.7 0.5 2014 12.3 13.5 13.6 1.3	1998	9.9	9.9	9.9	0.0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1999	13.2	14.1	14.9	1.8
2001 6.7 7.4 8.4 1.7 2002 12.0 13.4 15.9 3.8 2003 14.9 15.7 16.5 1.6 2004 8.1 9.0 10.0 1.8 2005 7.2 7.8 8.8 1.5 2006 14.8 16.7 18.1 3.3 2007 12.2 12.7 15.1 2.9 2008 12.3 12.4 16.3 3.9 2009 13.2 14.6 15.5 2.3 2010 7.9 9.6 12.2 4.3 2011 11.2 11.7 12.2 0.9 2012 8.3 9.1 13.2 4.9 2013 11.2 11.2 11.7 0.5 2014 12.3 13.5 13.6 1.3	2000	6.7	7.5	9.4	2.7
2002 12.0 13.4 15.9 3.8 2003 14.9 15.7 16.5 1.6 2004 8.1 9.0 10.0 1.8 2005 7.2 7.8 8.8 1.5 2006 14.8 16.7 18.1 3.3 2007 12.2 12.7 15.1 2.9 2008 12.3 12.4 16.3 3.9 2009 13.2 14.6 15.5 2.3 2010 7.9 9.6 12.2 4.3 2011 11.2 11.7 12.2 0.9 2012 8.3 9.1 13.2 4.9 2013 11.2 11.2 11.7 0.5 2014 12.3 13.5 13.6 1.3	2001	6.7	7.4	8.4	1.7
2003 14.9 15.7 16.5 1.6 2004 8.1 9.0 10.0 1.8 2005 7.2 7.8 8.8 1.5 2006 14.8 16.7 18.1 3.3 2007 12.2 12.7 15.1 2.9 2008 12.3 12.4 16.3 3.9 2009 13.2 14.6 15.5 2.3 2010 7.9 9.6 12.2 4.3 2011 11.2 11.7 12.2 0.9 2012 8.3 9.1 13.2 4.9 2013 11.2 11.2 11.7 0.5 2014 12.3 13.5 13.6 1.3	2002	12.0	13.4	15.9	3.8
2004 8.1 9.0 10.0 1.8 2005 7.2 7.8 8.8 1.5 2006 14.8 16.7 18.1 3.3 2007 12.2 12.7 15.1 2.9 2008 12.3 12.4 16.3 3.9 2009 13.2 14.6 15.5 2.3 2010 7.9 9.6 12.2 4.3 2011 11.2 11.7 12.2 0.9 2012 8.3 9.1 13.2 4.9 2013 11.2 11.2 11.7 0.5 2014 12.3 13.5 13.6 1.3	2003	14.9	15.7	16.5	1.6
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2004	8.1	9.0	10.0	1.8
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2005	7.2	7.8	8.8	1.5
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2006	14.8	16.7	18.1	3.3
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2007	12.2	12.7	15.1	2.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2008	12.3	12.4	16.3	3.9
2010 7.9 9.6 12.2 4.3 2011 11.2 11.7 12.2 0.9 2012 8.3 9.1 13.2 4.9 2013 11.2 11.2 11.7 0.5 2014 12.3 13.5 13.6 1.3	2009	13.2	14.6	15.5	2.3
2011 11.2 11.7 12.2 0.9 2012 8.3 9.1 13.2 4.9 2013 11.2 11.2 11.7 0.5 2014 12.3 13.5 13.6 1.3	2010	7.9	9.6	12.2	4.3
2012 8.3 9.1 13.2 4.9 2013 11.2 11.2 11.7 0.5 2014 12.3 13.5 13.6 1.3	2011	11.2	11.7	12.2	0.9
2013 11.2 11.2 11.7 0.5 2014 12.3 13.5 13.6 1.3	2012	8.3	9.1	13.2	4.9
2014 12.3 13.5 13.6 1.3	2013	11.2	11.2	11.7	0.5
	2014	12.3	13.5	13.6	1.3

Table F9: Annual Boxplot Statistics (Estimated HCO₃-, POBR)

Boxplots summarized by 5-Year Groups, Figure 7C

Tabl	e F10: An	inual Boxplot	t Statistics	(Estimated HCO ₃ -, BARN)
7	I O	1.	LIO.	IOD

Year	LQ	median	UQ	IQR
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
1999	13.7	14.4	14.7	0.9
2000	8.8	11.5	12.1	3.3
2001	11.9	12.5	13.3	1.4
2002	13.4	13.9	15.7	2.2
2003	14.4	15.3	15.5	1.1
2004	9.5	11.4	11.6	2.1
2005	10.2	10.9	12.3	2.1
2006	12.6	13.3	14.8	2.2
2007	11.9	13.0	14.0	2.0
2008	13.4	17.0	18.7	5.3
2009	14.7	14.9	15.5	0.8
2010	11.3	12.3	14.3	3.0
2011	15.3	17.0	18.8	3.5
2012	13.7	14.2	15.1	1.5
2013	12.0	13.2	14.8	2.7
2014	12.0	13.5	14.9	2.9

Boxplots summarized by 5-Year Groups, Figure 7C

$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	Year	LQ	median	UQ	IQR
1998 32.0 33.6 35.2 3.1 1999 39.3 43.1 45.3 6.0 2000 40.8 41.2 43.7 2.9 2001 43.1 43.4 47.3 4.2 2002 42.9 46.5 47.8 4.9 2003 48.6 50.6 53.0 4.4 2004 47.3 50.4 50.8 3.5 2005 45.3 47.7 51.7 6.4 2006 44.6 46.8 48.5 4.0 2007 51.1 54.1 55.3 4.2 2008 38.4 51.8 54.9 16.5 2009 56.8 57.0 58.9 2.1 2010 51.8 54.2 59.4 7.7 2011 58.6 62.5 69.1 10.4 2012 55.9 57.6 59.7 3.8 2013 58.0 61.1 62.5 4.5		(mg/L)	(mg/L)	(mg/L)	(mg/L)
1999 39.3 43.1 45.3 6.0 2000 40.8 41.2 43.7 2.9 2001 43.1 43.4 47.3 4.2 2002 42.9 46.5 47.8 4.9 2003 48.6 50.6 53.0 4.4 2004 47.3 50.4 50.8 3.5 2005 45.3 47.7 51.7 6.4 2006 44.6 46.8 48.5 4.0 2007 51.1 54.1 55.3 4.2 2008 38.4 51.8 54.9 16.5 2009 56.8 57.0 58.9 2.1 2010 51.8 54.2 59.4 7.7 2011 58.6 62.5 69.1 10.4 2012 55.9 57.6 59.7 3.8 2013 58.0 61.1 62.5 4.5	1998	32.0	33.6	35.2	3.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1999	39.3	43.1	45.3	6.0
2001 43.1 43.4 47.3 4.2 2002 42.9 46.5 47.8 4.9 2003 48.6 50.6 53.0 4.4 2004 47.3 50.4 50.8 3.5 2005 45.3 47.7 51.7 6.4 2006 44.6 46.8 48.5 4.0 2007 51.1 54.1 55.3 4.2 2008 38.4 51.8 54.9 16.5 2009 56.8 57.0 58.9 2.1 2010 51.8 54.2 59.4 7.7 2011 58.6 62.5 69.1 10.4 2012 55.9 57.6 59.7 3.8 2013 58.0 61.1 62.5 4.5	2000	40.8	41.2	43.7	2.9
2002 42.9 46.5 47.8 4.9 2003 48.6 50.6 53.0 4.4 2004 47.3 50.4 50.8 3.5 2005 45.3 47.7 51.7 6.4 2006 44.6 46.8 48.5 4.0 2007 51.1 54.1 55.3 4.2 2008 38.4 51.8 54.9 16.5 2009 56.8 57.0 58.9 2.1 2010 51.8 54.2 59.4 7.7 2011 58.6 62.5 69.1 10.4 2012 55.9 57.6 59.7 3.8 2013 58.0 61.1 62.5 4.5	2001	43.1	43.4	47.3	4.2
2003 48.6 50.6 53.0 4.4 2004 47.3 50.4 50.8 3.5 2005 45.3 47.7 51.7 6.4 2006 44.6 46.8 48.5 4.0 2007 51.1 54.1 55.3 4.2 2008 38.4 51.8 54.9 16.5 2009 56.8 57.0 58.9 2.1 2010 51.8 54.2 59.4 7.7 2011 58.6 62.5 69.1 10.4 2012 55.9 57.6 59.7 3.8 2013 58.0 61.1 62.5 4.5	2002	42.9	46.5	47.8	4.9
2004 47.3 50.4 50.8 3.5 2005 45.3 47.7 51.7 6.4 2006 44.6 46.8 48.5 4.0 2007 51.1 54.1 55.3 4.2 2008 38.4 51.8 54.9 16.5 2009 56.8 57.0 58.9 2.1 2010 51.8 54.2 59.4 7.7 2011 58.6 62.5 69.1 10.4 2012 55.9 57.6 59.7 3.8 2013 58.0 61.1 62.5 4.5	2003	48.6	50.6	53.0	4.4
2005 45.3 47.7 51.7 6.4 2006 44.6 46.8 48.5 4.0 2007 51.1 54.1 55.3 4.2 2008 38.4 51.8 54.9 16.5 2009 56.8 57.0 58.9 2.1 2010 51.8 54.2 59.4 7.7 2011 58.6 62.5 69.1 10.4 2012 55.9 57.6 59.7 3.8 2013 58.0 61.1 62.5 4.5	2004	47.3	50.4	50.8	3.5
2006 44.6 46.8 48.5 4.0 2007 51.1 54.1 55.3 4.2 2008 38.4 51.8 54.9 16.5 2009 56.8 57.0 58.9 2.1 2010 51.8 54.2 59.4 7.7 2011 58.6 62.5 69.1 10.4 2012 55.9 57.6 59.7 3.8 2013 58.0 61.1 62.5 4.5	2005	45.3	47.7	51.7	6.4
2007 51.1 54.1 55.3 4.2 2008 38.4 51.8 54.9 16.5 2009 56.8 57.0 58.9 2.1 2010 51.8 54.2 59.4 7.7 2011 58.6 62.5 69.1 10.4 2012 55.9 57.6 59.7 3.8 2013 58.0 61.1 62.5 4.5	2006	44.6	46.8	48.5	4.0
2008 38.4 51.8 54.9 16.5 2009 56.8 57.0 58.9 2.1 2010 51.8 54.2 59.4 7.7 2011 58.6 62.5 69.1 10.4 2012 55.9 57.6 59.7 3.8 2013 58.0 61.1 62.5 4.5	2007	51.1	54.1	55.3	4.2
2009 56.8 57.0 58.9 2.1 2010 51.8 54.2 59.4 7.7 2011 58.6 62.5 69.1 10.4 2012 55.9 57.6 59.7 3.8 2013 58.0 61.1 62.5 4.5	2008	38.4	51.8	54.9	16.5
2010 51.8 54.2 59.4 7.7 2011 58.6 62.5 69.1 10.4 2012 55.9 57.6 59.7 3.8 2013 58.0 61.1 62.5 4.5	2009	56.8	57.0	58.9	2.1
2011 58.6 62.5 69.1 10.4 2012 55.9 57.6 59.7 3.8 2013 58.0 61.1 62.5 4.5 2014 58.1 61.2 62.5 63.1	2010	51.8	54.2	59.4	7.7
2012 55.9 57.6 59.7 3.8 2013 58.0 61.1 62.5 4.5 2014 58.1 61.8 64.2 62.5	2011	58.6	62.5	69.1	10.4
2013 58.0 61.1 62.5 4.5 2014 58.1 61.8 64.2 62	2012	55.9	57.6	59.7	3.8
2014 59.1 (1.9 (4.2 (.2	2013	58.0	61.1	62.5	4.5
2014 38.1 01.8 64.3 6.3	2014	58.1	61.8	64.3	6.3

Table F11: Annual Boxplot Statistics (Estimated HCO3-, GFGB)

Boxplots summarized by 5-Year Groups, Figure 7C

Table F12: Annual Boxplot Statistics	(Estimated HCO ₃ ⁻ , GFGL)
Tuble I 12. Annual Domplot Statistics	

Year	LQ	median	UQ	IQR
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
1998	108.5	110.1	111.7	3.3
1999	94.5	107.0	125.2	30.8
2000	87.3	97.9	113.5	26.3
2001	106.4	129.2	148.0	41.6
2002	108.5	128.8	155.5	47.0
2003	97.9	115.4	141.2	43.3
2004	111.0	128.8	150.1	39.1
2005	103.9	124.4	139.7	35.8
2006	56.8	76.5	100.4	43.6
2007	86.5	123.7	158.9	72.4
2008	105.0	115.3	159.4	54.3
2009	120.9	131.1	154.3	33.4
2010	99.7	137.7	157.3	57.6
2011	98.2	141.4	146.5	48.3
2012	101.2	139.1	148.2	47.0
2013	104.9	147.5	159.7	54.9
2014	127.1	140.2	168.2	41.1

Boxplots summarized by 5-Year Groups, Figure 7C

Year	LQ	median	UQ	IQR
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
1998	0.7	0.7	0.7	0.0
1999	1.0	1.0	1.1	0.1
2000	0.5	0.6	0.7	0.2
2001	0.5	0.5	0.6	0.1
2002	0.9	1.0	1.2	0.3
2003	1.1	1.2	1.2	0.1
2004	0.6	0.7	0.7	0.1
2005	0.5	0.6	0.6	0.1
2006	1.1	1.2	1.3	0.2
2007	0.9	0.9	1.1	0.2
2008	0.9	0.9	1.2	0.3
2009	1.0	1.1	1.1	0.2
2010	0.6	0.7	0.9	0.3
2011	0.8	0.9	0.9	0.1
2012	0.6	0.7	1.0	0.4
2013	0.8	0.8	0.9	0.0
2014	0.9	1.0	1.0	0.1

Table F13: Annual Boxplot Statistics (Ca²⁺, POBR)

Boxplots summarized by 5-Year Groups, Figure 7D

Table F14: Annual Boxplot Statistics (Ca²⁺, BARN)

				<u> </u>
Year	LQ	median	UQ	IQR
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
1999	6.0	6.3	6.5	0.4
2000	3.9	5.0	5.3	1.4
2001	5.2	5.5	5.9	0.6
2002	5.9	6.1	6.9	1.0
2003	6.3	6.7	6.8	0.5
2004	4.2	5.0	5.1	0.9
2005	4.5	4.8	5.4	0.9
2006	5.5	5.8	6.5	1.0
2007	5.2	5.7	6.1	0.9
2008	5.9	7.5	8.2	2.3
2009	6.5	6.6	6.8	0.4
2010	5.0	5.4	6.3	1.3
2011	6.7	7.5	8.3	1.5
2012	6.0	6.2	6.7	0.6
2013	5.3	5.8	6.5	1.2
2014	5.3	5.9	6.5	1.3

Boxplots summarized by 5-Year Groups, Figure 7D

Year	LQ	median	UQ	IQR
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
1998	14.1	14.8	15.5	1.4
1999	17.3	19.0	20.0	2.6
2000	18.0	18.2	19.3	1.3
2001	19.0	19.1	20.9	1.9
2002	18.9	20.5	21.1	2.2
2003	21.4	22.3	23.4	2.0
2004	20.8	22.2	22.4	1.6
2005	20.0	21.0	22.8	2.8
2006	19.7	20.7	21.4	1.7
2007	22.5	23.8	24.4	1.9
2008	16.9	22.8	24.2	7.3
2009	25.0	25.1	26.0	0.9
2010	22.8	23.9	26.2	3.4
2011	25.8	27.5	30.5	4.6
2012	24.7	25.4	26.3	1.7
2013	25.6	26.9	27.5	2.0
2014	25.6	27.3	28.4	2.8

Table F15: Annual Boxplot Statistics (Ca²⁺, GFGB)

Boxplots summarized by 5-Year Groups, Figure 7D

Table F16: Annual Boxplot Statistics (Ca²⁺, GFGL)

Year	LQ	median	UQ	IQR
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
1998	47.8	48.6	49.3	1.4
1999	41.7	47.2	55.2	13.6
2000	38.5	43.2	50.1	11.6
2001	46.9	57.0	65.3	18.3
2002	47.8	56.8	68.6	20.7
2003	43.2	50.9	62.3	19.1
2004	49.0	56.8	66.2	17.2
2005	45.8	54.9	61.6	15.8
2006	25.1	33.7	44.3	19.2
2007	38.1	54.6	70.1	31.9
2008	46.3	50.8	70.3	24.0
2009	53.3	57.8	68.0	14.7
2010	44.0	60.7	69.4	25.4
2011	43.3	62.4	64.6	21.3
2012	44.6	61.3	65.4	20.7
2013	46.2	65.1	70.4	24.2
2014	56.1	61.8	74.2	18.1

Boxplots summarized by 5-Year Groups, Figure 7D

Year	LQ	median	UQ	IQR
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
1998	1.0	1.0	1.0	0.0
1999	0.8	0.8	0.9	0.1
2000	0.7	0.8	0.8	0.1
2001	0.5	0.5	0.6	0.1
2002	0.4	0.4	0.4	0.0
2003	0.8	0.8	0.8	0.0
2004	0.5	0.6	0.8	0.3
2005	0.6	0.8	0.8	0.2
2006	1.0	1.1	2.1	1.1
2007	0.5	0.6	0.7	0.2
2008	0.9	1.0	1.3	0.4
2009	0.8	0.9	1.1	0.3
2010	0.7	0.8	1.0	0.3
2011	0.9	1.0	1.1	0.2
2012	0.6	0.6	0.9	0.4
2013	0.6	0.7	0.8	0.1
2014	0.8	0.9	1.0	0.2

Table F17: Annual Boxplot Statistics (K⁺, POBR)

Boxplots summarized by 5-Year Groups, Figure 7E

Table F	18: Annual I	Boxplot	Statistics ($(K^+, BARN)$

Year	LQ	median	UQ	IQR
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
1999	1.6	1.6	1.6	0.1
2000	0.8	1.0	1.3	0.4
2001	1.0	1.2	1.3	0.3
2002	0.4	0.7	0.8	0.4
2003	1.5	1.6	1.7	0.2
2004	1.1	1.2	1.3	0.2
2005	1.1	1.3	1.4	0.3
2006	1.6	1.8	2.1	0.5
2007	1.3	1.4	1.5	0.3
2008	1.6	2.2	2.2	0.6
2009	1.7	1.8	1.9	0.2
2010	1.3	1.5	1.8	0.5
2011	1.8	2.2	2.3	0.5
2012	1.4	1.5	1.9	0.6
2013	0.9	1.2	1.6	0.7
2014	1.5	1.6	1.7	0.3

Boxplots summarized by 5-Year Groups, Figure 7E

$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	Year	LQ	median	UQ	IQR
1998 1.5 1.6 1.7 0.2 1999 1.8 1.9 2.3 0.5 2000 1.6 1.8 1.9 0.4 2001 1.7 1.8 2.1 0.4 2002 1.3 1.6 2.4 1.1 2003 1.9 1.9 1.9 0.1 2004 2.0 2.2 2.4 0.3 2005 2.1 2.3 2.8 0.6 2006 2.1 2.3 2.5 0.3 2007 1.9 2.4 3.1 1.2 2008 2.6 2.7 2.8 0.2 2010 2.5 2.7 2.9 0.4 2011 2.2 2.5 2.8 0.6 2012 2.3 2.5 2.7 0.4 2013 2.0 2.2 3.0 1.0 2014 2.8 3.0 3.0 0.2		(mg/L)	(mg/L)	(mg/L)	(mg/L)
1999 1.8 1.9 2.3 0.5 2000 1.6 1.8 1.9 0.4 2001 1.7 1.8 2.1 0.4 2002 1.3 1.6 2.4 1.1 2003 1.9 1.9 1.9 0.1 2004 2.0 2.2 2.4 0.3 2005 2.1 2.3 2.8 0.6 2006 2.1 2.3 2.5 0.3 2007 1.9 2.4 3.1 1.2 2008 2.6 2.7 2.8 0.2 2010 2.5 2.7 2.9 0.4 2011 2.2 2.5 2.8 0.6 2012 2.3 2.5 2.7 0.4 2013 2.0 2.2 3.0 1.0 2014 2.8 3.0 3.0 0.2	1998	1.5	1.6	1.7	0.2
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1999	1.8	1.9	2.3	0.5
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2000	1.6	1.8	1.9	0.4
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2001	1.7	1.8	2.1	0.4
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2002	1.3	1.6	2.4	1.1
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2003	1.9	1.9	1.9	0.1
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2004	2.0	2.2	2.4	0.3
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2005	2.1	2.3	2.8	0.6
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2006	2.1	2.3	2.5	0.3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2007	1.9	2.4	3.1	1.2
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2008	2.6	2.7	2.8	0.2
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2009	2.6	2.7	2.9	0.2
2011 2.2 2.5 2.8 0.6 2012 2.3 2.5 2.7 0.4 2013 2.0 2.2 3.0 1.0 2014 2.8 3.0 3.0 0.2	2010	2.5	2.7	2.9	0.4
2012 2.3 2.5 2.7 0.4 2013 2.0 2.2 3.0 1.0 2014 2.8 3.0 3.0 0.2	2011	2.2	2.5	2.8	0.6
2013 2.0 2.2 3.0 1.0 2014 2.8 3.0 3.0 0.2	2012	2.3	2.5	2.7	0.4
2014 2.8 3.0 3.0 0.2	2013	2.0	2.2	3.0	1.0
2017 2.0 5.0 5.0 0.2	2014	2.8	3.0	3.0	0.2

Table F19: Annual Boxplot Statistics (K⁺, GFGB)

Boxplots summarized by 5-Year Groups, Figure 7E

Table F20: Annual Boxplot Statistics (K⁺, GFGL)

Year	LQ	median	UQ	IQR
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
1998	2.1	2.2	2.4	0.3
1999	1.5	1.7	1.9	0.4
2000	1.5	1.5	2.0	0.5
2001	1.3	1.5	2.0	0.6
2002	1.7	1.8	2.1	0.5
2003	1.9	2.0	2.7	0.8
2004	1.7	2.0	2.3	0.5
2005	2.0	2.4	2.7	0.7
2006	2.0	2.5	2.7	0.7
2007	2.2	2.6	2.8	0.6
2008	2.2	2.4	2.5	0.4
2009	2.3	2.4	2.8	0.5
2010	1.9	2.3	2.6	0.7
2011	1.8	1.9	2.7	0.9
2012	1.6	1.7	2.0	0.4
2013	1.4	1.7	2.0	0.7
2014	2.0	2.2	2.4	0.4

Boxplots summarized by 5-Year Groups, Figure 7E

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EDUCATION	
Towson University, Towson, MD M.S. in Environmental Science Areas of Concentration: Water Resources Management and Assessment Thesis: Major Ions in Urban Streams: A Look at Concentrations Over Time and Across Land Cover	2017
University of Washington, Seattle, WA B.S. in Earth and Space Science Areas of Concentration: Geology Minor: History	2012
AWARDS	
Towson University: Dean's List University of Washington: Dean's List	September 2015 – June 2016 March 2011 – June 2012
WORK EXPERIENCE	
Towson University, Towson, MD Research Assistant Primary job duties: data analysis, current literature review, and research Co-author on papers and presentations	January 2016 – June 2017
Managed thesis project: collected >800 samples from an archive, organized samples for easy analysis, and maintained data integrity through extensive quality control and assurance procedures	
 The California Department of Resources Recycling and Recovery (CalRecycle), Sacramento, CA Environmental Scientist Primary job duties: research, data analysis, and assisting county level staff with reporting requirments Compiled technical reports on disposal issues in California for Executive Staff; wrote, presented, and managed a research project on tipping fees; analyzed data spatially with ArcGIS. 	October 2013 – April 2015
California's Department of Resources Recycling and Recovery (CalRecycle), Sacramento, CA Program Technician Primary job duties: data entry and management Assisted colleagues with data analysis, and report generation.	January – October 2013
PUBLICATIONS AND PAPERS	
"Major Ions in Urban Streams: A Look at Concentrations over Time and Across Land Cover" Thesis Defense, Towson, MD	April 13, 2017
"Increasing Major Ion Concentrations and Changing Ion Ratios in Urban Streams over a 15-Year Poster Presentation, Geologic Society of America Annual Northeastern Meeting,	r Period in Baltimore, MD"
Pittsburgh, PA	March 20, 2017
"The Evolution of Ion Chemistry in Urban Streams in the Maryland Piedmont and Implications for Presentation, Maryland Water Monitoring Council 22nd Annual Conference, North Linthicum, MD	or Freshwater Biota" December 2, 2016
"Using BES Data and Archived Samples to Examine Evolving Ion Chemistry in Urban Streams fr Poster Presentation, Baltimore Ecosystem Study Annual Meeting, Baltimore, MD	om 1999-2014 October 19, 2016

"Increasing Major Ion Concentrations and Changing Ion Ratios in Urban Streams over a 15-Year Period in Baltimore, MD"	
Presentation, Geologic Society of America Annual Meeting, Denver, CO	September 28, 2016
"Landfill Tipping Fees in California"	
Paper, The California Department of Resources Recycling and Recovery (CalRecycle),	
Sacramento, CA	February 1, 2015
<i>"Tipping Fees in California"</i> Presentation. The California Department of Resources Recycling and Recovery	
(CalRecycle) Monthly Public Meeting, Sacramento, CA	October 21, 2014

MEMBERSHIPS

Geologic Society of America