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BASELINE CONCENTRATIONS OF CONTAMINANTS OF EMERGING CONCERN IN THE LAKE THUNDERBIRD WATERSHED, PLANNING FOR INDIRECT POTABLE REUSE IN OKLAHOMA

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BASELINE CONCENTRATIONS OF CONTAMINANTS OF EMERGING CONCERN IN THE LAKE THUNDERBIRD WATERSHED, PLANNING FOR INDIRECT POTABLE REUSE IN OKLAHOMA

A THESIS APPROVED FOR THE
CONOCOPHILLIPS SCHOOL OF GEOLOGY AND GEOPHYSICS

BY

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Dedicated to my papa, mom, and dad for always encouraging me to work hard and supporting me in everything I have done or aspired to do.

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Abstract

The City of Norman, OK is planning an indirect potable reuse (IPR) project to augment their water supply. The IPR project involves transferring treated effluent from the Norman Water Reclamation Facility (NWRF) to Dave Blue Creek, which flows into Lake Thunderbird and acts as an environmental buffer. One of the major concerns for IPR projects is the presence of contaminants of emerging concern (CEC) in recycled wastewater. CEC are broadly defined as chemicals that can potentially enter the environment, but that are not routinely monitored and could pose health risks to humans or ecology. The objectives of this thesis research are to analyze baseline CEC concentrations in the lake, evaluate periodic tendencies, compare results to previous CEC studies, and identify probable sources for the detected CEC. Stakeholders can use the results to assess the effectiveness of the environmental buffering, and design necessary advanced water treatment at the NWRF before the IPR project commences.

Four water sampling events were completed at Lake Thunderbird in Norman, OK during 2016 and 2017 with each event representing a season. Water samples were collected at six lake sites and analyzed for 113 unique CEC including compounds in four categories: 1) industrials, 2) pesticides, 3) pharmaceuticals and personal care products (PPCP), and 4) “others”. Sub-watersheds were delineated and loading factor models were developed for each sub-watershed to assess potential CEC contributions based on land use, density of domestic wells (as a proxy for density of septic tanks), and density of storage tanks.

Eight, 21, 24, and 24 CEC were detected in June 2016, October 2016, January 2017, and April 2017 samples, respectively. The compound NP was detected in fall,

winter, and spring, making it the most frequently detected industrial compound. The pesticides atrazine and simazine were detected in every season, most likely because of year-round lawn or agricultural applications. Acesulfame-K (artificial sweetener) and DEET (insect repellant) were also detected in every season, those compound detections could be the result of runoff from residential areas or from recreational use of the lake. CEC are likely derived from seasonally variable sources, such as lawn applications and septic systems. Concentrations of atrazine, simazine, and 2, 4-D detected in Lake Thunderbird are well below EPA established maximum contaminant levels (MCLs) for drinking water. Nine other compounds detected in Lake Thunderbird are below non-federal health standards, available from the Minnesota Department of Health, which indicates that Lake Thunderbird water is likely safe for consumption with regard to CEC.

Comparison of Lake Thunderbird CEC concentrations to a microcosm study of Norman Water Reclamation Facility (NWRF) effluent in Dave Blue Creek sediment with photosynthetically active radiation (PAR) indicate that the environmental buffering may sufficiently reduce concentrations of CEC before they reach Lake Thunderbird during the planned IPR project. Future investigations should define the half-life and health standards that are presently unavailable for the 113 CEC analyzed in this study. Additional investigation, sampling, and analysis of current NWRF effluent discharge and receiving waters of the Canadian River would be beneficial for documenting environmental buffering effects.

Chapter 1. Introduction

In 2014, the (City of) Norman (OK) Utilities Authority produced a 2060 strategic water plan that projected a water shortage before the year 2020 (Figure 1). One augmentation option in the strategic water plan was to design an indirect potable reuse (IPR) project that would aid in recycling Norman's water (Norman Utilities Authority, 2014). The IPR project would consist of discharging treated effluent from the Norman Water Reclamation Facility (NWRF), which currently discharges into the Canadian River, into Dave Blue Creek, a tributary of Lake Thunderbird (Figure 2). Hypothetically, Dave Blue Creek and Lake Thunderbird, managed by the Central Oklahoma Master Conservancy District (COMCD), would serve as an environmental buffer that promotes natural degradation and attenuation of CEC before water reaches the water intake that provides water to Norman, Midwest City, and Del City. In preparation for a potential IPR project, COMCD contracted with researchers at the University of Oklahoma (OU) to evaluate baseline contaminants of emerging concern (CEC) in Lake Thunderbird and examine the data in context with other research related to CEC in the Lake Thunderbird watershed.

Water sampling was completed for six sites on the lake during each season to evaluate the water quality in Lake Thunderbird, and to establish a baseline that could be used in the design of water treatment goals. The samples were analyzed for CEC, which are defined as chemicals that are not commonly monitored in the environment but could have the potential to enter the environment and have harmful effects to humans and ecosystems (Alvarez et al., 2014). A suite of 98 compounds were analyzed during the summer (Jun 2016), fall (Oct 2016), winter (Jan 2017), and spring (Apr 2017), and

another suite of 43 compounds were analyzed during winter (Jan 2017), and spring (Apr 2017); which when combined amount to 113 unique compounds.

The compounds are categorized as 1) industrials, 2) pesticides, 3) pharmaceuticals and personal care products (PPCP), and 4) “other” (Murray et al., 2010). Compounds in the other category are chemicals that did not easily fit into the other three but could still be present in a water source, includes compounds such as caffeine (stimulant) and cotinine (an alkaloid of tobacco). The second suite of CEC included perfluorinated compounds (PFC), which were proposed by the OU principal investigator as a project modification because of numerous recent scientific reports documenting their occurrence and health hazards in water, as well as media attention that resulted when PFOA exceeded 400 ng/L in Hoosick Falls, NY water supply (EPA, 2017; Hoffman et al., 2010; Kannan et al., 2005; Post et al., 2012). The PFC have either never been analyzed in waters of Oklahoma or have never been detected and reported to the water quality database maintained in the USGS National Water Information System (NWIS).

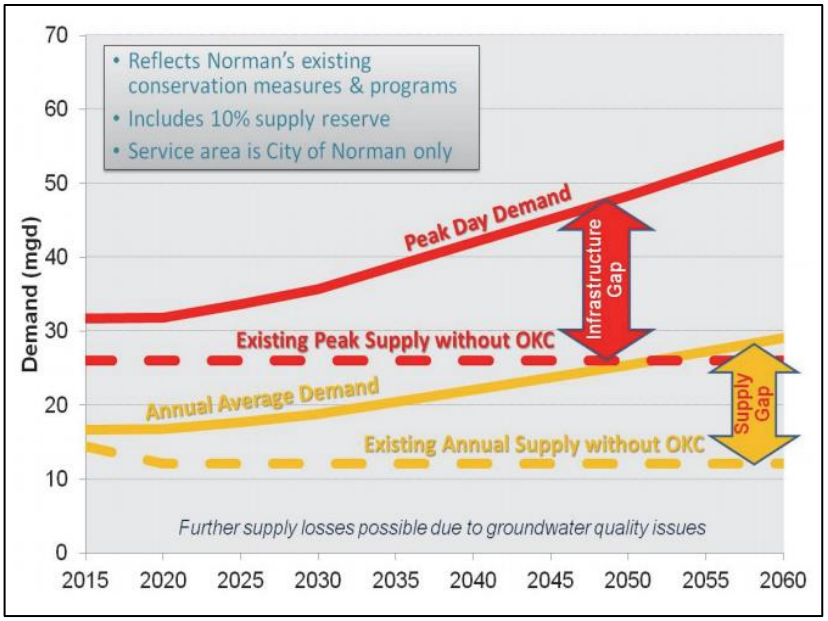

Figure 1. Water demand projections to the year 2060 and anticipated shortages in the water supply, representing the need for Norman to reuse water (Norman Utilities Authority, 2014).

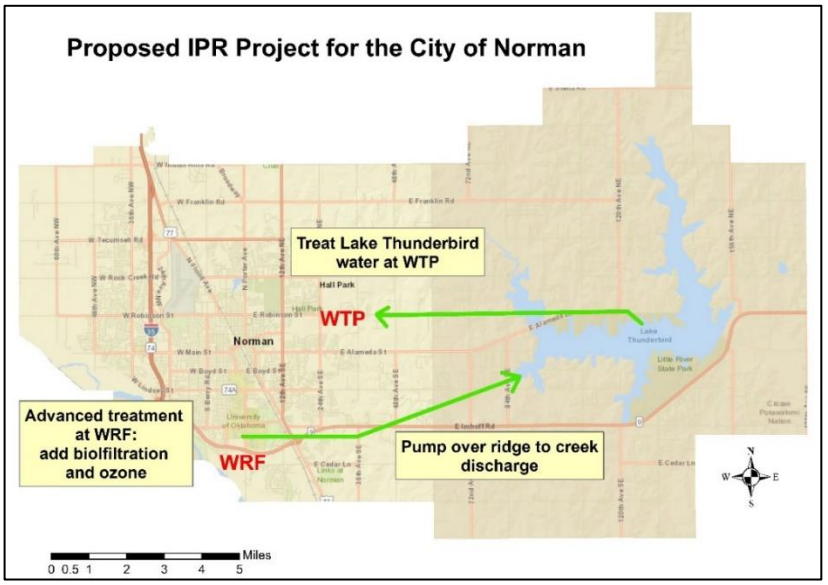

Figure 2. Schematic of the proposed IPR project of augmenting water in Lake Thunderbird, Norman, OK by treating the water at Norman's water reclamation facility (WRF), pumping the water into Dave Blue Creek, then sending it to the water treatment plant (WTP) (Modified from Norman Utilities Authority, 2014).

Chapter 2. Background

2.1 Contaminants of Emerging Concern

As previously stated, the compounds analyzed in this study fall into four classifications; 1) industrials, 2) pesticides, 3) PPCPs, and 4) others. The industrial compounds fall into three main categories, which include organophosphates, alkylphenols, and PFC. Organophosphates, such as tris-(2-chloro-, 1-methyl-ethyl)-phosphate (TCPP), tris- (2-chloroethyl)-phosphate (TCEP), and tris- (dichloro-iso-propyl)-phosphate (TDCP) are mainly used in polyurethane foam or concrete applications, and are reportedly carcinogenic (Li et al., 2014). They are sourced from sewage treatment plants, concrete, and liquid polyurethane spray (Andresen et al., 2004). Alkylphenols (bisphenol A - BPA, 4-nonylphenol - NP, 4-tert-octylphenol - OP) are endocrine disruptors (the compounds can affect hormone systems), like many of the pharmaceuticals and personal care products (PPCP) (Amiridou and Voutsda, 2011). The alkylphenols are thought to be sourced from septic systems, sewage treatment plants, and textile plant discharges and there are also instances of endocrine disruption (Rudel et al., 1998). The PFC are surfactants like PFBA (perfluorbutanoic acid), PFBS (perfluorobutanesulfonic acid), PFHxA (perfluorohexanoic acid), PFOA (perfluorooctanoic acid), PFOS (perfluorooctanesulfonic acid), and PFpeA (perfluoro-n-pentanoic acid); these compounds are used in shampoo, carpet coatings, foams, and paper (Giesy and Kannan, 2001).

Pesticides have been detected in surface water and groundwater samples across the US since the 1990s. Pesticides most prevalent in the environment are triazines (atrazine, simazine, and cyanazine) and acetanilides (Cohen et al., 1995). Herbicides in

drinking water and food may cause acute and chronic health problems to humans (Lichtenberg and Zimmerman, 1999). The triazine herbicides can cause breast cancer, two of which (atrazine and simazine) are listed on the EPA national primary drinking water regulations (NPDWR) (Table A 7). Cyanazine, a triazine herbicide, can cause genetic mutations and birth defects because it is a reproductive toxin (Cohen et al., 1995). These contaminants are usually sourced from runoff of crop lands or hay pasture lands.

Pharmaceuticals and personal care products (PPCPs) are unregulated, but the contaminants have been detected in drinking water supplies across the world since at least 1995 (Baronti et al., 2000). PPCPs are present in the environment predominantly from medicated humans and animals. Research indicates that 90% of antibiotics are excreted after consumption (Storteboom et al., 2010) and then can enter drinking water supplies from municipal wastewater discharge. Another issue is that livestock are heavily medicated with antibiotics and hormones that are also not completely absorbed, meaning runoff from livestock operations could also be contaminating drinking water, either directly from the animal excretion or indirectly through manure applications to agriculture (Boxall et al., 2003). These types of chemicals are also a threat because they can be endocrine disruptors, which sometimes lead to cancer, developmental disorders, and birth defects (Nikolaou et al., 2007).

"Other" compounds include DEET (insect repellant), sucralose (sugar substitute), cotinine (nicotine degradant), caffeine (stimulant), acesulfame-K (sugar substitute), 1,7-dimethylxanthine (caffeine metabolite), and theobromine (caffeine degradant). DEET is present in surface waters and is most likely the result of recreational use when humans are in direct contact with surface water, considering that it is only used on humans, but

can also be present in wastewater or as part of urban runoff (Tran et al., 2013). The EPA has defined DEET as a Group D carcinogen, meaning that some effects appear to be carcinogenic but there may not be evidence that is statistically significant. Although it is not a carcinogen, there have been many reports of children having seizures and neurotoxicity when in contact with DEET, so the EPA is investigating a potential direct link between the two (EPA, 1998), but to date there have been no definitive correlations.

Caffeine (including degradants/metabolites) and cotinine are both stimulants that are used worldwide by humans. They are both thought to be present in surface waters because they are sourced from leaking septic systems or wastewater contamination (Bradley et al., 2007). It is unknown if these contaminants have any severe impacts on humans at such small concentrations.

Sugar substitutes, like sucralose and acesulfame- K, are widespread in groundwater, surface water, and wastewater samples (Mawhinney et al. and Soh et al., 2011). Sucralose persists in the environment longer than acesulfame-K, making it a good anthropogenic marker, but the long-term low-dose toxicity effects have not been evaluated, which means it is unknown how this contaminant will affect human or ecological health if consumed over a long period of time (Soh et al., 2011).

2.2 Water Reuse

Recycled water has been widely accepted in the past for irrigation and agricultural purposes, but public concern is greater surrounding reuse for drinking water supply (Rodriguez et al., 2009). While it might not always be accepted, water sources are depleting, and potable reuse is more environmentally sustainable (AWWA, 2016). Water reuse/recycling can either be classified as direct potable reuse (DPR) or indirect potable

reuse (IPR). DPR involves the movement of purified water directly into an existing public water supply system (Figure 3). IPR requires the treatment of municipal wastewater to be discharged into a water source to augment the water supply (Figure 4), which acts as an environmental buffer (AWWA, 2016). In this case, the Dave Blue Creek stream system and residence in Lake Thunderbird would be acting as an environmental buffer whereby sorption, photodegradation, biodegradation, and attenuation would be reducing compound concentrations before the water is reintroduced into the City of Norman public water supply system.

Thornton (2017) analyzed the effectiveness of 15 days of sorption to Dave Blue Creek (DBC) sediment and photosynthetically active radiation (PAR) on reducing CEC concentrations in NWRF effluent. Thornton (2017) showed that both sorption to sediment and photodegradation are efficient in reducing or removing CEC concentrations, but photodegradation was more effective and could be very important for CEC removal (Table A 1).

IPR projects have been successful in multiple states including California, Arizona, Colorado, Texas, Florida, and Virginia, with California using these kinds of reuse systems for over 40 years (AWWA, 2016). Each state has its own guidelines for evaluating IPR as a viable option for their water resources, but each of them suggest continuous monitoring of water quality such as turbidity, nitrogen, and CEC compounds.

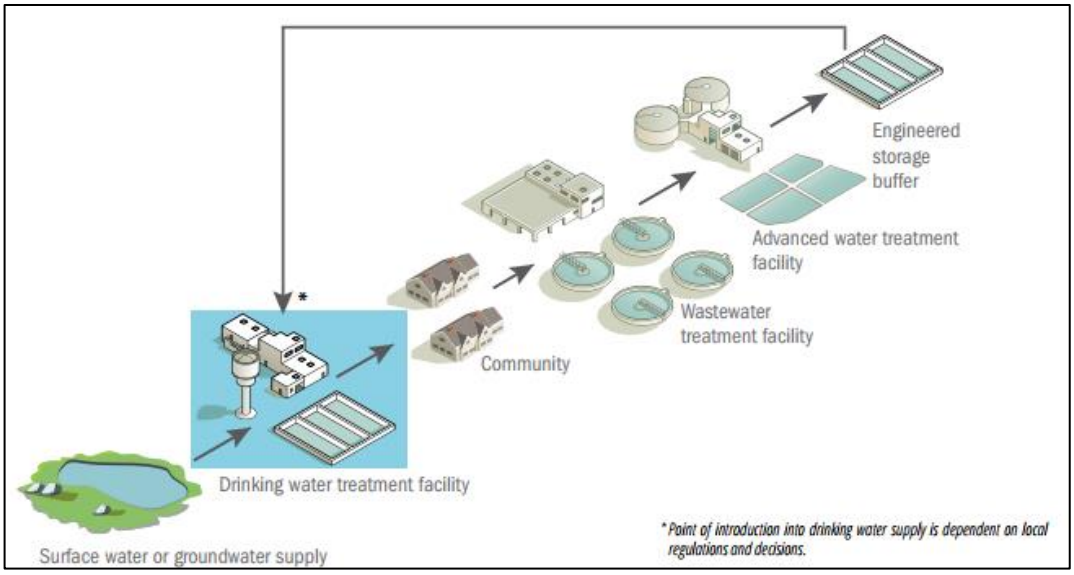

Figure 3. Schematic of a typical DPR project (AWWA, 2016).

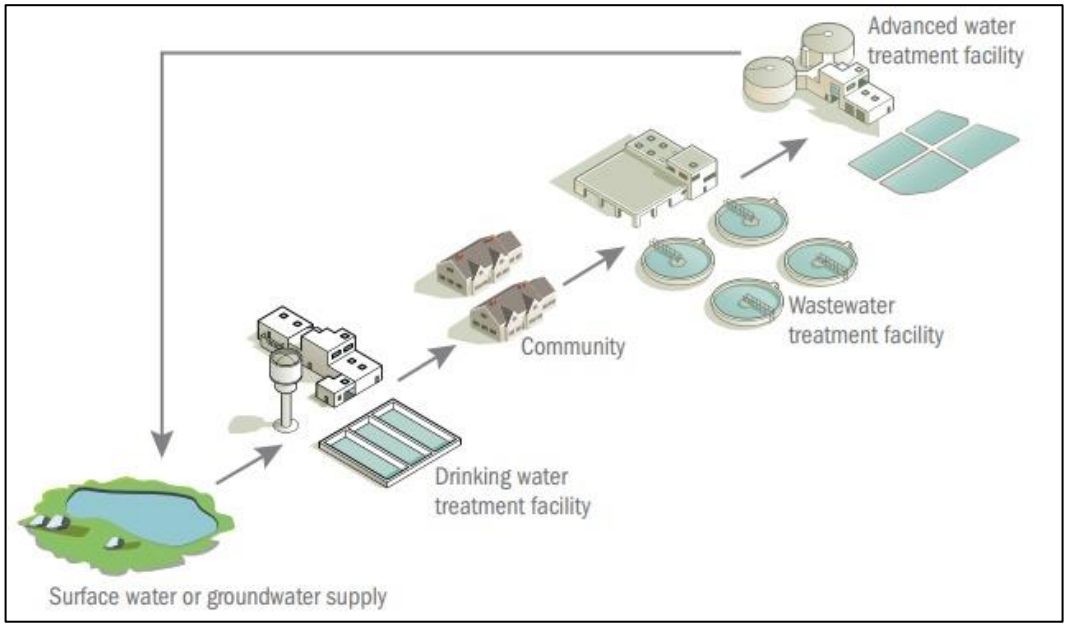

Figure 4. Schematic of a typical IPR project (AWWA, 2016).

2.3 NWIS Data

Only 66 CEC, out of the 113 analyzed in our study, had parameter codes in the U.S. Geological Survey (USGS) National Water Information System (NWIS) database

of water quality samples. A parameter code is a unique identifier used on the NWIS site that corresponds to a compound, the sample medium, and the units of measure. Among the 66 compounds with parameter codes, only 44 were detected in Oklahoma (Tables A 2–6). The absence of CEC data emphasizes that CEC are not commonly investigated. However, pesticides such as atrazine and simazine are commonly detected in water sources throughout Oklahoma.

2.4 Study Area

Lake Thunderbird is in central Oklahoma and captures runoff from parts of Cleveland and Oklahoma Counties. The multi-purpose reservoir, constructed in 1966 by the Bureau of Reclamation, has many uses including recreation, municipal water supply, ecosystem propagation, and flood control (OWRB, 2014). Lake Thunderbird has an area of 5,439 acres, volume of 105,838 acre-feet, shoreline of 59 miles (95 km), mean depth of 15 ft (4.7 m) water supply yield of 19.4 million gallons per day (MGD), and a mean monthly discharge of 74.5 cubic feet per second (cfs). Land use in the watershed includes residential (medium and high density), agriculture (generic and pasture), commercial, industrial, transportation, and open water (OWRB, 2001). Sixty percent of the watershed is agricultural and the majority of the remaining 40% is residential, which makes these land uses the focus of source investigations for CEC contamination by runoff. Industrials could be from runoff of storage tanks, septic systems, developed land, or cultivated land (Giesy and Kannan, 2001; Andresen et al., 2004; Li et al., 2014). PPCP entering the lake are possibly sourced from septic systems, developed land, or cultivated land (Baronti et al., 2000; Boxall et al., 2003; Nikolaou et al., 2007; Storteboom et al., 2010; Amiridou

and Voutsda, 2011). Pesticide contamination could be the result of runoff from developed, cultivated, or herbaceous land use (Cohen et al., 1995; Lichtenberg and Zimmerman, 1999). The other class of compounds are most likely sourced from septic systems and developed land only (Bradley et al., 2007; Mawhinney et al. and Soh et al., 2011; Tran et al., 2013).

As shown in Figure 5, the Lake Thunderbird watershed has several tributaries with the largest being the Little River. Other tributaries of the watershed include West Hog Creek, Hog Creek, West Elm Creek, Elm Creek, Kitchen Creek, Moore Creek, Rock Creek, Dave Blue Creek, Jim Blue Creek, and Clear Creek (OCC, 2008).

The wildlife present in Lake Thunderbird include sport fish and endemic fish. The sport fish include largemouth bass, white crappie, black crappie, blue catfish, channel catfish, flathead catfish, white bass, saugeye, bluegill sunfish, green sunfish, and redear sunfish. The endemic fish include common carp, small mouth buffalo, big mouth buffalo, river carp sucker, fresh water drum, spotted gar, gizzard shad, inland silverside, warmouth, longear sunfish, yellow bullhead, red shiner, blunt nose minnow, and mosquito fish (ODWC, 2008). Aquatic organisms of the lake will be important for any future studies on the effects of CEC on ecologic systems.

The reservoir is the main source of drinking water for the City of Norman, OK and augments water for the cities of Midwest City and Del City, OK, which have a combined population of 201,435 (OCC, 2008). Lake Thunderbird has been considered a sensitive water supply (SWS) since 2002, meaning that the lake is monitored for water quality parameters and may require treatment by COMCD under regulatory guidance by OWRB (OWRB, 2017). Lake Thunderbird is considered impaired due to excessive

chlorphyll-a (Chl-a) and turbidity, and low levels of dissolved oxygen (DO) (OWRB, 2015). Whilst the focus of this project is to analyze CEC concentrations, Chl-a and DO were also evaluated to document water quality indicators of interest for management of the lake.

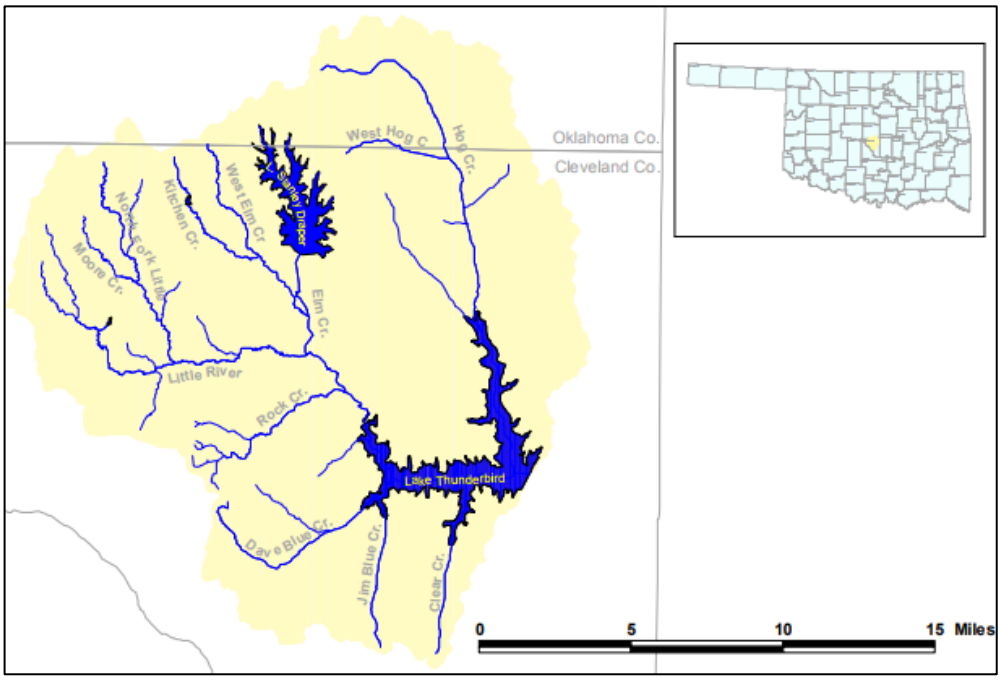

Figure 5. Schematic of the Lake Thunderbird Watershed (OCC, 2008).

2.5 CEC Treatment Approaches

In the original City of Norman IPR project plan, anticipated wastewater treatment techniques included biofiltration and ozone at the water reclamation facility (Figure 2). Lee et al. (2012) investigated the effects of treating 83 different PPCP, with PPCPs that are similar to the compounds in this study, using biofiltration and ozone. Ozone is used to treat PPCP because it forms hydroxyl radicals in the presence of natural organic matter that react quickly, which decreases the concentrations or completely degrades the PPCP or other micropollutants. Although the ozone method can reduce or remove PPCP, the

process can create disinfection by-products (DBP); therefore, biofiltration uses biologic material in conjunction with the ozone method to remove oxidation products that were generated. Lee et al. (2012) used ozone doses ranging from 0–12 mg/L and a biofilter media of anthracite (Figure 6).

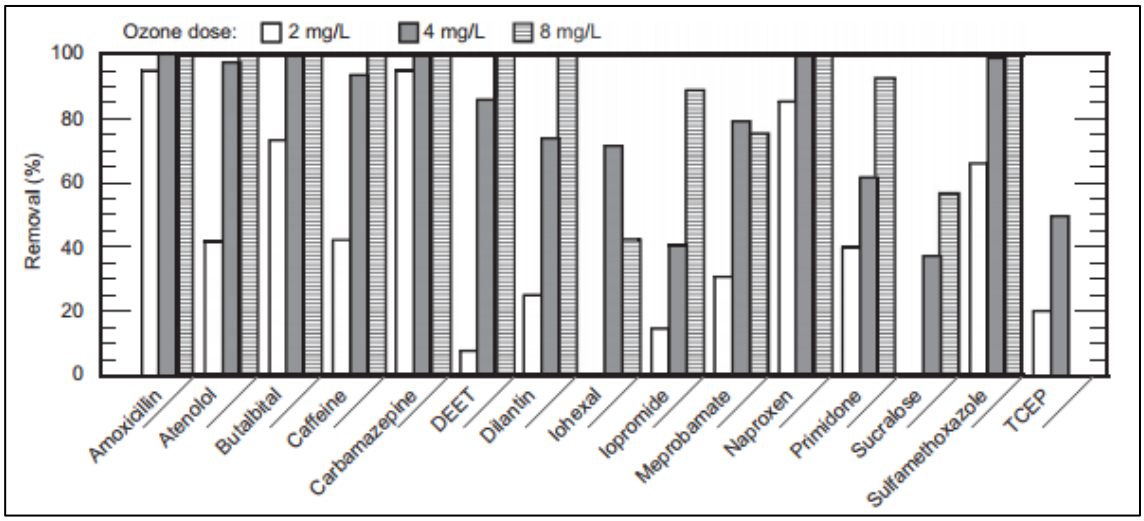

Figure 6. Results of removal of PPCP by the ozone dosages 2, 4, and 8 mg/L (Lee et al., 2012).

Lee et al. (2012) study of the treatment techniques showed that 52 of the PPCP were detected within the ozone contactor influent and had similar concentrations in the ozone and biofilter effluent, which indicated that the biofiltration did not remove or degrade the contaminants (Lee et al., 2012). The results for compound removal by ozone are shown in Figure 6, note that each compound shown was also analyzed in this study. Some CEC including amoxicillin, carbamazepine, and naproxen were rapidly removed even at the lowest ozone dosage. Other CEC such as iohexal, iopromide, meprobamate, primidone, sucralose, and TCEP were never completely removed at any of the ozone

dosages. Biofiltration has also been effective for the removal of pesticides (van der Aa et al., 2012).

Reverse osmosis (RO) with nanofiltration (NF), another treatment technology investigated for removal of CEC from wastewater in Norman, involves filtering water through a membrane to remove micropollutants. A study completed by Radjenović et al. (2008) concluded that RO/NF was very effective in removing PPCP, with a rejection >85% for uncharged solutes and >95% for negatively charged pharmaceuticals; researchers stated that the method could remove almost all the residues detected. RO has also been used to remove pesticides in water (Plakas and Karabelas, 2012), but difficulties arose due to membrane fouling.

Jones (2016) investigated the primary and secondary effluent from Norman's water resource recovery facility (WRRF) and reported that out of the 96 CEC analyzed, 82 were detected in primary effluent and 64 in secondary, which means the biodegradation is already occurring in the WRRF. Jones (2016) also concluded that NF met the available published and regulatory standards for CEC and found that it can remove many PPCP and industrial compounds but did not remove all. While the RO/NF method has been proven to be effective, Lee et al. (2012) argue that biofiltration and ozone is a better option because it is nearly as effective and has lower energy costs, lower waste production, higher water recovery, and lower maintenance costs.

The aforementioned advanced treatment methods can reduce or remove CEC, but with the results from Jones (2016) showing biodegradation is occurring in the WRRF, and Thornton's (2017) results of DBC sediment and PAR lights reducing or removing concentrations, advanced treatment might not be necessary. The environmental buffer

effect might be sufficient in reducing or removing CEC to regulatory and health standards.

2.6 Research Objectives & Hypotheses

The research objectives and hypotheses of this project are to (1) evaluate baseline CEC concentrations in Lake Thunderbird, Norman, OK; CEC have been found in other reservoirs in Oklahoma and in Norman's WRF, therefore those contaminants could be in Lake Thunderbird as well (2) examine seasonal and spatial variations; seasons with more rainfall will cause more runoff, i.e., there will be more pollution in the lake (3) compare CEC concentrations to established health standards, (4) synthesize CEC work completed by Thornton (2017) in Dave Blue Creek with CEC detected in Lake Thunderbird to assess potential environmental buffering effects of the planned IPR project, and (5) qualitatively assess potential sources of CEC in the Lake Thunderbird watershed and based on land use within each sub-watershed; land use type affects the type of CEC contaminating the lake.

Chapter 3. Methodology

Six locations (Sites 1, 4, 6, 7, 8, and 11), a subset of nine locations previously sampled by the Oklahoma Water Resources Board (OWRB) during water quality studies (OWRB, 2014 & 2015), were selected as the sample sites (Figure 7 and Table A 8). Four water sampling events were planned to represent each season: June 20, 2016 (summer), October 4, 2016 (fall), January 24, 2017 (winter), and April 6, 2017 (spring). Samples were taken seasonally to understand what role temperature and rainfall play in CEC detections. A hypothesis of how the seasons could affect CEC is that more rainfall would lead to more runoff causing more CEC detections in the lake (since many of the CEC are linked to runoff). Turnover of the lake from summer to fall and winter to spring, when the cold layer is on top, could reduce photodegradation of CEC, resulting in greater detections.

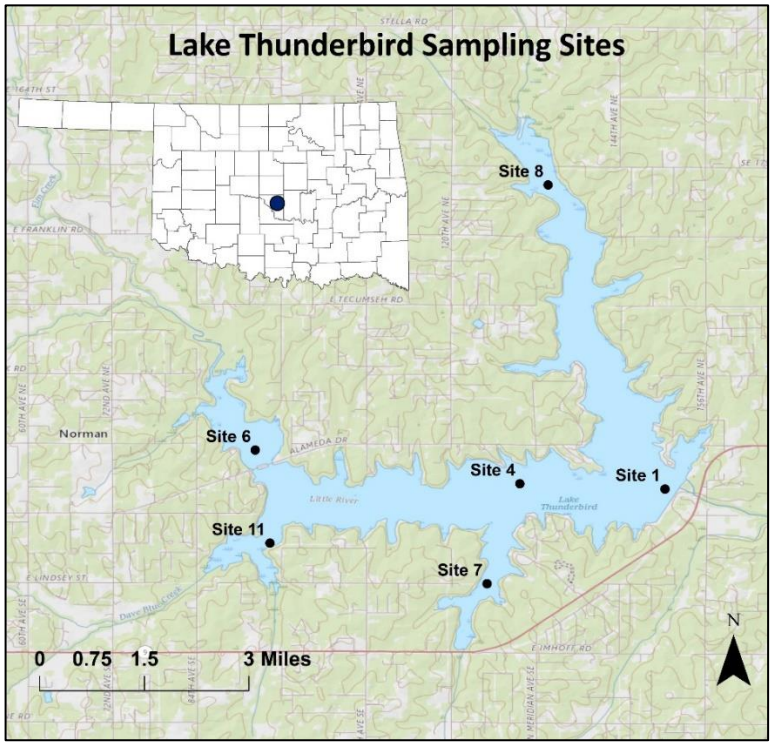

Figure 7. Sampling locations at Lake Thunderbird.

3.1 Field Parameters

Field parameters were measured at 2/3 depth using a Yellow Springs Instruments (YSI 6920) multi-parameter water quality sonde from the Center for Restoration of Ecosystems and Watersheds Lab (CREW) at OU. Parameters measured include temperature (Temp, °C), conductivity (Cond, µS/cm) which was used to calculate specific conductance (SpCond, mS/cm) at 25°C, total dissolved solids (TDS, mg/L), and salinity (Sal, ppt). The YSI 6920 was also used to measure resistivity (Resist, Ohm*cm), pH (-Log[H+]), oxidation-reduction potential (ORP, mV), chlorophyll-a (Chl-a) measured in µg/L and in Relative Fluorescence Units (RFU), and optical dissolved oxygen (ODO) expressed in percentage saturation (SAT) and as a concentration (mg/L).

3.2 Water Sampling for CEC

Since the compounds are measured in trace concentrations (ng/L or ppt), investigators were very careful not to use or touch products containing PPCP or other compounds such as acetaminophen or caffeine. Investigators also wore powderless nitrate gloves, and new gloves were used for every sampling location. Water samples were collected with a 1.2 L stainless steel Kemmerer water sampler that has Teflon-end seals (Figure 8). Samples were collected around 1/3, 2/3, and 3/3 depths. After sample collection at each depth, the Kemmerer sampler was emptied into a one-gallon glass container to form a composite sample of the water column. The Kemmerer water sampler was decontaminated between each site by rinsing with deionized water and passing through the vertical column of water at the next sampling site.

Figure 8. Stainless Steel 1.2 L Kemmerer water sampler.

After samples were composited into a one-gallon glass container, water was transferred into two 40 mL amber glass bottles (for EEA and WEST labs) that contained preservatives to avoid biological degradation of the compounds. The bottles were capped and shaken to combine the preservative and the sample. The samples were stored in a cooler to aid in sample preservation during the field sampling event. An equipment blank and blind duplicate (fall, winter, and spring) were also taken as quality control and quality assurance (QA/QC) samples. The equipment blank was collected by pouring deionized water into the Kemmerer sampler and into a specified equipment blank amber bottle. The purpose of an equipment blank is to assess whether contamination was introduced during the sampling process. Blind duplicates were used to determine the accuracy of the analytical method used, because while it is blind to the lab, the samplers know which site it was taken from and can then compare it to the reported values for that site.

After each sampling event, samples were packed on ice and shipped to labs for CEC analyses. The first suite of chemicals (Table A 9) were analyzed by Eurofins Eaton Analytical lab (EEA) for each sampling event and the second suite of chemicals (Table A 10) were analyzed by the University of Arizona Water & Energy Sustainable Technology (WEST) lab after the winter and spring sampling events.

3.3 CEC Analyses – Eurofins Eaton Analytical

The EEA lab externally analyzed the water samples using solid phase extraction and liquid chromatography/ tandem mass spectrometry (SPE - LC/MS/MS) endocrine disruptor mode (positive and negative) method to test the concentrations of the compounds, in accordance with EPA Method 544 (EPA, 2015). The method involved direct injection and a run time of less than 15 minutes. The water samples were 500 mL and immersed in an intracellular toxin solution and filtered, then the filter and filtrate were kept. The filter was in a solution of methanol that had 20% reagent water (water with low minerals and high resistivity) for a minimum of an hour at -20°C. Next, liquid was taken off the filter and added back into the original sample solution. The sample was then put through an SPE cartridge to extract the target compounds. After extraction, compounds were removed from the solid phase with methanol and 10% reagent water.

Extracts were subsequently evaporated with nitrogen in a heated water bath until they were dry, then refined to 1 mL volume with methanol and 10% reagent water. Once samples were refined to 1 mL, a 10 µL injection was made into an LC that contained a C8 (octylsilane) column for MS/MS. The acquired mass spectra and retention times for calibration standards acquired under identical LC/MS/MS conditions were compared, and

the concentrations were determined by external standard calibration (EPA, 2015). The MS was used in positive and negative modes to determine positive or negative ions.

3.4 CEC Analyses – University of Arizona WEST

The University of Arizona WEST lab sampling procedures were similar to the EEA lab in that the water samples collected by the Kemmerer were then transferred to amber vials. The vials contained 50 mg ascorbic acid and 1 g sodium azide to hinder possible microbial activity. The WEST samples also had to be cooled during shipment and were filtered through a 0.7 μm glass filter upon arrival to the facility. Samples were stored in darkness and kept on ice, then analyzed within 14 days of being received (Vanderford et al., 2011).

The WEST lab externally analyzed the water samples using ultra-high-performance liquid chromatography tandem mass spectrometry (UHPLC-MS/MS). The method the lab used was described in Anumol et al., (2013) and is summarized in this section. An automated SPE system was used to extract the samples with a 200 mg hydrophilic-lipophilic balance (HLB) cartridge. HLB cartridges were preconditioned with 5 mL of methyl tertiary-butyl ether (MTBE), then 5 mL of methanol and ultrapure water. After cartridges were prepared, compounds were removed with 5 mL of a 10/90 methanol/MTBE solution. Evaporation dried the extracts to less than 500 μl with a nitrogen flow, volumes were adjusted to 1 mL by adding methanol. Finally, the extracts were put into 2 mL vials and stored in darkness at 4°C until they were ready for UHPLC-MS/MS analysis.

Liquid chromatography was performed on 3 μL of sample extract using an Agilent 1290 binary pump with metal solvent fittings. The Agilent RRHD ZORBAX Eclipse Plus reverse phase C18 (octadecyl) was used to separate compounds in both the negative and positive electrospray ionization (ESI) modes. Next, mass spectrometry was executed with an Agilent 6460 triple quadrupole mass spectrometer. Analysis from both the electrospray ionization (ESI) positive and negative modes was performed using a multiple reaction model (MRM) method. Interpretation of the data was completed with the Agilent MassHunter software and monitoring of the labeled isotope recoveries, the retention time, and the ratio of the two transitions, which increased the accuracy of detection and reduced the possibility of false positives of the method (Anumol et al., 2013).

The WEST lab method detection limit (MDL), lowest concentration that is measurable, varied for each compound and each site. The MDL values were initially determined by removing samples from ultrapure water that contained target compounds two to three times the limit of quantification and spiking them with known concentrations. After being analyzed, the MDL was calculated by the multiplication of the standard deviation and the student's t-test value for n-1 degrees of freedom at 99% confidence (Anumol et al., 2013).

3.5 Horton vs. Thornton

Thornton's (2016) study that investigated the use DBC sediment and PAR light treatment to naturally degrade CEC in Norman's secondary effluent compared to the present study of ascertaining CEC in the lake (without effluent being introduced) is paramount to determine if IPR is achievable. First, the values of secondary effluent, before sediment or PAR light were added, were compiled. Next, the values of the effluent

after fifteen days with DBC sediment and effluent after fifteen days under PAR light were compared to the original secondary effluent values. Lastly, the values were compared to median values detected in Lake Thunderbird (Table A 1).

3.6 CEC Loading

A qualitative watershed loading factor model was created using ArcGIS. The term loading factor is meant to describe the possible sources of contamination, e.g. loading, by runoff into the lake, and the purpose of the model is to qualitatively assess which sub-watersheds have higher likelihood of contributing CEC to the lake by runoff based on land use. First, basemap features were downloaded for the Lake Thunderbird watershed in Cleveland and Oklahoma Counties. Next, potential sources of contamination were determined based on percentage of land uses within a sub-watershed, number storage tanks (gasoline and diesel) per acre, and number of domestic wells per acre (domestic wells were used as a proxy for septic tanks, since septic tank data cannot be retrieved). Pesticides are most likely from urban and agricultural runoff. Compounds from the industrials category could be sourced from urban runoff and leaking storage tanks. Sources for PPCP and hormone contamination could be derived from septic tanks, urban runoff, or agricultural runoff. Other compounds are most likely sourced from urban runoff and septic tanks.

After the main watershed and the land uses within it were mapped out, the sub-watersheds were delineated, and the possible loading factors were evaluated for each category of compound. For the purposes of this analysis, sub-watersheds were delineated for the tributaries that directly enter the lake (i.e. Little River, Hog Creek, Dave Blue

Creek, and Clear Creek). The sub-watersheds had different loading factors based on land use, and the different land uses were overlaid and weighted depending on what class of compound that map was focused on; an example would be PPCP contamination mostly sourced from developed land use, therefore developed land use would be the most heavily weighted loading factor.

Data for land use was retrieved from the USGS Land Cover Institute (LCI) website and digital elevation model (DEM) data was also collected from the USGS, but the The National Map (TNM) website (USGS, 2017). Storage tank (in use) data was gathered from the Oklahoma Department of Environmental Quality data viewer website (ODEQ, 2017). Lastly, watershed data was collected from the national hydrologic dataset of the USGS.

The thematic land use descriptions that were used in this analysis are as follows: developed land is any area that has a percentage of 30 or higher of constructed materials, like concrete, buildings, or asphalt which can be residential, commercial, or manufactured areas; herbaceous land is an area that is covered 75–100% by herbaceous vegetation and is often used for grazing; and cultivated lands include cultivated crops and hay pasture land cover that are characterized by planted vegetation for the production of food, fiber, or feed (USGS, 2017).

Sub-watersheds were delineated using a variety of spatial analysis tools in ArcGIS. First, a 10-m resolution DEM was downloaded and filled by removing imperfections or sinks in a surface raster (the 10-m DEM). Next, the flow direction tool was applied to create a raster of flow direction from a cell to its steepest downslope neighbor. Following flow direction, the flow accumulation tool was used to compute the

number of upstream cells from the flow direction raster that would contribute flow to every cell in the watershed. After flow accumulation, pour points (i.e. points of highest accumulation) were chosen for each sub-watershed to perform the snap pour point method by "snapping" the chosen pour points into the actual points of highest accumulation. Lastly, the watershed tool delineated the basins, or contributing areas, for the snapped pour points.

3.6.1 Modelling for Relative Loading

Relative loading (of CEC) from sub-watersheds was evaluated using an index-modeling approach that resembles the "export coefficient model" approach of Mattikalli and Richards (1996), whereby equations were created to weight the relative contributions of land use to CEC concentrations at the output into Lake Thunderbird. Two benchmark compounds were selected for each classification of analyte for each lab, based on highest number of detections. Equations were constructed using the most probable sources of runoff contamination, i.e. land use types or leaking tanks, for each type of compound (described in Chapter 2.4 "Study Area"). The loading factor variables were weighted by comparing the predicted loading factor to the observed median concentrations of benchmark compounds and adjusted to maximize the coefficient of determination (R^2) for the loading factor. All sampling sites have a corresponding sub-watershed except sites 1 and 4, therefore data for the entire watershed was used for those sites in the model for best fit, and if a site did not have a median concentration, ½ the MRL was used.

3.6.2 Equations for Relative Loading

Variables used to assess relative loading are as follows:

ST = # of in use storage tanks per acre

SS = # of domestic wells per acre (proxy for septic systems)

D = fraction of total developed land use

C = fraction of cultivated land use

H = fraction of herbaceous land use

For the industrial compounds, the following equation and benchmark compounds were used:

Equation: ST + SS + D + C

Benchmark compounds:

EEA

1. NP: three detections in fall, two in winter, two in spring
2. OP: three detections in fall

WEST

1. TCPP: three detections in spring
2. PFOS: five detections in winter, six in spring

NP and OP are used in commercial and household cleaning products, industrial processing, fabrics, shoes, paints and coatings, lotions, liquid cosmetics, and lawn care, crop protection products (Federal Register, 2014). TCPP is used as a flame retardant and for plastics. PFOS is used to make carpets, clothing, fabrics for furniture, paper packaging for food, materials that are resistant to water, grease or stains, firefighting at airfields, and in industrial processes (EPA, 2016). The industrial compounds evaluated in this study are

organophosphorus or alkylphenol compounds. The organophosphorus compounds are most likely sourced from developed land use (used for concrete, flame retardation, and pest control) and the alkyphenols are probably sourced from leaking storage tanks or septic systems (domestic well as proxy for septic tanks).

For the pesticide compounds, the following equation and benchmark compounds were used:

Equation: C + D + H

Benchmark Compounds:

EEA

1. Atrazine: six detections in summer, four in fall, six in winter and spring
2. Simazine: six detections in summer and fall, five detections in winter and spring

WEST

1. Atrazine: five detections in winter, six in spring
2. Simazine: five detections in winter, six in spring

Both atrazine and simazine are pesticides that are widely used in agriculture and developed areas (maintenance of roadsides, commercial areas, lawns, and gardens) as effective weed killers, which means runoff from those types of land are the most likely source of contamination (U.S. Geological Survey Circular 1225).

For the PPCP compounds, the following equation and benchmark compounds were used:

Equation: SS + D + C

Benchmark Compounds:

EEA

1. Clofibric acid: five detections in fall, six in winter, three in spring
2. Salicylic acid: three detections in winter, in spring

WEST

1. Iopromide: five detections in winter
2. Propylparaben: five detections in spring

Clofibric acid is used as a lipid regulator and salicylic acid is used for skin care; contamination most likely from runoff near pharmaceutical industries, households, livestock, or wastewater treatment plants (Boxall et al., 2012). Iopromide is an iodinated contrast medium and has been detected in wastewater treatment facilities (Schulz et al., 2008) and propylparaben is used as a stabilizer, bactericide, and flame retardant; it has been detected in industrial runoff and wastewater treatment facilities (Martins et al., 2017).

For the other compounds, the following equation and benchmark compounds were used:

Equation: SS + D

Benchmark Compounds:

EEA

1. DEET: six detections in summer, fall, and winter; five in spring

2. Acesulfame-K: six detections in summer, four in fall, two in winter, five in spring

WEST

1. DEET: five detections in winter, six in spring
2. Acesulfame-K: five detections in winter, six in spring

The other CEC group consists of an insect repellant (DEET), stimulants, and some artificial sweeteners; since those products are exclusively used by humans, it is plausible that they are only sourced from urban runoff and leaking septic tanks. The principal pathway for DEET to enter a drinking water environment is through sewage effluent from washing off humans and excretion by humans (Costanzo et al., 2007). There is a strong correlation between acesulfame-K concentrations in surface waters near heavier population (Muller et al., 2011), because it is generally a constituent of effluent from wastewater treatment plants (Lange et al., 2012).

Chapter 4. Results and Discussion

4.1 CEC Detections – Eurofins Eaton Analytical

More CEC were detected in fall than in the other seasons for the EEA lab, while the fewest CEC were detected in the summer. In the summer there was one industrial detect, two pesticides, one PPCP, and three other detects. Fall sampling event detections included three industrials, nine pesticides, seven PPCP (two of those being hormones), and three others. Winter had the second most detections with one industrial, nine pesticides, five PPCP including a hormone, and four other compounds. One industrial, ten pesticides (most of any season), four PPCP, and three others were detected in the Spring sampling event. Results of the compound concentrations for each season at all six sites can be found in Tables A 11–14 and Figures B 1–32.

4.1.1 Industrial Compounds

The industrial compounds detected include BPA, NP, OP, and TDCPP. BPA was present at three sites in the summer, but not in any of the other seasons; it is considered an alkyphenol and an endocrine disruptor and is used as a monomer for polycarbons and epoxy resins (Kuch and Ballschmiter, 2001). It was probably only detected in the summer because of higher recreational use of the lake in the summer, considering BPA is mostly used in plastic containers. A toxicological summary for BPA completed in 2015 by the Minnesota Department of Health (MDH) quantified the short term non-cancer health standard of BPA to be 100,000 ng/L and a sub-chronic non-cancer health standard of 20,000 ng/L (MDH, 2015); the highest concentration measured in this study was 120 ng/L, substantially lower than the health standard concentrations.

NP was the most common industrial compound, detected in the fall, winter, and spring. Aside from industrial use, NP is used in many residential and commercial products (Federal Register, 2014). The frequent detections of NP could be related to septic systems or from runoff of lawns/crops due to its applications which could have been used year-round; another hypothesis is that NP is more resistant to degradation than the other industrial chemicals considering the others were only detected in the fall. A toxicological summary for NP completed in 2015 by the MDH determined the short term non-cancer health standard of NP to be 100,000 ng/L, sub-chronic non-cancer health standard of 40,000 ng/L, and chronic non-cancer health standard of 20,000 ng/L (MDH, 2015); the highest concentration reported from the present analysis was 530 ng/L and did not exceed the health standards suggested by MDH (2015).

OP and TDCPP were detected only in the fall. As previously stated, OP is used in industrial, residential, and commercial products. A toxicological summary for OP completed in 2015 by the MDH ascertained that the short term non-cancer health standard of 100,000 ng/L, sub-chronic non-cancer health standard of 400,000 ng/L, and chronic non-cancer health standard of 100,000 ng/L (MDH, 2015); 410 ng/L was the highest concentration detected for OP and did not exceed any health standards. TDCPP is used for polyurethane foams, plastics, and fabrics. A toxicological summary for TDCPP completed in 2013 by the MDH resolved a sub-chronic non-cancer health standard of 20,000 ng/L, and chronic non-cancer health standard of 9,000 ng/L (MDH, 2013); the only value detected in the present analysis was 180 ng/L, therefore lower than the health standards. These chemicals possibly were detected in fall samples because of to higher levels of rainfall in September and October than in the summer months.

4.1.2 Pesticide Compounds

The pesticides detected include 2,4-D, atrazine, bromacil, cyanazine, DACT, DEA, DIA, diuron, OUST, quinoline, and simazine. Atrazine and simazine, herbicides of the triazine family, were detected during every season. Triazine herbicides are used to control weeds and conceivably could have contaminated the lake from residential surface water or agricultural runoff. These pesticides have been related to acute and chronic problems with humans and in ecosystems; they have also been linked to several types of cancer (Cohen et al., 1995; Lichtenberg and Zimmerman, 1999; Leeuwen et al., 1999). Atrazine has specifically been linked to disruptions in menstrual cycle functions (Cragin et al., 2011), positively linked with stomach cancer incidents (Leeuwen et al., 1999), can be toxic to fish (Nwani et al., 2010), and cause hermaphroditism and demasculinize male frogs in concentrations as little as 1,000 ng/L (Hayes et al., 2001); levels of atrazine from the present study did not exceed 1,000 ng/L – the highest reported value was 26 ng/L. The levels for atrazine never exceeded the EPA drinking level standard of 4,000 ng/L (Table A 6). Simazine levels were also lower than EPA drinking level standard of 3,000 ng/L (Table A 6), if the compound had exceeded those levels it could cause issues with blood in humans, but the highest value detected was 1,400 ng/L in the spring season. Cyanazine, another member of the triazine herbicides, had one detection in fall. However, cyanazine production has been banned in the U.S. since 1999 and illegal to use since 2002 (EPA, 2000). The unexpected detection of cyanazine may have been the result of a continuing source of cyanazine in the sub-watershed. DACT, DIA, and DEA are

chlorometabolites of the triazine herbicides and presumably persisted in the environment through fall, winter, and spring after summer applications of the parent compounds.

Bromacil, 2,4-D, and Diuron were detected in the fall, winter, and spring. Bromacil is another weed killer and exposure to it has been shown to slow weight gain in dogs, increase incidence of thyroid cysts and tumors in rats, and eye irritation, it is also considered persistent and highly mobile in the environment (EPA, 1996). A weed-killing herbicide, 2,4-D, can cause issues with kidneys, the liver, or adrenal glands. The EPA health standard for 2,4-D is 70,000 ng/L (Table A 6), the standard was never exceeded in this study because the highest value documented was 200 ng/L. Diuron is considered a pre-emergent herbicide to control grasses and weeds, it is usually paired with a surfactant. Diuron is considered persistent in the environment and the estimated health standard for acute (non-cancer) effects is 67,100 ng/L and chronic (cancer) effects is 47,100 ng/L (EPA, 2001). The health standards for diuron were not exceeded in the present study because the highest value attained was 260 ng/ L in the spring season. Diuron is used year-round in residential and agricultural areas and thus detected in nearly every season. Because there is less rainfall in the summer, there is less runoff, and this possibly results in non-detects for diuron in summer.

Quinoline was detected in winter and spring, it is used in petroleum practices, coal processing, wood preservation, solvents, and paints. It biodegrades quickly in aquatic systems (21-day half-life in summer, 160-day half-life in winter), therefore it could have been degraded microbially or photolytically in the summer and fall seasons after initial entrance into the lake from runoff (EPA, 2001). Human health standards for quinoline

were not available. OUST was detected at every site in spring, possibly due to higher uses in that season and more runoff; human health standards were not available for OUST.

4.1.3 PPCP Compounds

Several PPCP compounds were detected including clofibric acid, gemfibrozil, ibuprofen, iohexol, lincomycin, meclofenamic acid, salicylic acid, triclocarban, and trimethoprim. Clofibric acid, used as a lipid regulator (Boxall et al., 2012), was the most frequently detected PPCP, occurring in the fall, winter, and spring. Salicylic acid, used for skin care, was also frequently detected in spring and winter. The only PPCP detected in summer was iohexol, an X-Ray contrast media has been shown to cause cancer by enhancing genotoxicity and cell mutation (Jeong et al., 2017). The aforementioned compounds (clofibric acid, salicylic acid, and iohexal) do not have water-based health standards.

Lincomycin, triclocarban, and trimethoprim were detected at one site in the fall. Lincomycin is an antibiotic, widely used for swine, that could be entering waterways through agrarian land use or leaking septic tanks; there are no health standards for this contaminant (USGS, 2014). Ibuprofen, used as an anti-inflammatory medicine for humans, was detected in fall and winter at one site. The primary pathway for ibuprofen to enter a water way is through wastewater effluent (Bound and Voulvoulis, 2006); health standards could not be found for ibuprofen.

Triclocarban is an antibacterial and disinfectant, it has the potential to enter streams downslope of wastewater treatment facilities. A risk assessment completed by the MDH (2013) determined the chronic non-cancer health standard to be 100,000 ng/L;

the only detection in the present study was 5.1 ng/L. Trimethoprim is also an antibacterial, often is used alongside antibiotics, it can enter the environment through agricultural runoff or leaking septic tanks. The health standard determined by the MDH (2015) to be 4,000 ng/L; the only value obtained by the EEA lab (9.9 ng/L) was well below this standard.

Meclofenamic acid, medication used to relieve pain, was only detected in the winter, and most likely entered water systems through runoff from leaking septic tanks. Health standards could not be acquired for Meclofenamic acid. Gemfibrozil is used to lower cholesterol and triglyceride levels in pancreatitis patients. It was detected in the spring in our study and has been detected in wastewater effluent and marine receiving waters elsewhere (Vidal-Dorsch et al., 2012). There are currently no available health standards for gemfibrozil.

The hormone compounds detected, which are a subcategory of the PPCP compounds, were andorostenedione, estriol, estrone, and testosterone. There were no hormones detected in the summer. Andorostenedione and testosterone were detected in fall, estriol in winter, and estrone in spring. Andorostenedione and testosterone are androgens, while estriol and estrone are estrogens. Hormone contamination can cause endocrine disruption or cancer (USGS, 2014). These compounds could have entered waterways from agricultural runoff, leaking septic tanks, or effluent from wastewater treatment facilities. Drinking water standards for hormones are not established.

4.1.4 Other Compounds

Compounds from the other class that were detected include acesulfame-K, caffeine, cotinine, and DEET. Acesulfame-K and DEET were detected in each season, which is reasonable considering that these chemicals are probably used in every season and would be constituents of urban runoff. Acesulfame-K does not have a health standard, but the health standard for DEET is 200,000 ng/L (MDH, 2013) which is much higher than any concentrations (7.7-55 ng/L) detected in the present study. Caffeine was detected in the fall, winter, and spring. Cotinine was detected in the summer and winter. Neither caffeine nor cotinine have drinking water standards.

4.2 CEC Detections – University of Arizona WEST

More CEC were detected, by the analytical methods of the WEST lab, in spring than in winter. In the spring, two industrials, two pesticides, four PPCPs, and two other compounds were detected. Winter resulted in two industrial detections, two pesticides, three PPCPs, and two other compounds. Results of the compound concentrations for spring and winter at all six sites can be found in Tables A 15–16 and Figures B 33-45.

4.2.1 Industrial Compounds

Industrial compounds detected by the WEST lab include PFHxA, PFOS, and TCPP. PFHxA is used for protective fire resistance, repellency against oil, grease, and water, used in cleanings, textiles, leather, paper, paints, and wire insulation (EPA, 2012). PFOS is used to make carpets, clothing, fabrics for furniture, paper packaging for food, materials that are resistant to water, grease or stains, firefighting at airfields, and in

industrial processes (EPA, 2016). TCPP is used for flame retardation and is most likely sourced from developed areas; it has been shown to be resistant to ozone as a remediation or treatment technology (Pisarenko et al., 2012). The compounds PFOS and PFHxA are PFC and they are persistent in the environment. Studies (described in Chapter 2.4 "Study Area") have shown that these compounds are linked to higher cholesterol levels in humans, reduced immune responses, thyroid disease, kidney cancer, and testicular cancer. The health standard for PFOS is 27 ng/L, which was not exceeded in this study considering the highest value reported was 3.1 ng/L. Health standards have not been established for PFHxA (MPCA, 2008) and could not be found for TCPP.

4.2.2 Pesticide Compounds

The only pesticide compounds detected by WEST were atrazine and simazine with frequent detections in winter and spring. Results were similar to the EEA lab values. Possible runoff sources and toxic effects of these compounds are mentioned in "4.1.2 Pesticide Compounds".

4.2.3 PPCP Compounds

The PPCP compounds detected were diltiazem, hydrochlorothiazide, iopromide, meprobamate, propylparaben, and trimethoprim. Iopromide is an iodinated contrast medium (Schulz et al., 2008), it was the most frequently detected PPCP from the WEST lab. There currently are not any available drinking water standards for iopromide. As previously stated, trimethoprim is an antibacterial, it was detected once in winter and once in spring. The health standard for trimethoprim is 4,000 ng/L; values from WEST lab (0.9

and 3.6 ng/L) also did not exceed the standard. Hydrochlorothiazide was detected at a few sites in winter, it is used in the treatment of hypertension and does not have a drinking water health standard.

Propylparaben is used as a stabilizer, bactericide, and flame retardant (Martins et al., 2017), and was the second most frequently detected PPCP, but it was only detected in spring. Health standards could not be obtained for propylparaben. Diltiazem, a calcium channel blocker used to prevent chest pain, was detected at one site in the spring. Studies have shown that diltiazem can cause chronic kidney disease in rats, but toxicity levels in humans could not be found (Ismail et al., 2017). Meprobamate, used for treating anxiety disorders, was only detected in spring and does not have a drinking water standard.

4.2.4 Other Compounds

Other compounds detected by WEST were acesulfame-K and DEET, detected frequently in winter and spring are similar to the EEA results; analysis of these contaminants mentioned in "4.1.4 Other Compounds".

4.3 Field Parameters

Results from the field parameters illustrate that the most substantial changes detected in any of the parameters were in chlorophyll-a (Chl-a), oxidizing-reducing potential (ORP), and optical dissolved oxygen (ODO). The highest concentrations of Chl-a were measured in the fall with one anomalously high concentration in spring. Chl-a increases could be caused by nutrient enrichment enhancing algal biomass, decreases could be because of nutrient depletion (Harper, 1992).

High concentrations of Chl-a, exceeding 10 µg/L (EPA, 2016), contributed to Lake Thunderbird becoming a SWS. Chl-a levels exceeded the recommended levels at two sites in summer, five sites in fall, six sites in winter, and two sites in spring. Therefore, before proceeding with indirect potable reuse, the City of Norman may need to enforce phosphorous and nitrogen criteria in accordance with OAC 785:45-5-10(7) (EPA, 2016) which could be achieved by imposing phosphorous-free fertilizer rules or by keeping organic matter out of the street, so the fertilizers do not enter drains; if citizens do not comply they could be fined.

ORP was highest (oxidizing) in summer and winter and lowest (reducing) in spring and fall. Differences in ORP values could be due to bacterial activity, more bacterial activity could mean higher ORP and vice versa (Hunting et al., 2013). ODO concentrations were high in summer, winter, and spring and lowest in fall. The dip in ODO during the fall could perhaps be the result of excessive algae growth, because when algae die the process take up DO (MPCA, 2009) – which is consistent with higher levels of Chl-a. The ODO results correspond to the season with the highest number of CEC detections, homologous with the Chl-a spike. In 2011, a supersaturated dissolved oxygen injection system (SDOX) was emplaced to aid the deficiency of dissolved oxygen in the lake, and as of 2014 the SDOX had improved levels of DO to meet EPA requirements; even though DO has met requirements, it can still be affected by algae growth, therefore nutrient reduction should still be a mitigation focus to prevent low DO in the future (OWRB, 2014).

Thermal stratification, and the turnover of the lake, could also be playing a part in seasonal changes in compound detections. Stratification in the summer has the

epilimnion layer (warm water) on top that cannot move through the hypolimnion (cold dense water) which means the water cannot mix and photosynthesis cannot occur in the hypolimnion layer of the lake. The lake turns over from summer to fall, then again in winter to spring, meaning the hypolimnion layer becomes the top layer (Elci, 2008). The summer and winter seasons in this study had the fewest detections, while the fall and spring had the most; the higher detections could be due to mixing of sediment (to which contaminants have attached) when the lake turns over along with the reduced effect of photosynthesis. Tables for the field parameter results are in Tables A 17–28, corresponding figures are in Figures D 1–12.

4.4 CEC Loading Mapping

Four sub-watersheds were defined by the snap pour point method (Figure 9): 1) Hog Creek, which coincides with Site 8 and includes West Hog Creek and Hog Creek; 2) Clear Creek, that corresponds to Site 7 and only encompasses Clear Creek; 3) Dave Blue Creek, which equates to Site 11 and is comprised of Dave Blue Creek and Jim Blue Creek; and 4) Little River, the largest sub-watershed containing Stanley Draper Lake, Elm Creek, West Elm Creek, Kitchen Creek, North Fork Little River, Little River, and Rock Creek – corresponding to Site 6. The loading assessments (Tables A 29–32) were based on the land use fractions, storage tanks per acre, and domestic wells per acre for each sub-watershed (Figures 10 & 11).

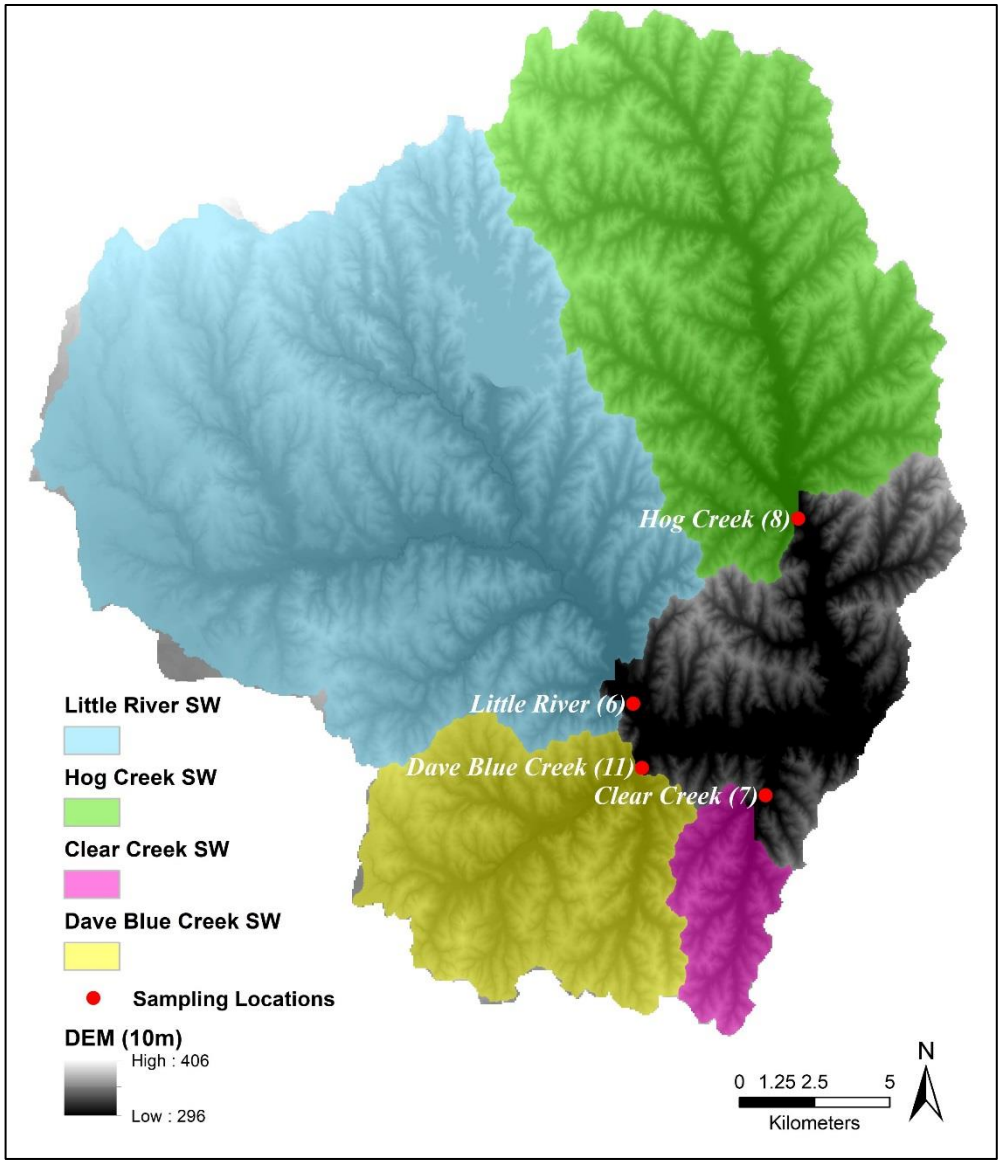

Figure 9. Delineated sub-watersheds based on sampling sites.

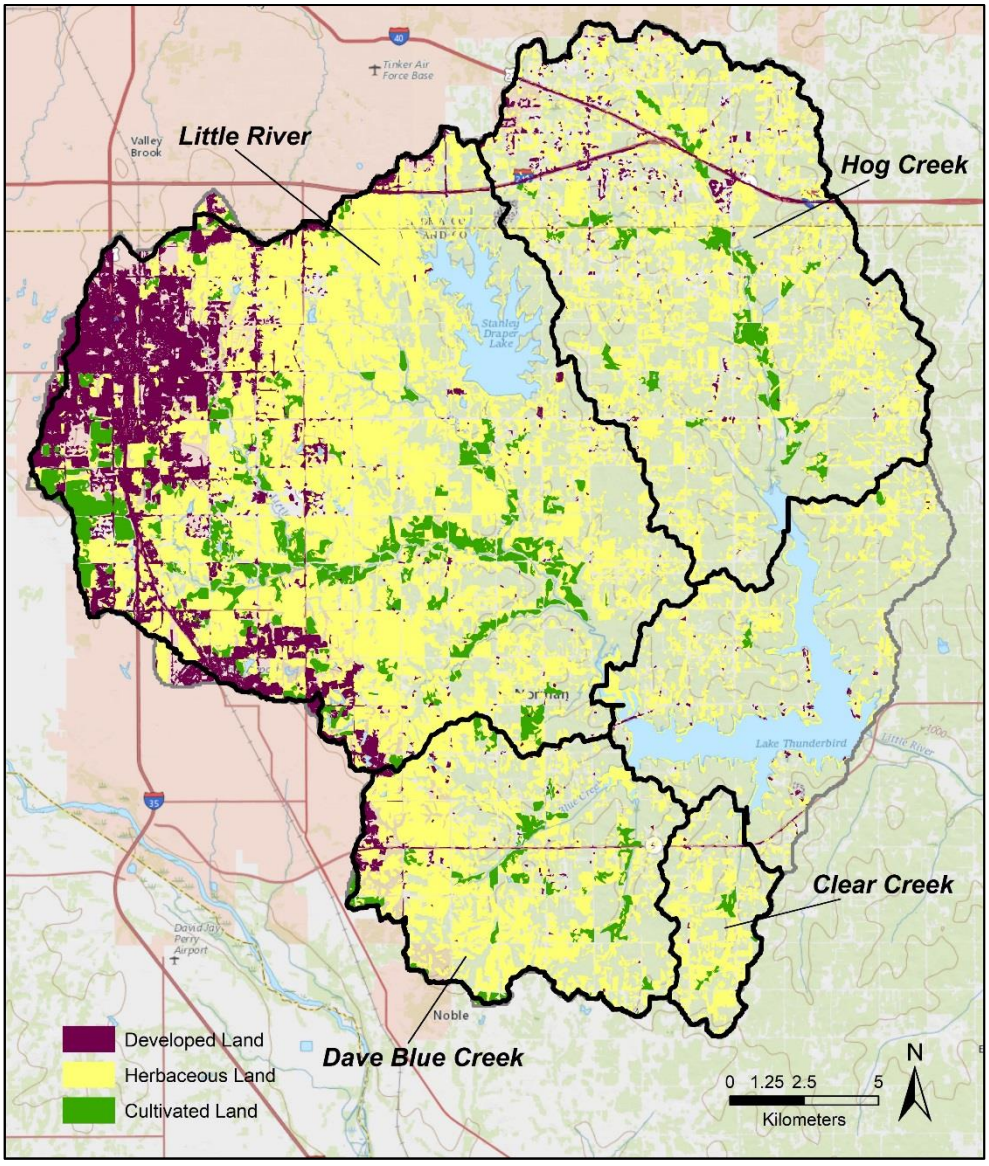

Figure 10. Sub-watersheds and land uses used to assess potential CEC loading.

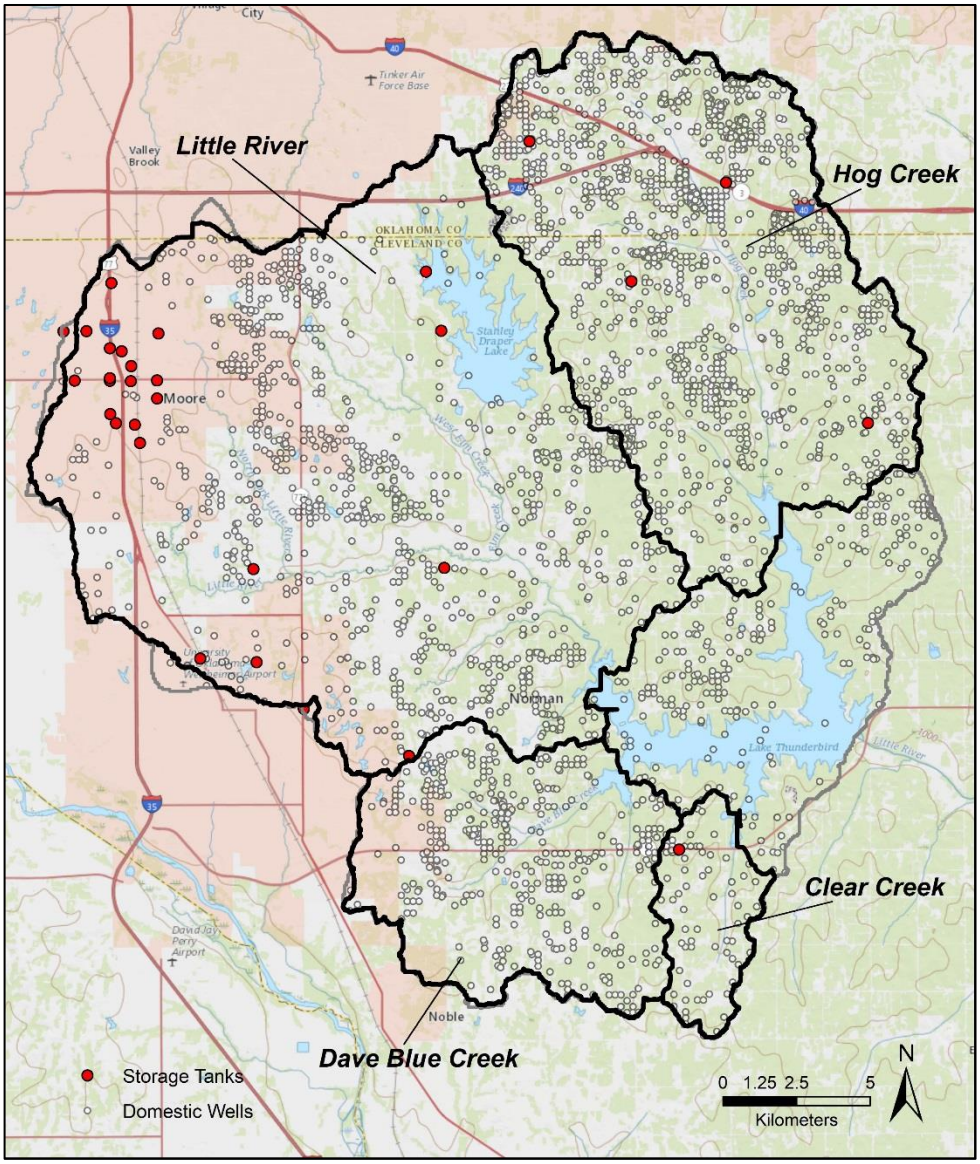

Figure 11. Domestic wells, storage tanks, and outlines of sub-watersheds.

The loading factors (derived by adjusting the land use weighting coefficients to maximize the R^2) and the corresponding equations for each benchmark compound are listed in Table A 33 and represented graphically in Figures E 1–12. Variable definitions are as follows:

LF = loading factor

ST = # of in use storage tanks per acre

SS = # of domestic wells per acre (proxy for septic systems)

D = fraction of total developed land use

C = fraction of cultivated land use

H = fraction of herbaceous land use

4.4.1 Industrial Coefficients

NP: LF = 0.1 ST + 0.001 SS + 0.9 D + 3 C; $Conc_{NP}$ = 9.3638 LF + 48.906; R^2 = 0.9573

OP: LF = 1700 ST + 46 SS + 3 D + 0.009 C; $Conc_{OP}$ = 57.856 LF; R^2 = 0.9043

TCPP: LF = 0.001 ST + 1000 SS + 0.01 D + 0.01 C; $Conc_{TCPP}$ = 5.7975 LF; R^2 = 0.5460

PFOS: LF = 0.1 ST + 0.1 SS + 1.1 D + 9 C; $Conc_{PFOS}$ = 0.8247 LF + 2.0117; R^2 = 0.7111

The non-point source variable (land use) that most affected NP was cultivated land, with developed land possibly having less of an impact. OP was the opposite, with developed land weighting heavier, apparently. TCPP was equally affected by both non-point contamination sources. PFOS was more influenced by cultivated land than developed land, perhaps due to soils being a great sink for PFC (EPA, 2016). The point source variables (septic systems and storage tanks) for NP did not have a large impact, but the coefficient was lower for leaking septic systems than storage tanks, most likely due to its use in plastics. Storage tanks and septic systems were the heaviest weighted coefficients for OP, with storage tanks having more of an impact. TCPP was possibly most affected by septic systems, and least affected by storage tanks. PFOS was not nearly as affected by septic systems as TCPP. The Little River sub-watershed had the highest median concentrations for all the benchmark compounds. Overall, cultivated land was the

highest contributing non-point source factor to loading of industrial CEC, which means that best management practices in areas of cultivated land could have the greatest impact on reducing industrial CEC to Lake Thunderbird.

4.4.2 Pesticide Coefficients

Atrazine: LF = 4.8 C + 2 D + 0.45 H; $Conc_{Atrazine}$ = -1.8855 LF + 10.995; R^2 = 0.9756

Simazine: LF = 4.4 C + 0.01 D + 7.7 H; $Conc_{Simazine}$ = 57.703 LF + 201.73; R^2 = 0.7633

Atrazine was most likely sourced from runoff from cultivated and domestic land with the Little River sub-watershed having the highest median concentrations, whereas herbaceous land did not contribute substantially to loading. Simazine was also highly influenced by cultivated land, but moreso by herbaceous land possibly because it is considered a selective pesticide and is used widely for tall grasses. Reducing the use of atrazine and simazine as weed-killers for cultivated land, and simazine for herbaceous land could mitigate some of the pesticide loading to Lake Thunderbird.

4.4.3 PPCP Coefficients

Clofibric acid: LF = 1 SS + 0.001 D + 3.1 C; $Conc_{Clofibricacid}$ = 176.72 LF; R^2 = 0.8752

Salicylic acid: LF = 0.01 SS + 0.1 D + 500 C; $Conc_{Salicylicacid}$ = 12.894 LF + 28.042; R^2 = 0.6839

Iopromide: LF = 6.5 SS + 1.4 D + 0.2 C; $Conc_{Iopromide}$ = -9.3209 LF + 5.465; R^2 = 0.6558

Propylparaben: LF = 0.001 SS + 0.01 D + 200 C; $Conc_{Propylparaben}$ = -0.759 LF + 16.838; R^2 = 0.4228

The Little River sub-watershed had the highest median concentrations for every PPCP benchmark compound, which is reasonable because the Little River sub-watershed has the highest proportion of residential and developed areas. Clofibric acid, salicylic acid, and propylparaben were most strongly related (most heavily weighted coefficient) to the proportion of cultivated land, but it was the smallest for iopromide. Clofibric and salicylic acids have been detected in livestock runoff (Boxall et al., 2012), therefore that is probably the reason that the cultivated land had such an impact. The bulk point source impact for iopromide was apparently from septic systems (assuming that domestic wells are a good proxy), which corresponds to previous studies detecting the iopromide in wastewater effluent (Schulz et al., 2008), but it was not compared to any other point source of pollution. The PPCP loading factors had overall lower R^2 values than the industrial or pesticide compounds, hence there could be a contributing loading factor not in the current loading factor equation – could possibly be from recreational use and excretion into the lake that was not quantified.

4.4.4 Other Coefficients

DEET: LF = 4 SS + 1.2 D; $Conc_{DEET}$ = 52.312 LF + 24.834; R^2 = 0.6674

Acesulfame–K: LF = 0.001 SS + 1 D; $Conc_{Acesulfame\text{-}K}$ = 68.546 LF + 25.496; R^2 = 0.3560

DEET and acesulfame-K, like the PPCP compounds, also did not have strong R^2 values, especially the latter contaminant. The Little River sub-watershed again had higher median concentrations than the other sub-watersheds. DEET was most heavily affected by septic systems and acesulfame-K by developed land. The same issue could be arising with this equation as with the PPCP equation, not being able to gauge the effect of

recreational use on the lake as a loading factor. In the case of the other benchmark compounds, it would not even need to be excretion, it could be from entering the lake with DEET on one's skin or spilling an item containing acesulfame-K.

Chapter 5. Conclusions

Out of the 113 CEC compounds analyzed, 40 were detected in Lake Thunderbird. The EEA lab analysis had the most detections in fall (22) and the fewest in summer (7). The WEST lab analysis resulted in more detections in spring (10) than in winter (9). In total, 54% of industrial compounds analyzed were detected, 55% of pesticides, 25% of PPCP, and 57% of others. None of the detected compounds exceeded an established health standard for concentrations in drinking water, out of the 12 available. However, numerous CEC detected in this study do not currently have a drinking water standard.

A recommendation to the City of Norman and COMCD would be to continue to collect samples during each season and analyze for the most frequently detected compounds and metabolites (benchmark compounds and others mentioned in Chapter 4). When possible, discrete depth sampling would also be informative to better understand the role of stratification in the CEC detections. Another suggestion would be to either adopt the MDH drinking suggested water standards as a rule for Norman for the CEC, or to complete similar toxicological assessments focused on the compounds detected in this study. Chl-a levels will also need to be tracked since the levels were higher than the EPA recommends for a SWS, and phosphorous and nitrogen criterion need to be emplaced. The lake turnover effect, specifically related to its impact on micropollutants, should also be investigated further.

After weighting the loading factors for each benchmark compound, it is apparent that cultivated land has the greatest impact on CEC loading to Lake Thunderbird. Alternative weed-killers and crop protectors that are less toxic should partially replace the ones discussed in this study to lower contamination levels. Septic systems (domestic

wells as a proxy) also had heavy coefficients for loading factors for some PPCP and other contaminants; therefore, septic tanks could be a major contributor of those pollutants that are ultimately transported to the lake. A suggestion for preventing further contamination via septic tank discharge would be to compile and evaluate relevant septic system locations and information, since that data could not be attained and apparently contributes to PPCP in the watershed. The effect of septic systems as a potential loading factor for CEC could be reduced by expanding the municipal wastewater treatment system to encompass current rural septic system users.

The highest median concentrations came from the Little River sub-watershed, therefore if there are investigations of loading into Lake Thunderbird in the future, the Little River sub-watershed should be the target sub-watershed for additional characterization and best management practices. The sub-watershed model discussed in this study was qualitative, to make this model quantitative would need to include soil types, slopes, and rainfall data.

From the results of this investigation, an IPR project seems feasible with the current information and health standards at hand. When comparing CEC concentrations of effluent after 15 days of natural processes with DBC sediment and PAR light (Thornton, 2017) with median concentrations in the Lake, indications are that the environmental buffering effect could be sufficient to degrade and attenuate CEC below health standards or to trace concentrations.

Future work should investigate the relationship between Chl-a and ODO with the micropollutants in this study, since anonymously higher values of those parameters coincided with higher frequency of CEC detection. A biological investigation of the

accumulated toxins in the fish species of the lake (described in Chapter 2.4) should also be completed since it is a recreational lake and the pollutants could be entering human systems by the consumption of fish. Another analysis that could potentially benefit the City of Norman would be to complete microcosm studies for each creek and river entering the lake, similar to the study with Dave Blue Creek sediment (Thornton, 2017). An effort to sample and analyze the present NWRF effluent discharge and receiving waters of the Canadian River could also be used to evaluate natural degradation and attenuation that is occurring under current water management practices.

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Appendix A: Tables

Table A 1. Concentrations detected in Lake Thunderbird were higher for 10 out of 11 benchmark compounds when compared to concentrations observed by Thornton (2017) after 15-day microcosm studies with Dave Blue Creek sediment and Photosynthetically Active Radiation (PAR). Blue text indicates lower (cleaner), red is higher (dirtier), and orange is unknown, respectively, than water in Lake Thunderbird.

Class	Benchmark Compound	DBC Initial (ng/L)	DBC Sediment - 15 Days (ng/L)	PAR Initial (ng/L)	PAR - 15 Days (ng/L)	Lake Thunderbird Median Concentrations (ng/L) from Horton (2018)
Industrial	NP	1500	<100	280	240	305-400
	OP	120	<50	<50	<50	150-220
	TCPP	390	<100	560	720	250-290
	PFOS	NA	NA	NA	NA	2.1-2.9
Pesticide	Atrazine	<5	<5	<5	6	9.30-10.35
	Simazine	2200	620	300	<5	360-432.5
PPCP	Clofibric acid	17	7.5	<5	<5	19-53
	Salicylic acid	<100	<100	580	100	330-515
	Iopromide	<5	<5	5.4	<5	2.4-4.5
	Propylparaben	<20	<20	<5	<5	6-15
Other	Acesulfame-K	6600	400	140	54	20.00-36.25
	DEET	62	89	<10	15	30.25-37.75

Table A 2. NWIS industrial compound detection amounts in Oklahoma and medium the compound was discovered (USGS, 2017).

Class	Compound	Medium	Detections
Industrial	4-nonylphenol (NP)	Spring	1
		Stream	14
		Well	5
	4-tert-Octylphenol (OP)	Spring	1

Class	Compound	Medium	Detections
Industrial	4-tert-Octylphenol (OP)	Stream	14
		Well	5
	Bisphenol-A (BPA)	Spring	1
		Stream	14
		Well	2

Table A 3. NWIS pesticide compound detection amounts in Oklahoma and the medium the compound was discovered (USGS, 2017).

Class	Compound	Medium	Detections
Pesticide	Atrazine	Combined Sewer	1
		Lake	2
		Spring	11
		Stream	80
		Well	284
	Bromacil	Combined Sewer	1
		Lake	2
		Spring	12
		Well	214
		Stream	49
	Cyanazine	Combined Sewer	1
		Lake	2
	Cyanazine	Spring	10
		Stream	65
		Well	283
	Diuron	Stream	1

Table A 4. NWIS PPCP compound detection amounts in Oklahoma and the medium the compound was discovered (USGS, 2017).

Class	Compound	Medium	Detections
PPCP	Acetaminophen	Well	10
	Albuterol	Well	10
	Atenolol	Well	7

Class	Compound	Medium	Detections
PPCP	Azithromycin	Stream	1
	Benzophenone	Well	3
		Stream	2
	Carbamazepine	Well	10
		Stream	1
	Carisoprodol	Well	7
	Chloramphenicol	Stream	1
	Cimetidine	Well	7
	Dehydronifedipine	Well	19
	Diazepam	Well	7
	Diltiazem	Well	19
	Diphenhydramine	Well	10
	Erythromycin	Stream	1
		Well	7
	Hydrocortisone	Well	7
	Ibuprofen	Stream	1
	Lidocaine	Well	7
	Lincomycin	Stream	1
	Meprobamate	Well	7
	Prednisone	Well	7
	Propranolol	Well	7
	Sulfadiazine	Stream	1
	Sulfadimethoxine	Stream	1
		Well	7
	Sulfamethazine	Stream	1
	Sulfamethizole	Well	7
	Sulfamethoxazole	Stream	1
	Sulfamethoxazole	Well	10
	Sulfathiazole	Stream	1
	Theophylline	Well	7
	Triclosan	Stream	14
		Well	5
		Spring	1
	Trimethoprim	Stream	1
		Well	10
	Warfarin	Well	10

Table A 5. NWIS hormone compound detection amounts in Oklahoma and the medium the compound was discovered (USGS, 2017).

Class	Compound	Medium	Detections
Hormone	Estrone	Stream	1
		Well	7
	Testosterone	Stream	1
		Well	7

Table A 6. NWIS other compound detection amounts in Oklahoma and the medium the compound was discovered (USGS, 2017).

Class	Compound	Medium	Detections
Other	1,7-Dimethylxanthine	Well	10
	Caffeine	Stream	22
		Spring	1
		Well	27
	Cotinine	Spring	1
		Stream	14
		Well	12
	DEET	Spring	1
		Stream	14
		Well	5

Table A 7. Compound listed under the EPA NPDWR, with the maximum contaminant level (MCL) in ng/L, the maximum detection in this study, potential health effects, and potential sources (EPA, 2017).

Contaminant	MCL (ng/L)	Highest Concentration (ng/L) for Present Study	Health Effects	Sources
Atrazine	3,000	26	Cardiovascular system or reproductive problems	Runoff from herbicide used on row crops
2-4 D	70,000	200	Kidney, liver, or adrenal gland problems	Runoff from herbicide used on row crops

Contaminant	MCL (ng/L)	Highest Concentration (ng/L) for Present Study	Health Effects	Sources
Simazine	4,000	1,400	Problems with Blood	Herbicide Runoff

Table A 8. Site identifier, longitude, latitude, and site name (OWRB, 2014 & 2015).

Identifier	Longitude	Latitude	Site Name
Site 1	-97.220786	35.223229	Dam
Site 4	-97.250944	35.224328	Sec 25
Site 6	-97.305880	35.231323	Little Arm River
Site 7	-97.257755	35.203538	Clear Creek Arm
Site 8	-97.245082	35.286420	Hog Creek Arm
Site 11	-97.302846	35.211994	Dave Blue Creek Arm

Table A 9. List of 98 compounds analyzed by EEA lab including the class, method reporting limit (MRL), and the common use of that compound; all compounds were measured in ng/L. Yellow are compounds analyzed by both labs, gray are EEA unique compounds.

Class	MRL	Compound	Common Use
Industrial	10	BPA (Bisphenol A)	Plasticizer
	100	NP (4-nonylphenol)	Surfactant
	50	OP (4-tert-octylphenol)	Surfactant
	10	TCEP (Tris(2-chloroethyl) phosphate)	Flame Retardant
	100	TCPP (Tris(1,3-dichloro-2-propyl) phosphate)	Flame Retardant
	100	TDCPP (Tris(1,3-dichloroisopropyl) phosphate)	Flame Retardant
Pesticide	5	2,4-Dichlorophenoxyacetic Acid	Herbicide
	5	Atrazine	Triazine Herbicide
	5	Bendroflumethiazide	Triazide
	5	Bromacil	Herbicide
	5	Chloridazon	Enzyme

Class	MRL	Compound	Common Use
Pesticide	5	Chlorotoluron	Herbicide
	5	Cyanazine	Triazine Herbicide
	5	DACT (Diaminochlorotriazine)	Triazine Degradant
	5	DEA (Deethylatrazine)	Triazine Degradant
	5	DIA (Deisopropylatrazine)	Triazine Degradant
	5	Diuron	Herbicide
	100	Isoproturon	Herbicide
	5	Linuron	Herbicide
	5	Metazachlor	Herbicide
	5	Metolachlor	Herbicide
	5	OUST	Herbicide
	5	Propazine	Triazine Herbicide
	5	Quinoline	Phosphate Pesticide
	5	Simazine	Triazine Herbicide
	5	Thiabendazole	Fungicide and Parasiticide
PPCP	5	Acetaminophen	Analgesic
	5	Albuterol	Anti-Asthmatic
	20	Amoxicillin (semi-quantitative)	Antibiotic
	5	Atenolol	Beta Blocker
	20	Azithromycin	Antibiotic
	5	Bezafibrate	Lipid Regulator
	5	Butalbital	Analgesic-NSAID
	5	Butylparaben	Preservative
	5	Carbadox	Antibiotic
	5	Carbamazepine	Anticonvulsant
	5	Carisoprodol	Muscle Relaxant
	10	Chloramphenicol	Antibiotic
	5	Cimetidine	H2 Blocker
	5	Clofibric Acid	Lipid Regulator and Herbicide
	5	Dehydronifedipine	Blood Pressure Drug Metabolite
	5	Diazepam	Valium Anti-Anxiety
	5	Diclofenac	Anti-Inflammatory
	20	Dilantin	Anti-Seizure
	5	Diltiazem	Calcium Blocker
	10	Erythromycin	Antibiotic
	20	Ethylparaben	Preservative
	10	Flumeqine	Antibiotic
	10	Fluoxetine (Prozac)	Antidepressant

Class	MRL	Compound	Common Use
PPCP	5	Gemfibrozil	Lipid Regulator
	10	Ibuprofen	Analgesic-NSAID
	10	Iohexol	X-ray Contrast Agent
	5	Iopromide	X-ray Contrast Agent
	5	Isobutylparaben	Preservative for Skin Care Products
	5	Ketoprofen	Anti-Inflammatory
	5	Ketorolac	Anti-Inflammatory
	5	Lidocaine	Analgesic
	10	Lincomycin	Antibiotic
	20	Lopressor (Metoprolol)	Beta Blocker
	5	Meclofenamic Acid	Anti-Inflammatory
	5	Meprobamate	Anti-Anxiety
	20	Methylparaben	Preservative as Antifungal in Cosmetics
	10	Naproxen	Analgesic-NSAID
	20	Nifedipine	Calcium Blocker
	10	Oxolinic acid	Antibiotic
	5	Pentoxifylline	Blood thinner
	5	Phenazone	Analgesic
	5	Primidone	Anticonvulsant
	5	Propylparaben	Preservative
	100	Salicylic Acid	Phenolic Acid
	5	Sulfachloropyridazine	Sulfa Antibiotic
	5	Sulfadiazine	Sulfa Antibiotic
	5	Sulfadimethoxine	Sulfa Antibiotic
	5	Sulfamerazine	Sulfa Antibiotic
	5	Sulfamethazine	Sulfa Antibiotic
	5	Sulfamethizole	Sulfa Antibiotic
	5	Sulfamethoxazole	Sulfa Antibiotic
	5	Sulfathiazole	Sulfa Antibiotic
	20	Theophylline	Anti-Asthmatic
	5	Triclocarban	Antibacterial
	10	Triclosan	Antibacterial
	5	Trimethoprim	Antibiotic
	5	Warfarin	Anticoagulant
Hormone	5	Andorostenedione	Steroid Hormone
	5	EE2 (17 Alpha-ethynylestradiol)	Contraceptive Hormone
	5	Estradiol	Hormone
	5	Estriol	Steroid Hormone

Class	MRL	Compound	Common Use
Hormone	5	Estrone	Estrogenic Hormone
	5	Norethisterone	Steroid Hormone
	5	Progesterone	Steroid Hormone
	10	Testosterone	Steroid Hormone
Other	10	1,7-Dimethylxanthine	Caffeine Degradant
	20	Acesulfame-K	Artificial Sweetener
	5	Caffeine	Stimulant
	10	Cotinine	Nicotine Degradant
	10	DEET (N,N-Diethyl-meta-toluamide)	Mosquito Repellant
	100	Sucralose	Sugar Substitute
	10	Theobromine	Caffeine Degradant

Table A 10. List of 43 compounds analyzed by Arizona WEST lab including the class and the common use of that compound; all compounds were measured in ng/L. Yellow are compounds analyzed by both labs, gray are WEST unique compounds.

Class	Compound	Common Use
Industrial	Benzotriazole	Anticorrosion Agent
	BPA (Bisphenol A)	Plasticizer
	PFBA (Perfluorbutanoic Acid)	Surfactant
	PFBS (Perfluorobutanesulfonic Acid)	Surfactant
	PFHxA (Perfluorohexanoic Acid)	Surfactant
	PFOA (Perfluorooctanoic Acid)	Surfactant
	PFOS (Perfluorooctanesulfonic Acid)	Surfactant
	PFpeA (Perfluoro-n-pentanoic Acid)	Surfactant
	TCEP (Tris(2-chloroethyl) phosphate)	Flame Retardant
	TCPP (Tris(1,3-dichloro-2-propyl) phosphate)	Flame Retardant
Pesticide	Atrazine	Herbicide
	Simazine	Triazine Herbicide
PPCP	Atenolol	Beta Blocker
	Benzophenone	Sunscreen
	Carbamazepine	Anticonvulsant
	Clofibric Acid	Lipid Regulator and Herbicide
	Dexamethasone	Glucocorticoid
	Diclofenac	Anti-Inflammatory
	Diltiazem	Calcium Blocker
	Diphenhydramine	Antihistamine
	Fluoxetine (Prozac)	Antidepressant
	Gemfibrozil	Lipid Regulator
	Hydrochlorothiazide	High Blood Pressure

Class	Compound	Common Use
PPCP	Hydrocortisone	Glucocorticoid
	Ibuprofen	Analgesic-NSAID
	Iohexol	X-ray Contrast Media
	Iopamidol	X-ray Contrast Media
	Iopromide	X-ray Contrast Media
	Meprobamate	Anti-Anxiety
	Naproxen	Analgesic-NSAID
	Prednisone	Glucocorticoid
	Primidone	Anticonvulsant
	Propranolol	Beta Blocker
	Propylparaben	Preservative
	Sulfamethoxazole	Sulfa Antibiotic
	Triclocarban	Antibacterial
	Triclosan	Antibacterial
	Trimethoprim	Antibiotic
Hormone	Testosterone	Steroid Hormone
Other	Acesulfame-K	Artificial Sweetener
	Caffeine	Stimulant
	DEET (N,N-Diethyl-meta-toluamide)	Insect Repellant
	Sucralose	Sugar Substitute

Table A 11. List of compounds detected by EEA for summer, including class of compound, MRL, and site # at the top; an "*" indicates a degradant and italics means the compound was analyzed by both labs. All values reported in ng/L, no duplicate was taken this season.

Summer (June 2016)								
Class	Compound	MRL	1	4	6	7	8	11
Industrial	*BPA*	10			40	78		120
Pesticide	*Atrazine*	5	10	10	11	11	9.7	12
	Simazine	5	420	420	250	400	380	380
PPCP	*Iohexol*	10			220			10
Other	*Acesulfame-K*	20	67	51	95	34	40	34
Other	*Cotinine*	10	12		22	10	15	10
	DEET	10	35	34	78	46	42	42

Table A 12. List of compounds detected by EEA for fall, including class of compound, MRL, site #, and duplicate at the top; an "*" indicates a degradant and italics means the compound was analyzed by both labs. All values reported in ng/L, duplicate was for site 1.

Fall (October 2016)									
Class	Compound	MRL	1	4	6	7	8	11	Dup
Industrial	NP	100		500	480		500		530
	OP	50		410	220		150		140
	TDCPP	100		180					
Pesticide	2,4-D	5			19	37	21	28	
	Atrazine	5	11			9.3	11	8.1	
	Bromacil	5		20	25	18		15	14
	Cyanazine	5						6.8	
	DACT *	5		33	20				48
	DEA *	5			5.3				
	DIA *	5	50	70	81	90	36	99	60
	Diuron	5		11	12	18		16	9.5
	Simazine	5	310	390	390	370	340	340	380
PPCP	*Clofibric Acid*	5		5.5	7.5	42	8.9	35	6
	Ibuprofen	10					36		
	Lincomycin	10		30					46
	Triclocarban	5				5.1			
	Trimethoprim	5			9.9				
Hormone	Andorostenedione	5			5.2				
	Testosterone	10						5.8	
Other	*Acesulfame-K*	20		22	36		97	48	25
	Caffeine	5				14		30	
	DEET	10	55	49	47	49	45	45	52

Table A 13. List of compounds detected by EEA for winter, including class of compound, MRL, site #, and duplicate at the top; an "*" indicates a degradant and italics means the compound was analyzed by both labs. All values reported in ng/L, duplicate was for site 6.

Winter (January 2017)									
Class	Compound	MRL	1	4	6	7	8	11	Dup
Industrial	NP	100		290		320			
Pesticide	2,4-D	5	11	6.8	160			42	
	Atrazine	5	9.3	8.4	8.4	11	8	8.2	9.2
	Bromacil	5	19	15	24	14	14	13	21
	DACT *	5				24			31
	DEA *	5	8.2	6.9	5.6	31	5.5	6.5	29

Winter (January 2017)									
Class	Compound	MRL	1	4	6	7	8	11	Dup
Pesticide	DIA *	5	180	140	160	260	95	110	330
	Diuron	5	14	13	11	12	13	12	9.2
	Quinoline	5			15	5.3	8.6	6	11
	Simazine	5	480	450		500	470	810	
PPCP	*Clofibric Acid*	5	23	21	53	19	19	27	52
	Ibuprofen	10					36		
	Meclofenamic Acid	5			7.4				
	Salicylic Acid	100			790		490	650	120
Hormone	Estriol	5				7	6.2		5.8
Other	*Acesulfame-K*	20	20		21				41
	Caffeine	5			31	5.3		5	22
	Cotinine	10	12	11	24	13	14	14	14
	DEET	10	26	26	28	20	25	23	44

Table A 14. List of compounds detected by EEA for spring, including class of compound, MRL, site #, and duplicate at the top; an "*" indicates a degradant and italics means the compound was analyzed by both labs. All values reported in ng/L, duplicate was for site 6.

Spring (April 2017)									
Class	Compound	MRL	1	4	6	7	8	11	Dup
Industrial	NP	100					110		100
Pesticide	2,4-D	5	91	120	42	100	200	66	49
	Atrazine	5	12	15	25	16	29	25	32
	Bromacil	5	8.8	15	75	7	6.2	38	82
	DACT *	5	18		110		15	36	80
	DEA *	5	10	12	16	7.2	17	12	10
	DIA *	5	120	120	270	110	97	190	260
	Diuron	5	32	46	210	21	29	120	260
	OUST	5	19	110	1300	74	9.2	980	1300
	Quinoline	5			10	8.1		5.2	10
	Simazine	5	490	670		500	470	1100	1400
PPCP	*Clofibric Acid*	5			190		50	170	
	Gemfibrozil	5				6.2			
	Salicylic Acid	100		330	240		230	280	670
Hormone	Estrone	5			11				
Other	*Acesulfame-K*	20	50	25	46	27	30		
	Caffeine	5			24	11		17	20
	DEET	10	20	18	11		16	12	

Table A 15. List of compounds detected by WEST for winter, including class of compound, site #, and duplicate at the top; an "<" indicates a compound lower than MDL and italics means the compound was analyzed by both labs. All values reported in ng/L, duplicate was for site 6.

Winter (January 2017)								
Class	Compound	1	4	6	7	8	11	Dup
Industrial	PFHxA	< 14	< 14	24	< 14	< 14	16	<14
	PFOS	1.5	3.1	1.3	1.7	1.4	1.6	1.7
Pesticide	*Atrazine*	8	8.6	6.8	8.5	6.1	7.2	26
	Simazine	110	120	430	88	110	160	380
PPCP	Hydrochlorothiazide	4.1	< 2.6	< 2.3	< 2.7	3.6	3.4	<2.4
	Iopromide	1.9	2.1	2.7	3.4	3	4.5	4.3
	Trimethoprim	< 1.1	< 1	< 1.2	< 1.2	< 1	0.9	<1.1
Other	*Acesulfame -K*	17	18	23	15	19	18	26
	DEET	18	16	29	17	13	14	7.7

Table A 16. List of compounds detected by WEST for spring, including class of compound, site #, and duplicate at the top; an "<" indicates a compound lower than MDL and italics means the compound was analyzed by both labs. All values reported in ng/L, duplicate was for site 6.

Spring (April 2017)								
Class	Compound	1	4	6	7	8	11	Dup
Industrial	PFOS	2.6	2.3	2.9	2.4	2.1	2.5	1.5
	TCPP	95	250	< 21	< 21	< 23	290	<22
Pesticide	*Atrazine*	12	11	20	11	21	21	22
	Simazine	220	42	630	240	190	530	690
PPCP	*Diltiazem*	< 1.7	21	< 1.5	< 1.5	< 1.5	< 1.8	<1.5
	Meprobamate	< 2.6	< 1.2	< 2.6	< 2.6	4.6	2.7	2.7
	Propylparaben	17	65	< 6	15	8	6	11
	Trimethoprim	< 1.6	< 1.6	2.3	< 1.5	< 1.6	3.6	<1.3
Other	*Acesulfame -K*	26	26	27	23	24	26	29
	DEET	25	40	18	24	22	24	18

Table A 17. Temperature values for each site and season.

Temperature (°C)				
Site	**Summer**	**Fall**	**Winter**	**Spring**
Site 1	23.58	22.34	6.75	15.62
Site 4	25.59	22.59	7.20	15.46

Temperature (°C)				
Site	Summer	Fall	Winter	Spring
Site 6	29.98	22.99	8.72	15.29
Site 7	28.73	23.45	7.43	15.77
Site 8	31.68	23.13	8.53	15.56
Site 11	29.15	23.6	8.49	14.61

Table A 18. Specific conductance values for each site and season.

Specific Conductance (mS/cm)				
Site	Summer	Fall	Winter	Spring
Site 1	0.397	0.368	0.377	0.390
Site 4	0.394	0.365	0.379	0.385
Site 6	0.521	0.364	0.448	0.387
Site 7	0.389	0.368	0.378	0.388
Site 8	0.392	0.356	0.381	0.385
Site 11	0.415	0.365	0.403	0.347

Table A 19. Conductivity values for each site and season.

Conductivity (µS/cm)				
Site	Summer	Fall	Winter	Spring
Site 1	386	349	246	320
Site 4	398	348	250	315
Site 6	571	350	309	315
Site 7	416	357	251	319
Site 8	442	344	261	316
Site 11	448	355	276	278

Table A 20. Resistivity values for each site and season.

Resistivity (Ohm*cm)				
Site	Summer	Fall	Winter	Spring
Site 1	2590	2870	4070	3120
Site 4	2510	2870	4000	3170
Site 6	1750	2860	3240	3180
Site 7	2400	2800	3980	3130
Site 8	2260	2910	3830	3170
Site 11	2230	2810	3630	3590

Table A 21. Total dissolved solids values for each site and season.

Total Dissolved Solids (mg/L)				
Site	**Summer**	**Fall**	**Winter**	**Spring**
Site 1	258	239	245	254
Site 4	256	237	246	250
Site 6	339	237	291	251
Site 7	253	239	246	252
Site 8	255	232	247	250
Site 11	270	237	262	226

Table A 22. Salinity values for each site and season.

Salinity (ppm)				
Site	**Summer**	**Fall**	**Winter**	**Spring**
Site 1	1.90E-07	1.80E-07	1.80E-07	1.90E-07
Site 4	1.90E-07	1.70E-07	1.80E-07	1.90E-07
Site 6	2.50E-07	1.70E-07	2.20E-07	1.90E-07
Site 7	1.80E-07	1.80E-07	1.80E-07	1.90E-07
Site 8	1.80E-07	1.70E-07	1.80E-07	1.90E-07
Site 11	2.00E-07	1.70E-07	1.90E-07	1.70E-07

Table A 23. pH values for each site and season.

pH (-Log[H+])				
Site	**Summer**	**Fall**	**Winter**	**Spring**
Site 1	7.51	8.7	8.41	8.42
Site 4	7.55	8.76	8.44	8.36
Site 6	8.15	8.45	8.55	8.19
Site 7	8.43	8.04	8.55	8.45
Site 8	8.54	8.82	8.64	8.35
Site 11	8.39	8.29	8.56	8.18

Table A 24. Oxidation-reduction potential values for each site and season.

Oxidation-Reduction Potential (mV)				
Site	**Summer**	**Fall**	**Winter**	**Spring**
Site 1	55.9	-106	156	-34.0
Site 4	179	-109	125	-31.0
Site 6	177	-91.0	93.0	-37.0
Site 7	107	-66.7	135	-30.0
Site 8	177	-113	98.0	-34.0

Oxidation-Reduction Potential (mV)				
Site	**Summer**	**Fall**	**Winter**	**Spring**
Site 11	169	-82.0	77.0	7.00

Table A 25. Chlorophyll-A values as a concentration for each site and season.

Chlorophyll-A (µg/L)				
Site	**Summer**	**Fall**	**Winter**	**Spring**
Site 1	4.10	196	15.2	2.90
Site 4	4.30	179	13.7	61.3
Site 6	13.3	187	33.9	4.70
Site 7	9.30	176	22.0	10.5
Site 8	6.30	138	21.1	3.60
Site 11	28.4	161	22.9	6.20

Table A 26. Chlorophyll-A values in relative fluorescence for each site and season.

Chlorophyll-A (RFU)				
Site	**Summer**	**Fall**	**Winter**	**Spring**
Site 1	1.10	16.2	3.60	0.700
Site 4	1.10	14.9	3.30	14.5
Site 6	3.30	12.5	8.10	1.10
Site 7	2.30	8.50	5.30	2.50
Site 8	1.60	15.9	5.00	0.800
Site 11	6.90	11.5	5.50	1.50

Table A 27. Optical dissolved oxygen in saturation for each site and season.

Optical Dissolve Oxygen (%SAT)				
Site	**Summer**	**Fall**	**Winter**	**Spring**
Site 1	6.80	3.90	96.4	97.0
Site 4	18.6	3.60	99.1	92.8
Site 6	83.1	3.00	99.9	88.6
Site 7	94.8	2.00	103	93.5
Site 8	93.7	3.80	105	94.9
Site 11	84.9	2.70	99.4	90.8

Table A 28. Optical dissolved oxygen as a concentration for each site and season, winter values are missing due to instrument error.

Optical Dissolved Oxygen (mg/L)				
Site	**Summer**	**Fall**	**Winter**	**Spring**
Site 1	0.58	4.25	NA	9.64
Site 4	1.52	5.95	NA	9.26
Site 6	6.27	6.94	NA	8.87
Site 7	7.32	6.47	NA	9.26
Site 8	6.88	7.49	NA	9.45
Site 11	6.51	7.21	NA	9.23

Table A 29. Sub-watershed loading factor assessment for industrial class contaminants, area in acres.

Site	Storage Tanks/Acre	Domestic Wells/Acre	Fraction of Developed	Fraction of Cultivated	Loading Factor
Entire	0.0003	0.039	0.079	0.054	17.23
Little River	0.00048	0.022	0.141	0.082	24.50
Clear Creek	0.00058	0.015	0.006	0.022	4.36
Hog Creek	0.00077	0.013	0.025	0.032	7.06
Dave Blue Creek	0	0.024	0.024	0.054	10.23

Table A 30. Sub-watershed loading factor assessment for pesticide class contaminants; areas in acres.

Site	Fraction of Cultivated	Fraction of Herbaceous	Fraction of Developed	Loading Factor
Entire	0.054	0.368	0.079	50.10
Little River	0.082	0.431	0.141	65.37
Clear Creek	0.022	0.396	0.006	42.41
Hog Creek	0.032	0.311	0.025	36.75
Dave Blue Creek	0.054	0.437	0.024	51.53

Table A 31. Sub-watershed loading factor assessment for PPCP class contaminants; areas in acres.

Site	Domestic Wells/Acre	Fraction of Cultivated	Fraction of Developed	Loading Factor
Entire	0.022	0.054	0.079	15.50
Little River	0.013	0.082	0.141	23.56
Clear Creek	0.039	0.022	0.025	8.56
Hog Creek	0.024	0.032	0.024	8.02
Dave Blue Creek	0.015	0.054	0.006	7.54

Table A 32. Sub-watershed loading factor assessment for other class contaminants; areas in acres.

Site	Domestic Wells/Acre	Fraction of Developed	Loading Factor
Entire	0.022	0.079	10.10
Little River	0.013	0.141	15.40
Clear Creek	0.039	0.025	6.36
Hog Creek	0.024	0.024	4.80
Dave Blue Creek	0.015	0.006	2.10

Table A 33. Half-lives of benchmark compounds in aqueous environments.

Class	Compound	Estimated Half-Life in Water
Industrial	NP	10-15 hours *(Canada, 2002)*
	OP	6.9 hours *(Environment Agency UK, 2005)*
	TCPP	Not available
	PFOS	3.3 years *(Worley et al., 2017)*
Pesticide	Atrazine	> 200 days *(U.S. Department of Health, 2003)*
	Simazine	145 days *(Environmental Monitoring Branch, 2004)*
PPCP	Clofibric acid	2 days *(Kunkel and Radke, 2011)*
	Iopromide	3.1 days *(Kalsch, 1999)*
	Propylparaben	9.6-32.5 hours *(Haman et al., 2015)*
	Salicylic acid	Not available
Other	Acesulfame-K	7-9 days *(Gan et al., 2014)*
	DEET	5-15 days *(ECHA, 2010)*

Appendix B: Graphs of Compounds

Industrial Compounds – EEA

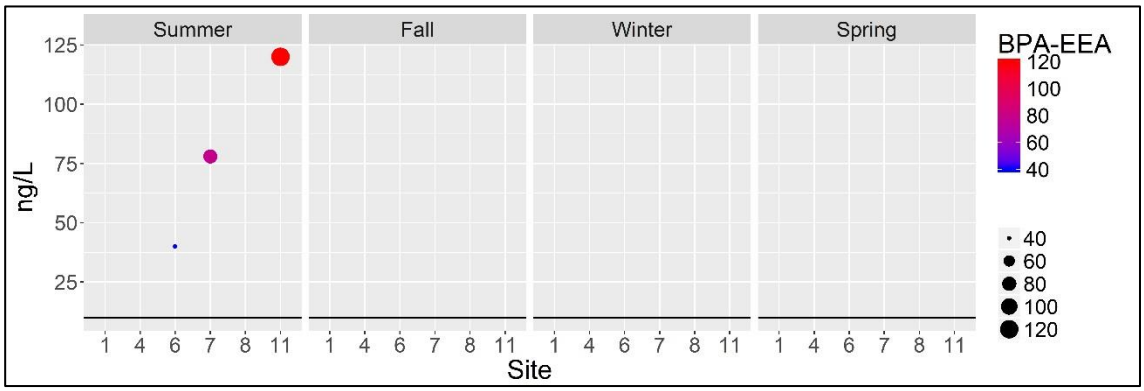

Figure B 1. BPA detections in ng/L for each season (EEA lab results).

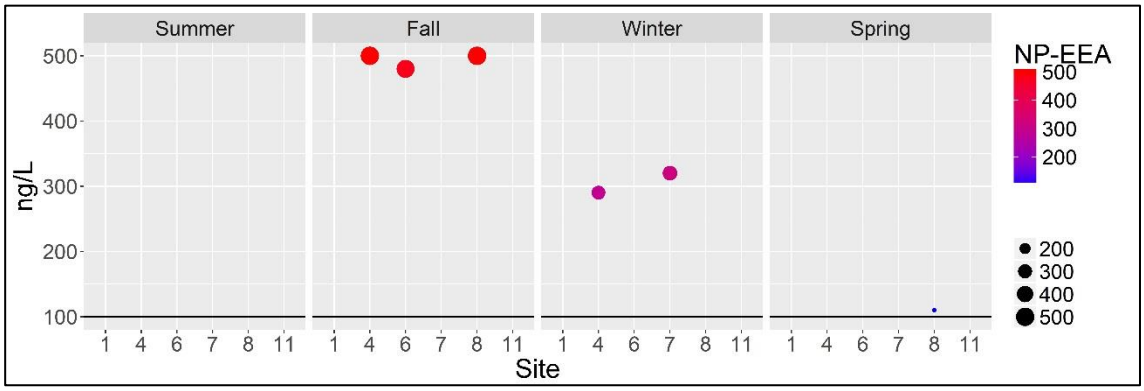

Figure B 2. NP detections in ng/L for each season (EEA lab results).

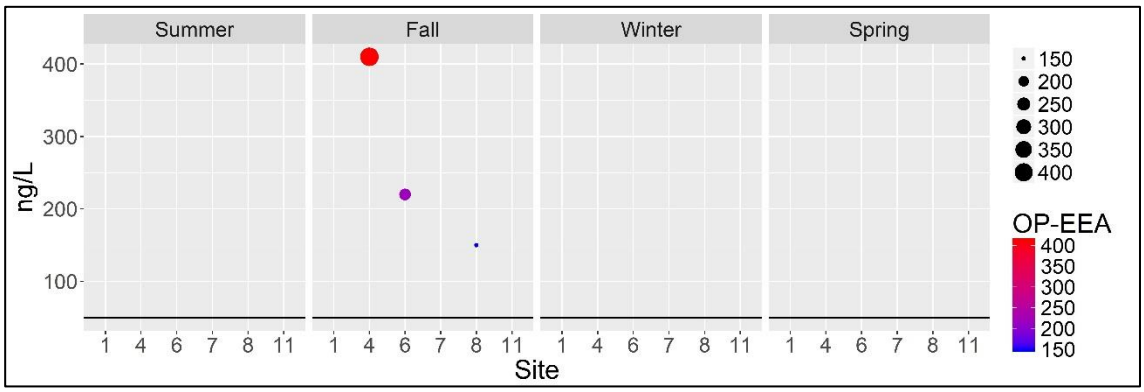

Figure B 3. OP detections in ng/L for each season (EEA lab results).

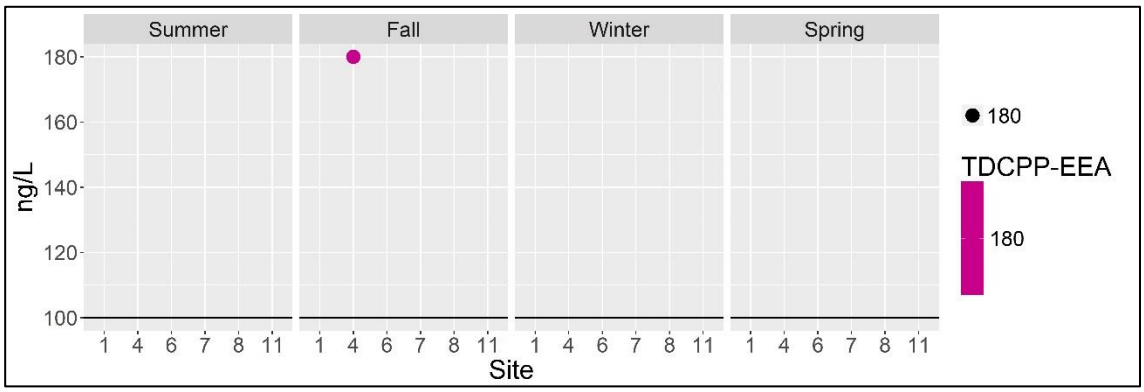

Figure B 4. TDCPP detections in ng/L for each season (EEA lab results).

Pesticide Compounds – EEA

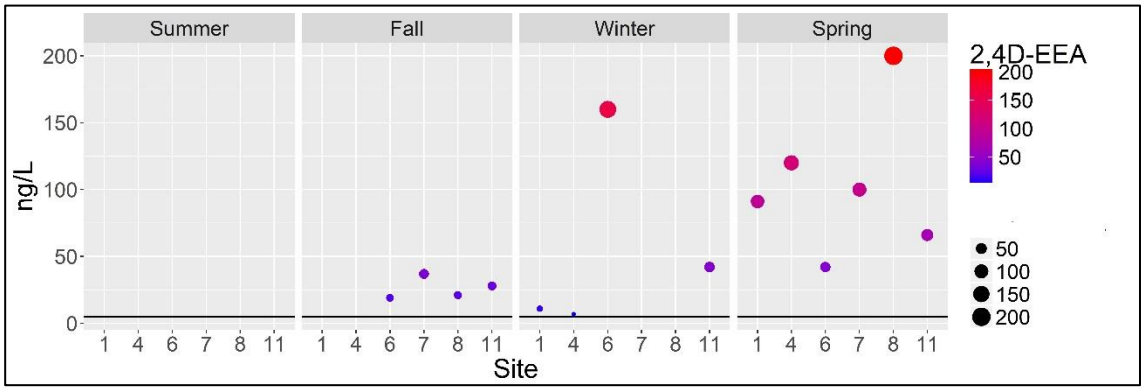

Figure B 5. 2,4-D detections in ng/L for each season (EEA lab results).

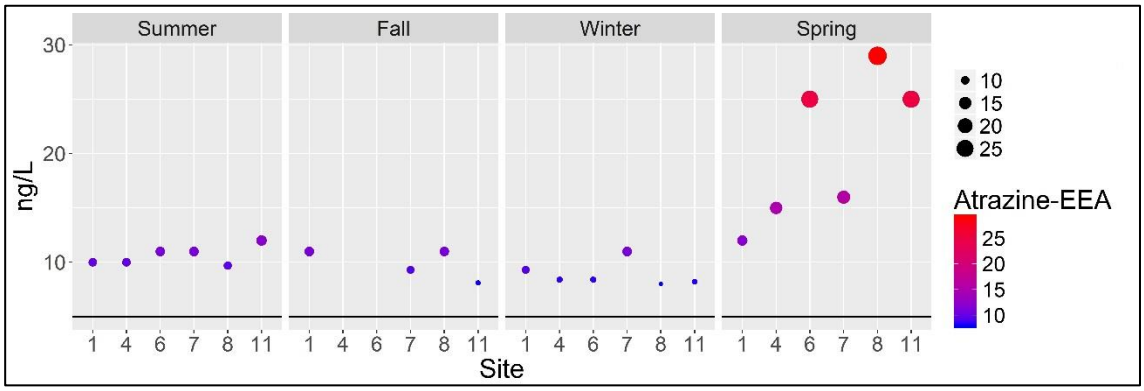

Figure B 6. Atrazine detections in ng/L for each season (EEA lab results).

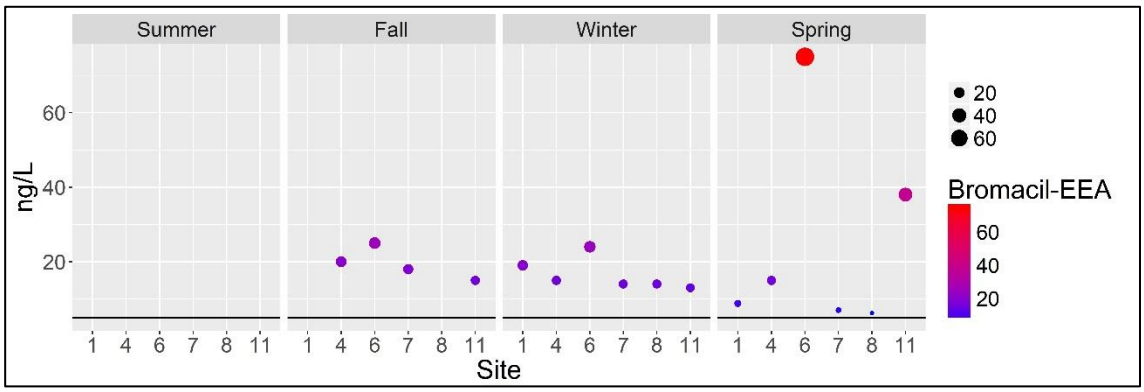

Figure B 7. Bromacil detections in ng/L for each season (EEA lab results).

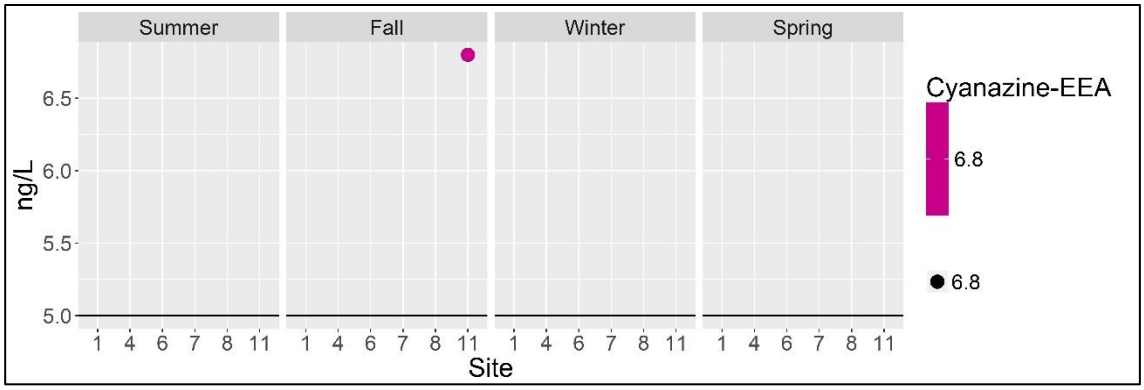

Figure B 8. Cyanazine detections in ng/L for each season (EEA lab results).

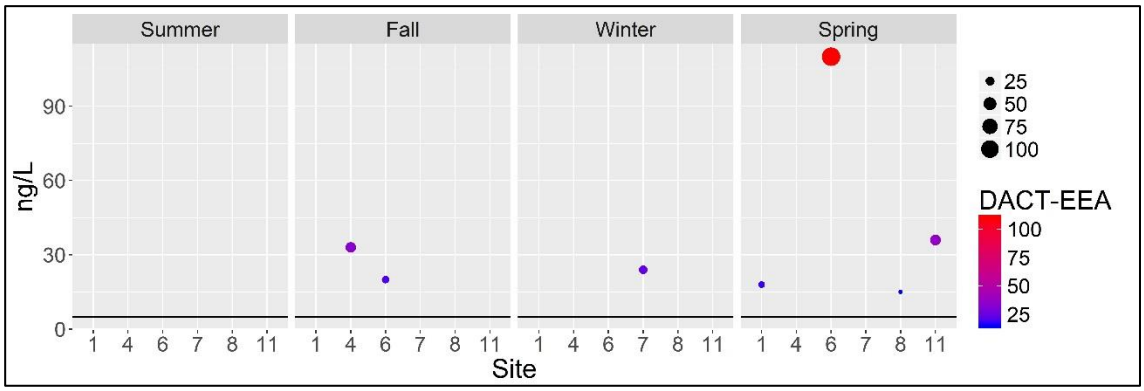

Figure B 9. DACT detections in ng/L for each season (EEA lab results).

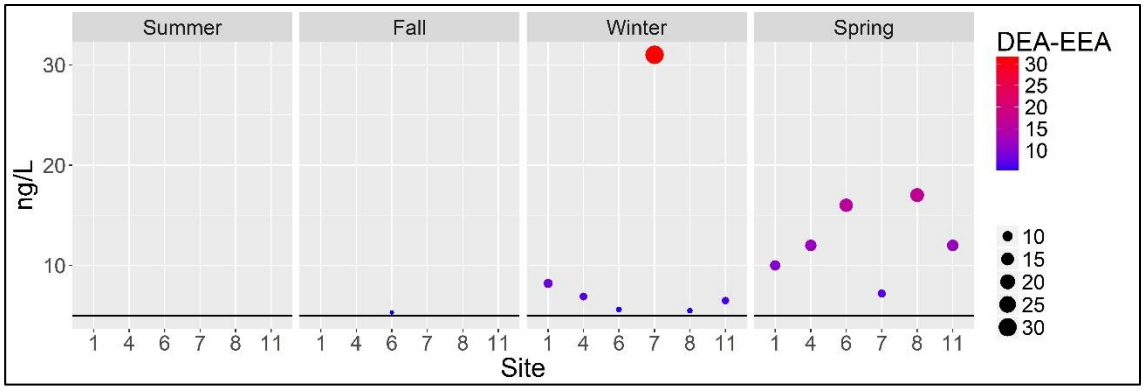

Figure B 10. DEA detections in ng/L for each season (EEA lab results).

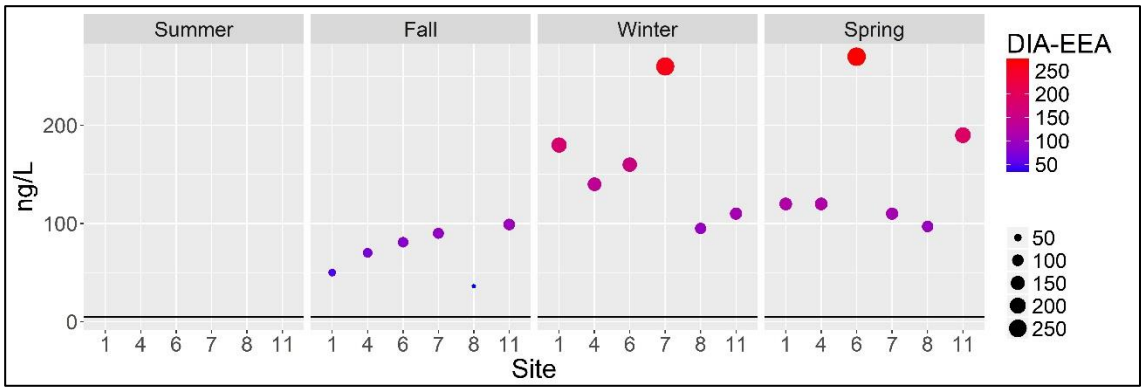

Figure B 11. DIA detections in ng/L for each season (EEA lab results).

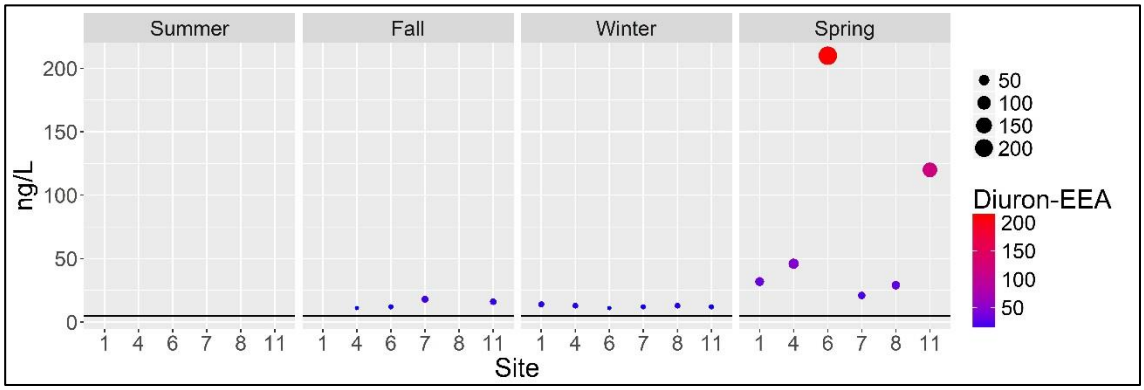

Figure B 12. Diruon detections in ng/L for each season (EEA lab results).

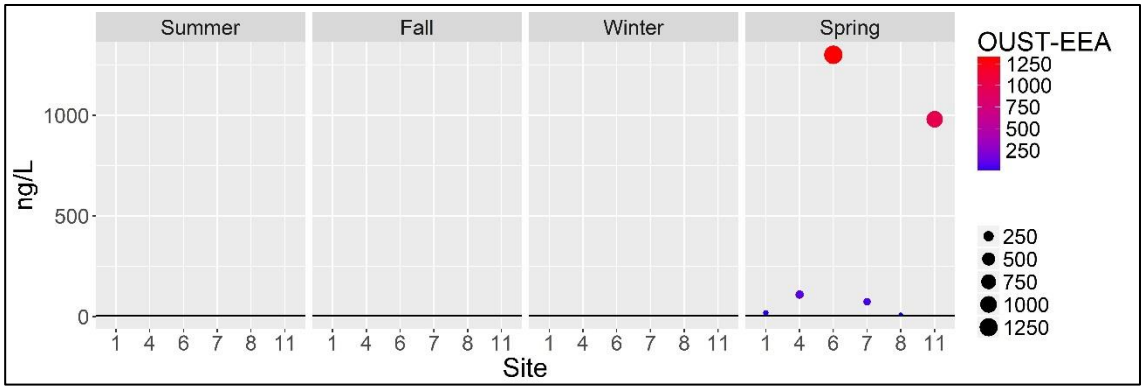

Figure B 13. OUST detections in ng/L for each season (EEA lab results).

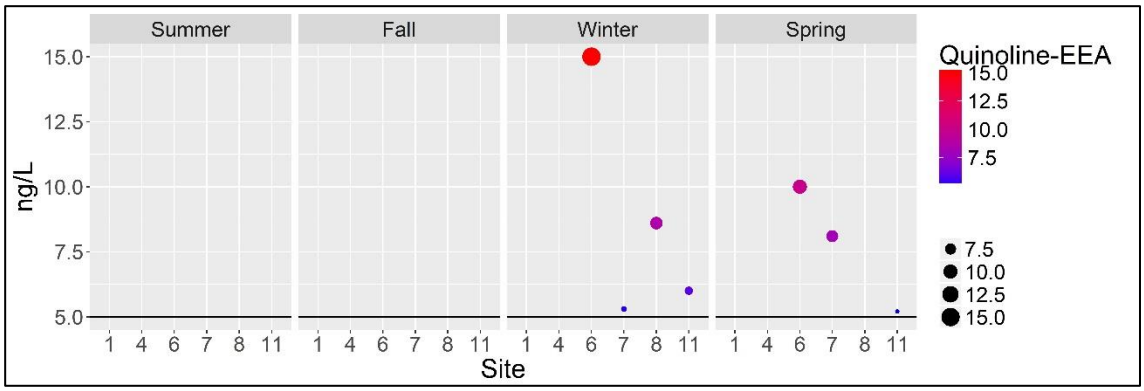

Figure B 14. Quinoline detections in ng/L for each season (EEA lab results).

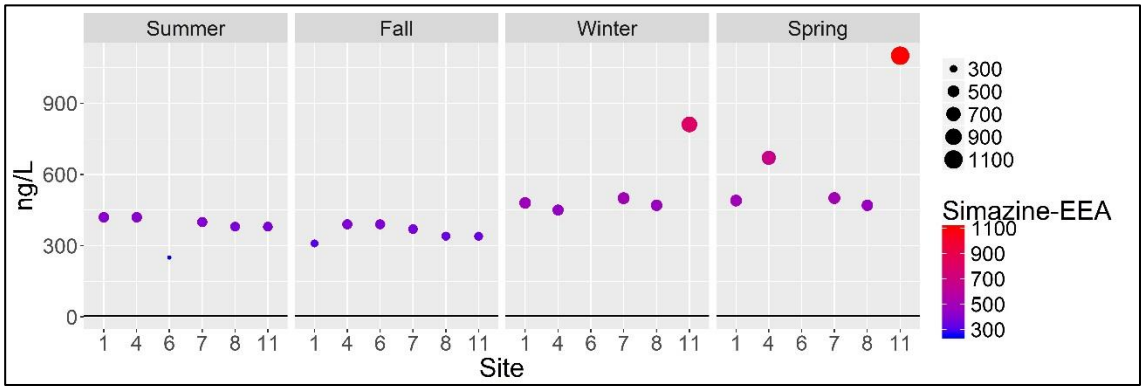

Figure B 15. Simazine detections in ng/L for each season (EEA lab results).

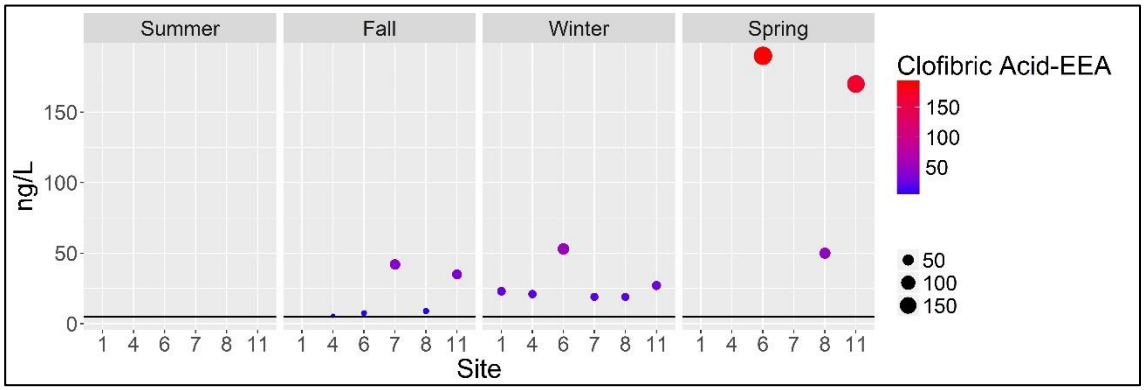

Figure B 16. Clofibric acid detections in ng/L for each season (EEA lab results).

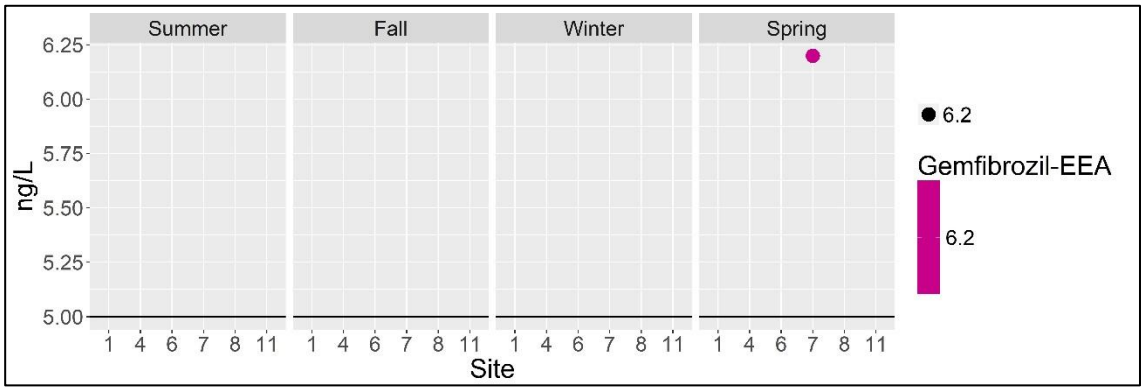

Figure B 17. Gemfibrozil detections in ng/L for each season (EEA lab results).

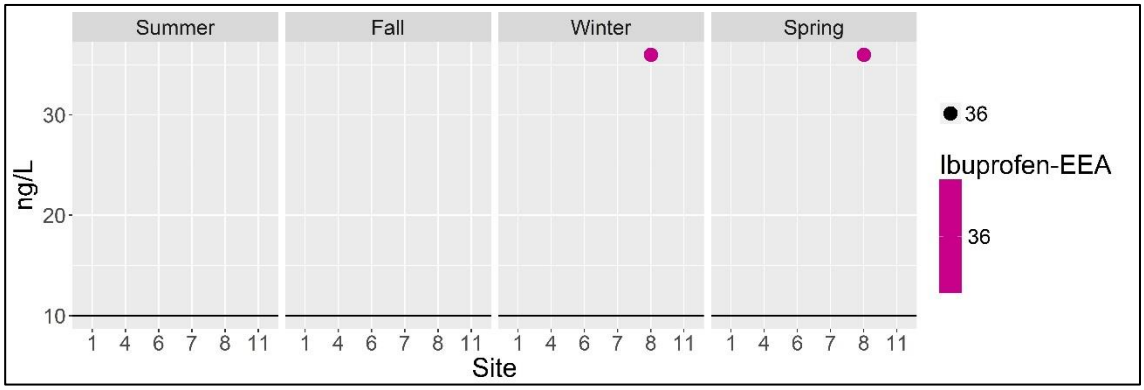

Figure B 18. Ibuprofen detections in ng/L for each season (EEA lab results).

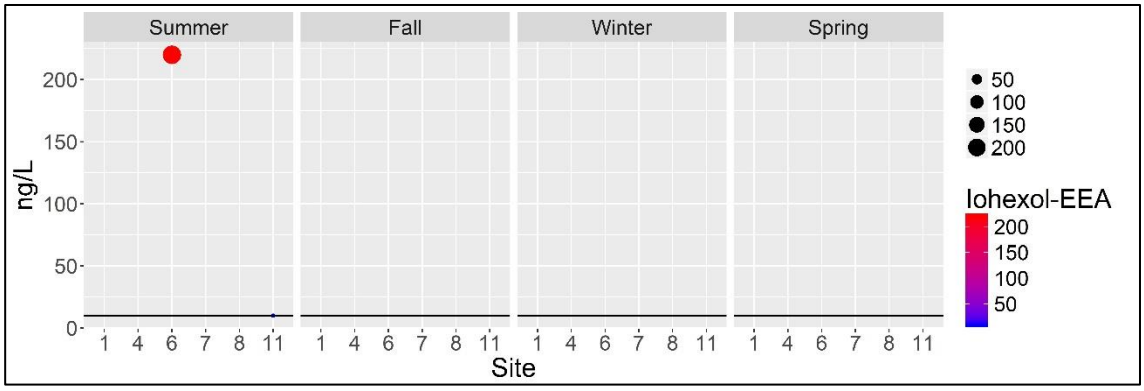

Figure B 19. Iohexal detections in ng/L for each season (EEA lab results).

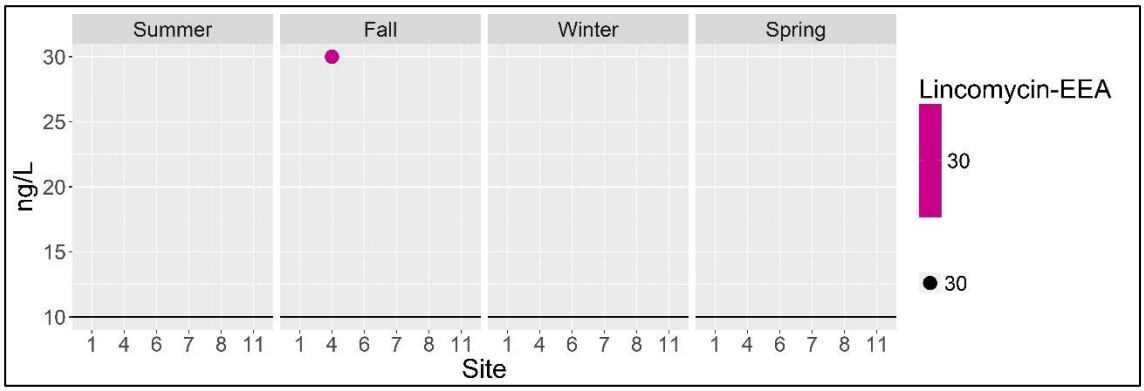

Figure B 20. Lincomycin detections in ng/L for each season (EEA lab results).

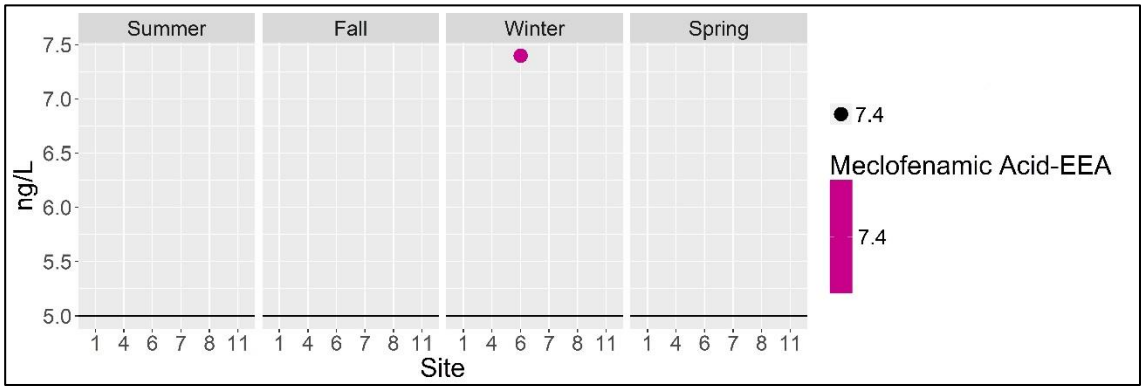

Figure B 21. Meclofenamic acid detections in ng/L for each season (EEA lab results).

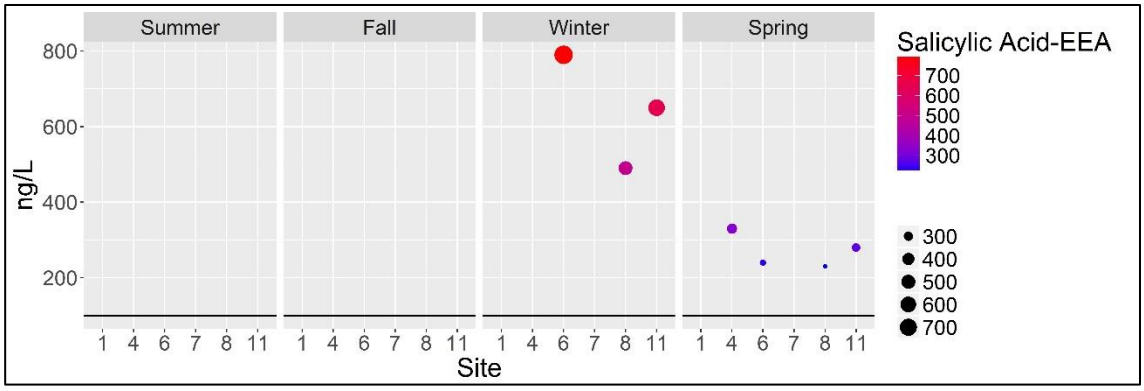

Figure B 22. Salicylic acid detections in ng/L for each season (EEA lab results).

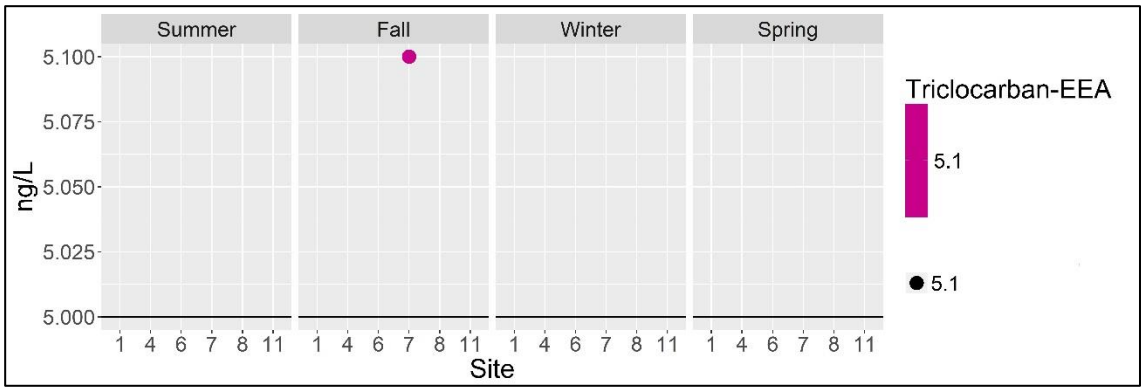

Figure B 23. Triclocarban detections in ng/L for each season (EEA lab results).

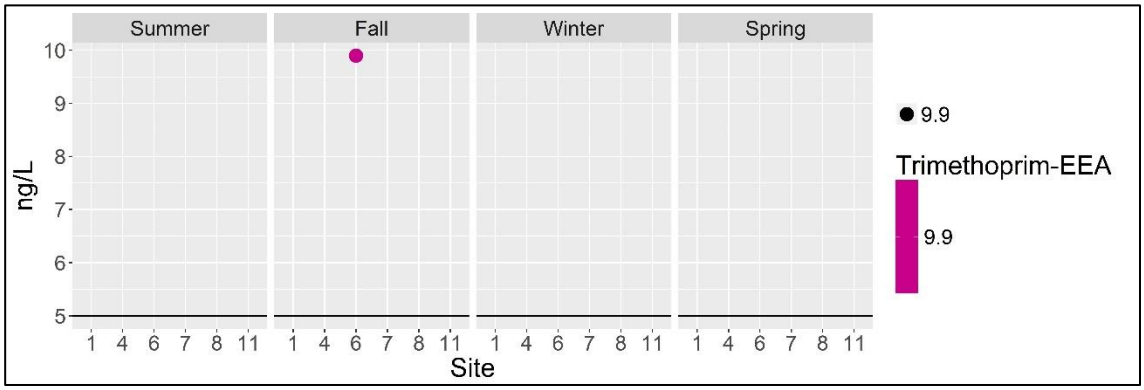

Figure B 24. Trimethoprim detections in ng/L for each season (EEA lab results).

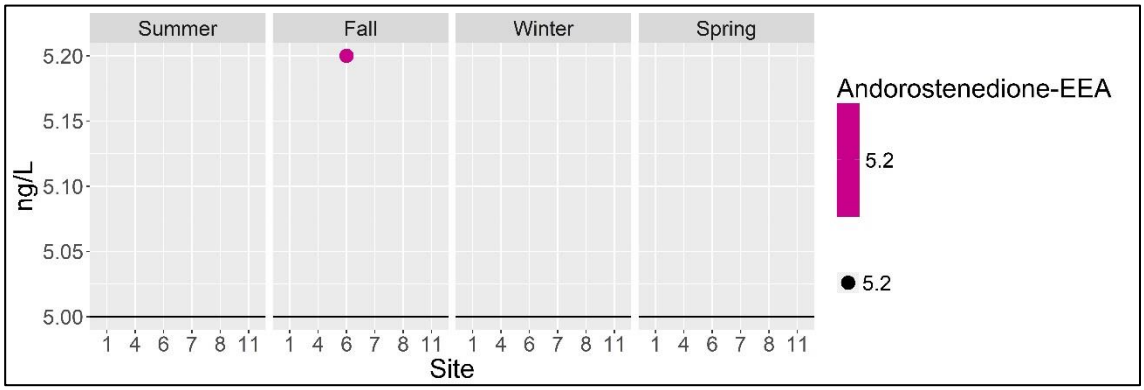

Figure B 25. Andorostenedione detections in ng/L for each season (EEA lab results).

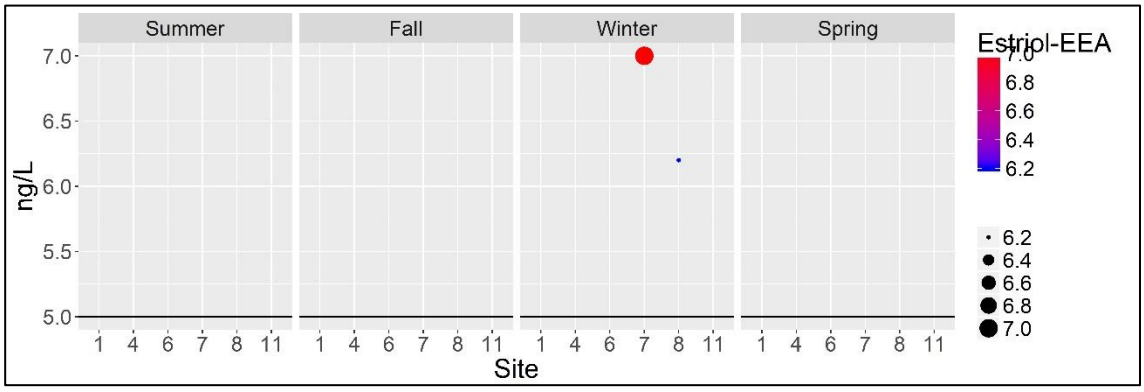

Figure B 26. Estriol detections in ng/L for each season (EEA lab results).

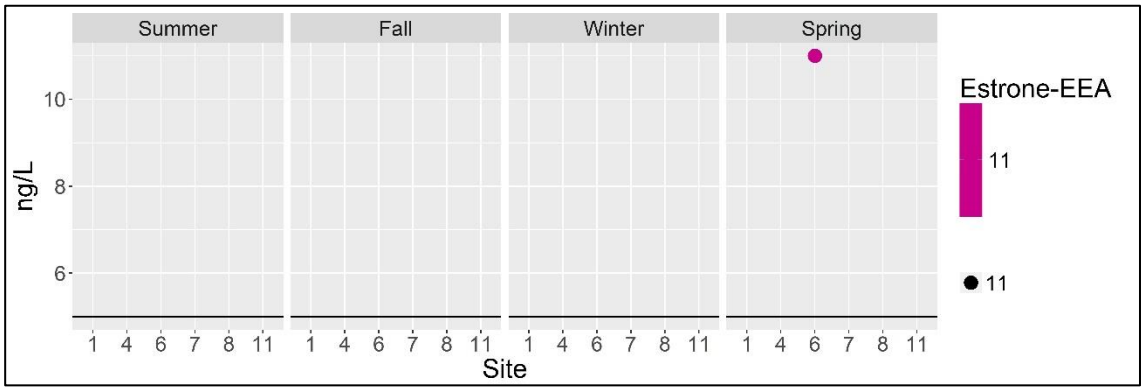

Figure B 27. Estrone detections in ng/L for each season (EEA lab results).

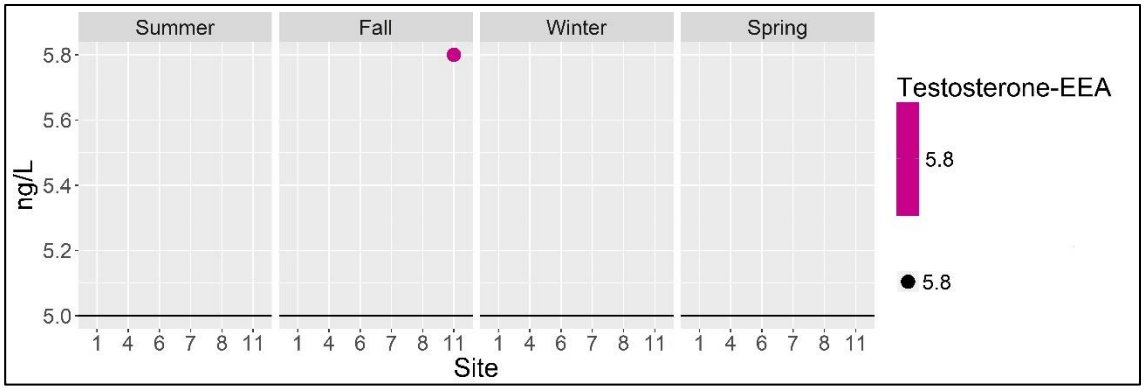

Figure B 28. Testosterone detections in ng/L for each season (EEA lab results).

Other Compounds – EEA

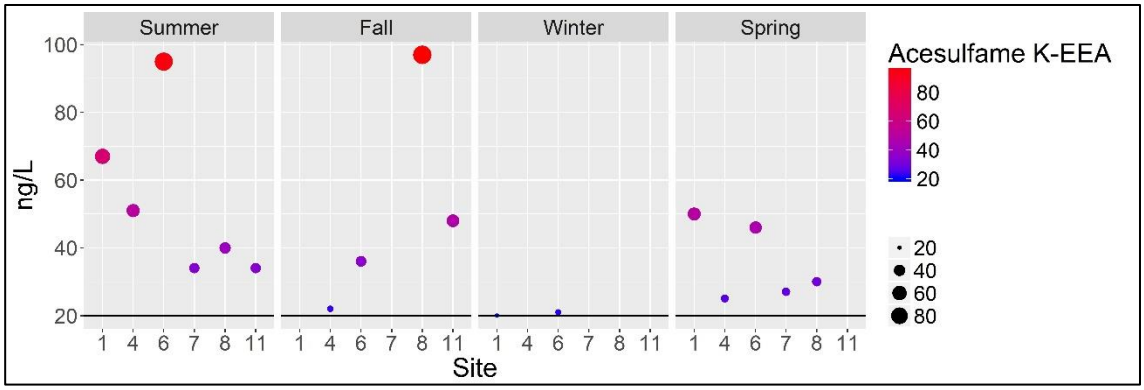

Figure B 29. Acesulfame-K detections in ng/L for each season (EEA lab results).

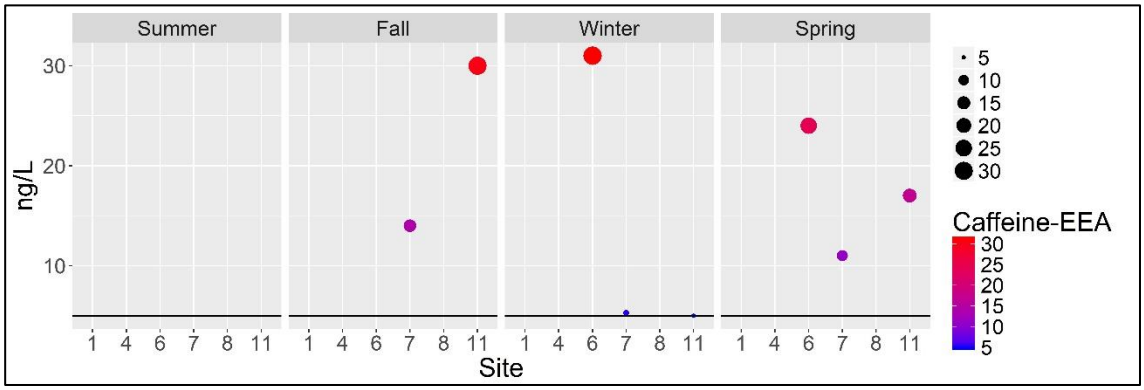

Figure B 30. Caffeine detections in ng/L for each season (EEA lab results).

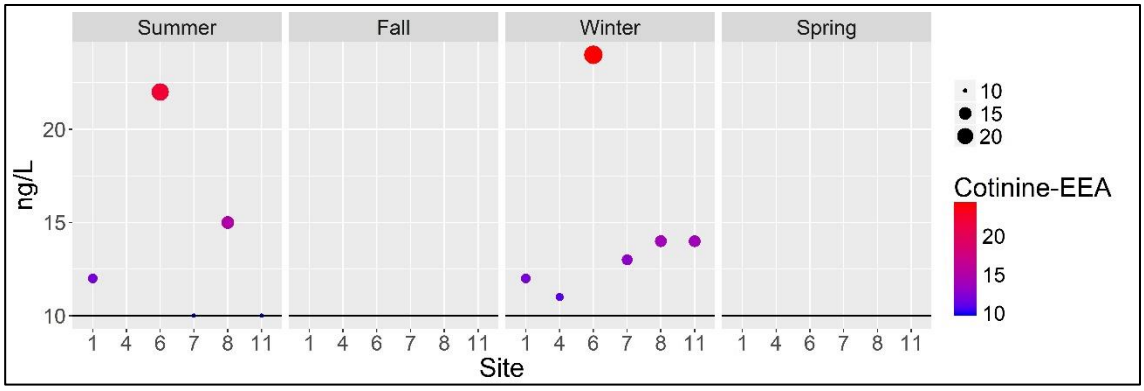

Figure B 31. Cotinine detections in ng/L for each season (EEA lab results).

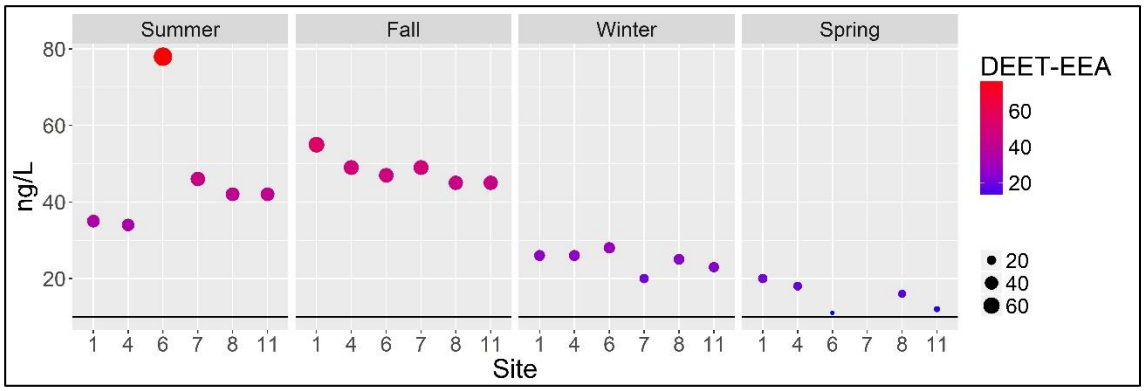

Figure B 32. DEET detections in ng/L for each season (EEA lab results).

Industrial Compounds – WEST

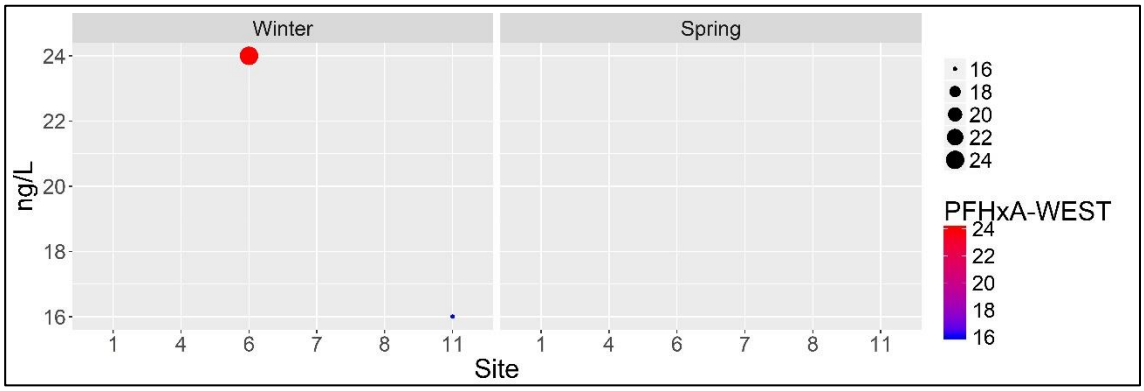

Figure B 33. PFHxA detections in ng/L for winter and spring (WEST lab results).

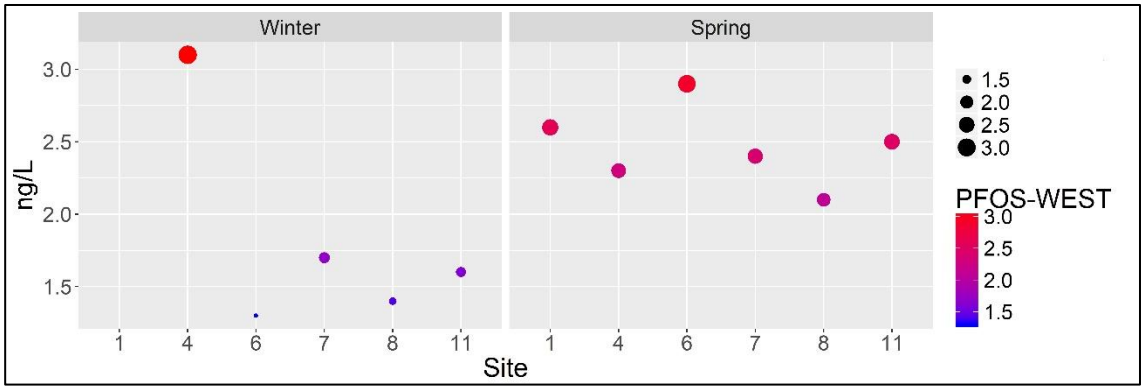

Figure B 34. PFOS detections in ng/L for winter and spring (WEST lab results).

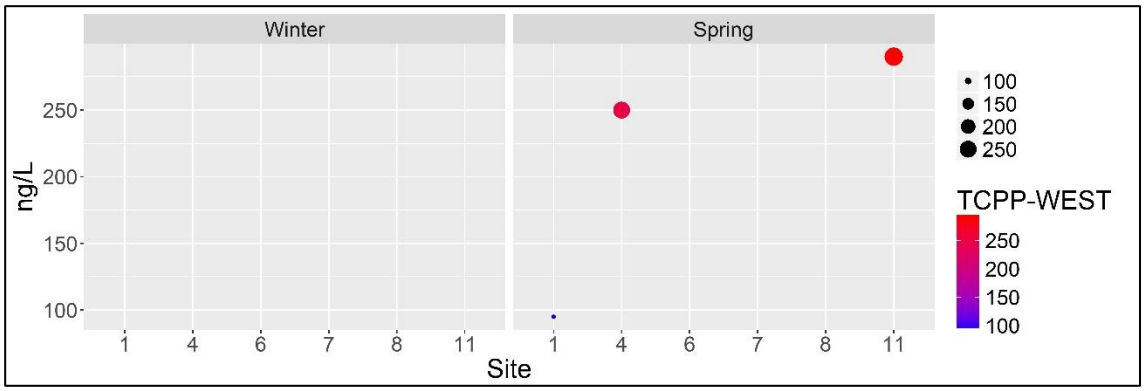

Figure B 35. TCPP detections in ng/L for winter and spring (WEST lab results).

Pesticide Compounds – WEST

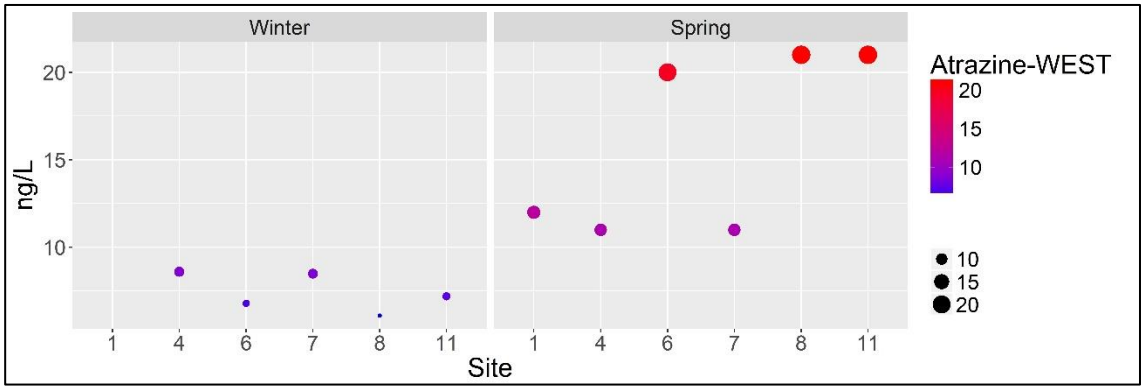

Figure B 36. Atrazine detections in ng/L for winter and spring (WEST lab results).

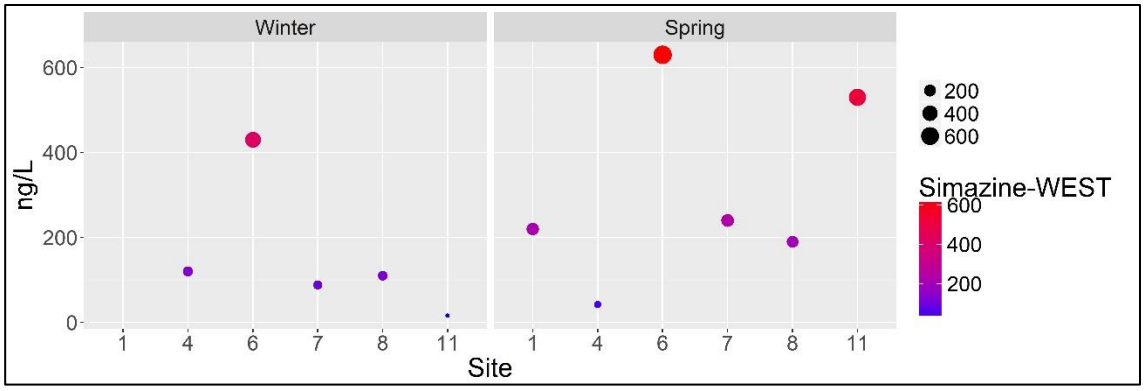

Figure B 37. Simazine detections in ng/L for winter and spring (WEST lab results).

PPCP Compounds – WEST

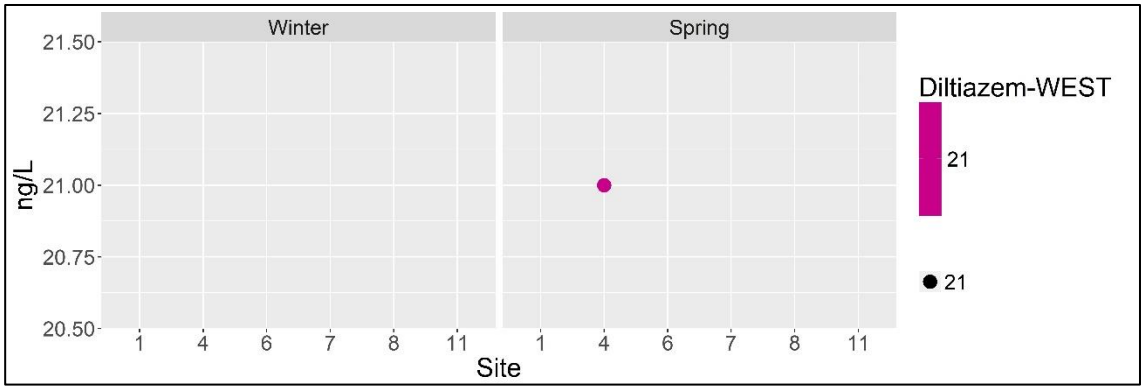

Figure B 38. Diltiazem detections in ng/L for winter and spring (WEST lab results).

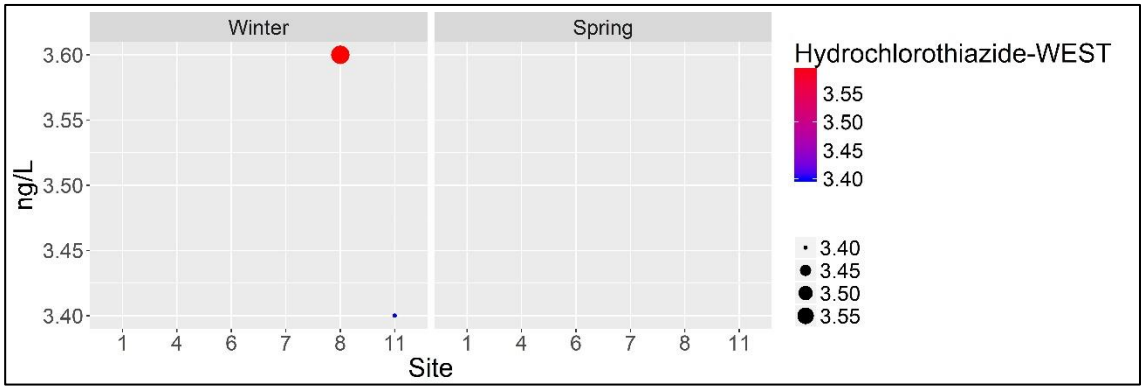

Figure B 39. Hydrochlorothiazide detections in ng/L for winter and spring (WEST lab results).

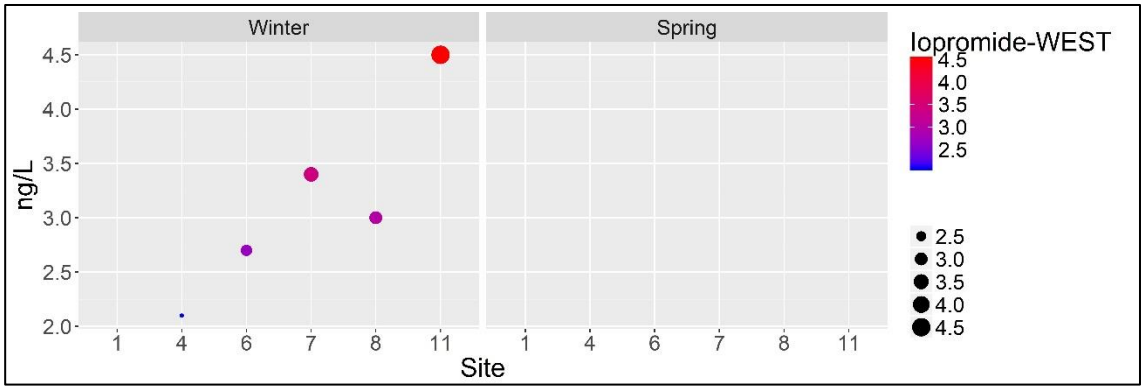

Figure B 40. Iopromide detections in ng/L for winter and spring (WEST lab results).

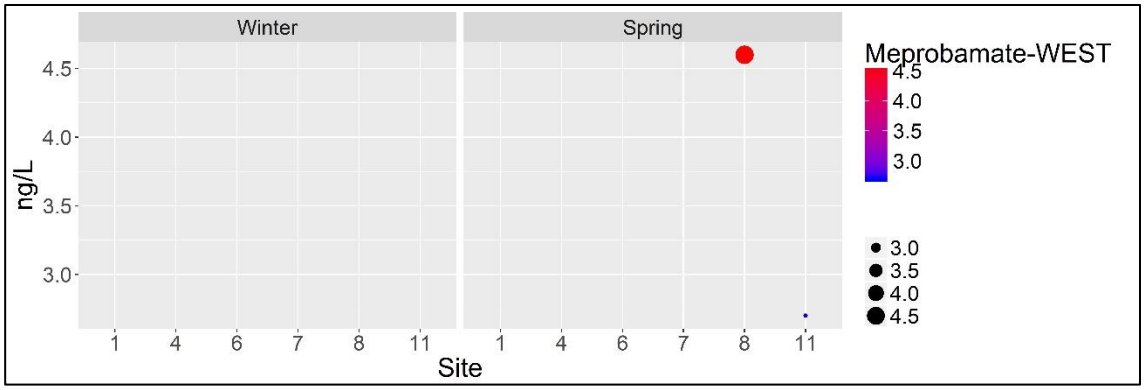

Figure B 41. Meprobamate detections in ng/L for winter and spring (WEST lab results).

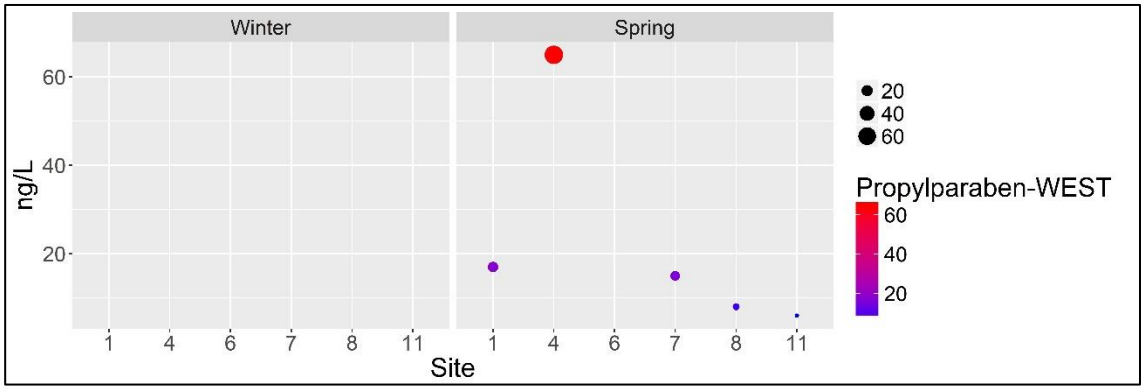

Figure B 42. Propyl paraben detections in ng/L for winter and spring (WEST lab results).

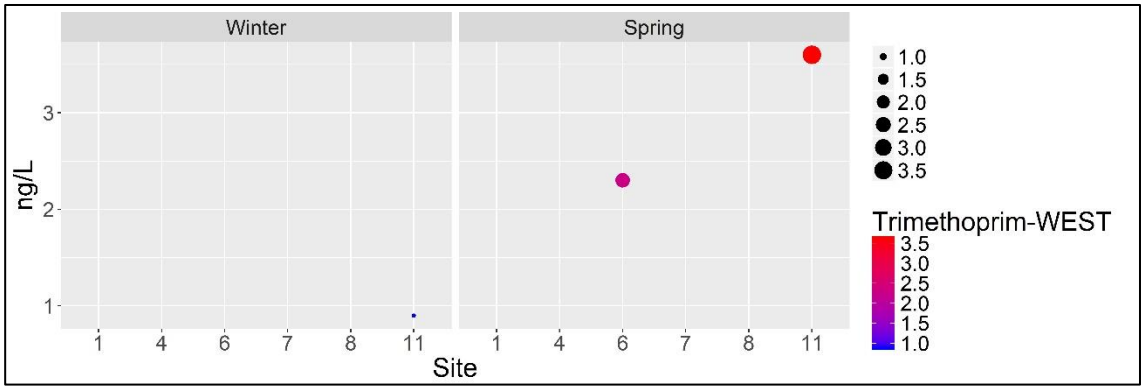

Figure B 43. Trimethoprim detections in ng/L for winter and spring (WEST lab results).

Other Compounds –WEST

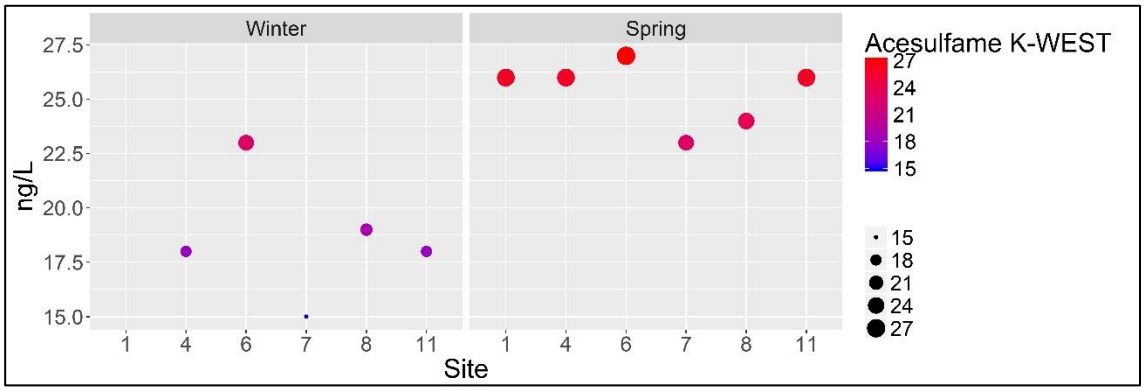

Figure B 44. Acesulfame K detections in ng/L for winter and spring (WEST lab results).

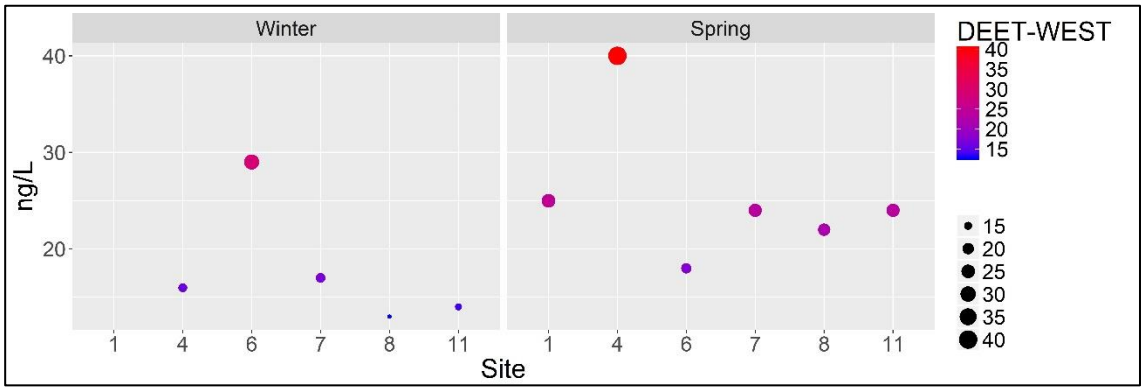

Figure B 45. DEET detections in ng/L for winter and spring (WEST lab results).

Appendix C: Codes for R

C.1 Code to make graphs for compounds analyzed by EEA lab

```
#set the working directory

#check to see if it's in the right place:

getwd()


library(Amelia)

library(plotly)

library(reshape2)


#clean environment

rm(list=ls())


#read data:

gsa=read.csv("CompoundsEEA.csv") #first row has "MRL" values #gsa is the folder my

data is in, CompoundsEEA is the excel file

names(gsa)


#change factor levels for subsequent plotting

gsa$Season=factor(gsa$Season,levels                                                =

c("Summer","Fall","Winter","Spring","MRL"),ordered = TRUE)

gsa$Site=factor(gsa$Site,levels = c("1","4","6","7","8","11","MRL"),ordered = TRUE)
```

```
#create dataframes for each class
#industrial=gsa[c("BPA...EEA","NP...EEA","OP...EEA","TDCPP...EEA","Site","Seaso
n")]
#pesticide=gsa[c("X2.4.D...EEA","Atrazine...EEA","Bromacil...EEA","Cyanazine...EE
A","DACT...EEA","DEA...EEA","DIA...EEA","Diuron...EEA","OUST...EEA","Quinol
ine...EEA","Simazine...EEA","Site","Season")]
#ppcp=gsa[c("Clofibric.Acid...EEA","Ibuprofen...EEA","Iohexol...EEA","Lincomycin..
.EEA","Meclofenamic.Acid...EEA","Salicylic.Acid...EEA","Triclocarban...EEA","Trim
ethoprim...EEA","Site","Season")]
#hormone=gsa[c("Andorostenedione...EEA","Estriol...EEA","Estrone...EEA","Testoste
rone...EEA")]
#other=gsa[c("Acesulfame.K...EEA","Caffeine...EEA","Cotinine...EEA","DEET...EEA
","Site","Season")]

missmap(gsa[2:25,1:32])

##########################
##########################Single plot- manually enter every contaminant
##########################
p = ggplot(gsa[2:25,], aes(x=Site, y=Estriol...EEA,col=Estriol...EEA,
size=Estriol...EEA)) + geom_point()+geom_hline(yintercept = gsa[1,"Estriol...EEA"])
#p = p + scale_color_gradient2(low="blue",mid="white",high="red")
p = p + scale_color_gradient(low="blue",high="red")
```

```
p
# Divide by season, going horizontally and wrapping with 4 columns
p = p + facet_wrap( ~ Season, ncol=4)
p = p + theme(text = element_text(size=20))
p = p + labs(colour = "Estriol-EEA", y="ng/L")
p = ggplotly(p)
p

ggsave("Estriol.EEA.png", width = 12, height = 4, units = c("in"),dpi = 600)
p
##########################
##########################
##########################
#change the dataframe scheme
gsa_long=melt(gsa)
p

#loop through all columns:
#loop will only label them with “contaminant name…lab” not “contaminant name-lab”
feat=names(gsa)
feat=feat[1:32]
#contaminants names
```

```
contname=c("Bromacil...EEA","X2.4.D...EEA","Diuron...EEA","OUST...EEA","Simaz
ine...EEA","Atrazine...EEA","Cyanazine...EEA","DIA...EEA","DACT...EEA","DEA...
EEA","Quinoline...EEA","BPA...EEA","NP...EEA","OP...EEA","TDCPP...EEA","Clof
ibric.Acid...EEA","Gemfibrozil...EEA","Iohexol...EEA","Ibuprofen...EEA","Lincomyci
n...EEA","Meclofenamic.Acid...EEA","Salicylic.Acid...EEA","Trimethoprim...EEA","
Triclocarban...EEA","Testosterone...EEA","Andorostenedione...EEA","Estriol...EEA","
Estrone...EEA","DEET...EEA","Acesulfame.K...EEA","Cotinine...EEA","Caffeine...EE
A")
for (plt in seq_along(feat)){
  p=ggplot(gsa[2:25,], aes(x=Site, y=gsa[2:25,plt],col=gsa[2:25,plt], size=gsa[2:25,plt]))
+ geom_point() +
    geom_hline(yintercept = gsa[1,plt])+
    scale_color_gradient(low="blue",high="red")+
    labs(colour = contname[plt], size = "                    .")+
    guides(size = guide_legend(reverse=TRUE,order = 1))+
    # Divide by season, going horizontally and wrapping with 4 columns
    facet_wrap( ~ Season, ncol=4) +
    theme_get()+
    theme(text = element_text(size=20)) +
    scale_y_continuous(feat[plt],limits=c(0, max(1.1*gsa[2:25,plt])))

  ggsave(paste(feat[plt],".png"), width = 12, height = 4, units = c("in"),dpi = 600)
  rm(p)
```

```
  print(gsa[1,plt])
}
```

C.2 Code to make graphs for compounds analyzed by Arizona WEST lab

```
#set the working directory
#check to see if it's in the right place:
getwd()

library(Amelia)
library(plotly)
library(reshape2)

#clean environment
rm(list=ls())

#read data:
gsa=read.csv("CompoundsWEST.csv")
#gsa is the folder my data is in, CompoundsWEST is the excel file
names(gsa)

#change factor levels for subsequent plotting
gsa$Season=factor(gsa$Season,levels = c("Winter","Spring"),ordered = TRUE)
```

```
gsa$Site=factor(gsa$Site,levels = c("1","4","6","7","8","11"),ordered = TRUE)

#create dataframes for each class
#industrial=gsa[c("PFHxA...WEST","PFOS...WEST","Site","Season")]
#pesticide=gsa[c("Atrazine...WEST","Simazine...WEST","Site","Season")]
#ppcp=gsa[c("Diltiazem...WEST","Hydrochlorothiazide...WEST","Iopromide...WEST"
,"Meprobamate...WEST","Propylparaben...WEST","Trimethoprim...WEST","Site","Sea
son")]
#other=gsa[c(Acesulfame.K...WEST","DEET...WEST","Site","Season")]

missmap(gsa[2:12,1:12])

############################
############################Single plot - manually enter every contaminant
############################
p = ggplot(gsa[2:12,], aes(x=Site, y=Trimethoprim...WEST,col=Trimethoprim...WEST,
size=Trimethoprim...WEST)) + geom_point(yintercept =
gsa[1,"Trimethoprim...WEST"])
#p = p + scale_color_gradient2(low="blue",mid="white",high="red")
p = p + scale_color_gradient(low="blue",high="red")

p
# Divide by season, going horizontally and wrapping with 4 columns
```

```
p = p + facet_wrap( ~ Season, ncol=2)
p = p + theme(text = element_text(size=20))
p = p + labs(colour = "Trimethoprim-WEST", y="ng/L")
p = ggplotly(p)
p
ggsave("Trimethoprim.WEST.png", width = 12, height = 4, units = c("in"),dpi = 600)
p
##########################
##########################
##########################
#change the dataframe scheme
gsa_long=melt(gsa)
p


#loop through all columns:
#loop will only label them with “contaminant name…lab” not “contaminant name-lab”
feat=names(gsa)
feat=feat[1:12]
#contaminants names
contname=c("Simazine...WEST","Atrazine...WEST","PFHxA...WEST","PFOS...WEST
","TCPP...WEST","Diltiazem...WEST","Hydrochlorothiazide...WEST","Iopromide...W
EST","Meprobamate...WEST","Propylparaben...WEST","Trimethoprim...WEST","Tricl
ocar,"DEET...WEST","Acesulfame.K...WEST")
```

```
for (plt in seq_along(feat)){
  p=ggplot(gsa[2:12,], aes(x=Site, y=gsa[2:12,plt],col=gsa[2:12,plt], size=gsa[2:12,plt]))
+ geom_point()(yintercept = gsa[1,plt])+
    scale_color_gradient(low="blue",high="red")+
    labs(colour = contname[plt], size = "                    .")+
    guides(size = guide_legend(reverse=TRUE,order = 1))+
    # Divide by season, going horizontally and wrapping with 4 columns
    facet_wrap( ~ Season, ncol=2) +
    theme_get()+
    theme(text = element_text(size=20)) +
    scale_y_continuous(feat[plt],limits=c(0, max(1.1*gsa[2:12,plt])))

  ggsave(paste(feat[plt],".png"), width = 12, height = 4, units = c("in"),dpi = 600)
  rm(p)

  print(gsa[1,plt])
}
```

Appendix D: Graphs for Field Parameters

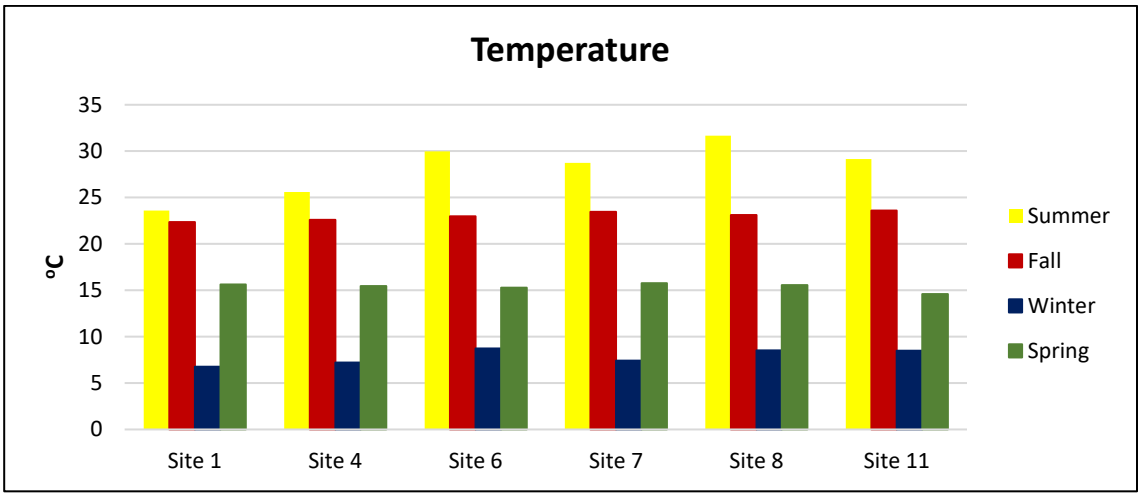

Figure D 1. Temperature values for every site and season.

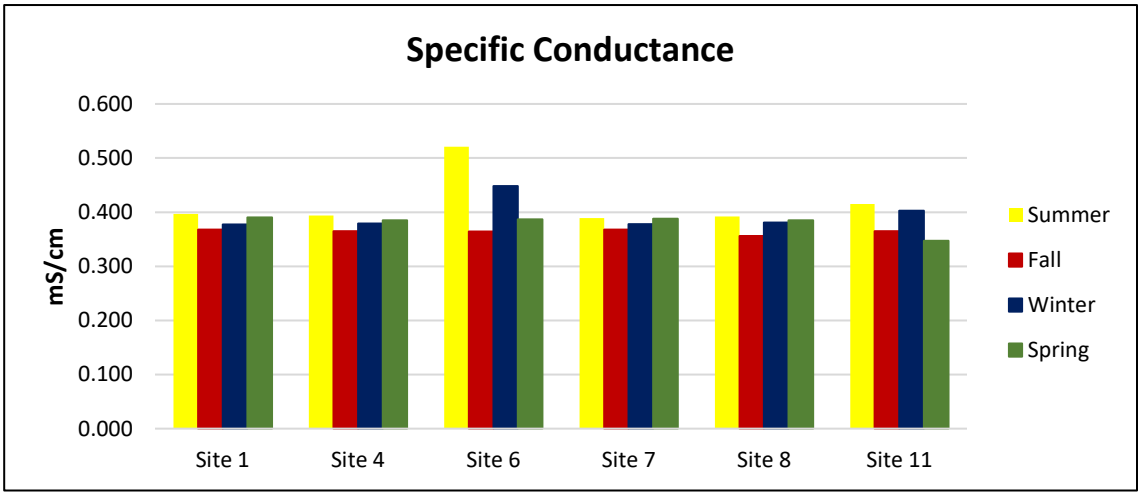

Figure D 2. Specific conductance values for every site and season.

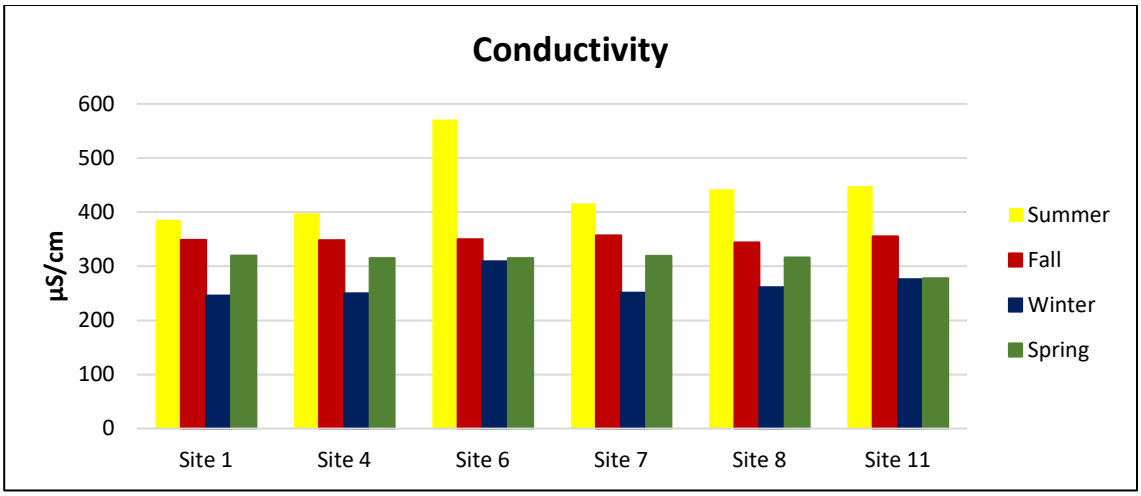

Figure D 3. Conductivity values for every site and season.

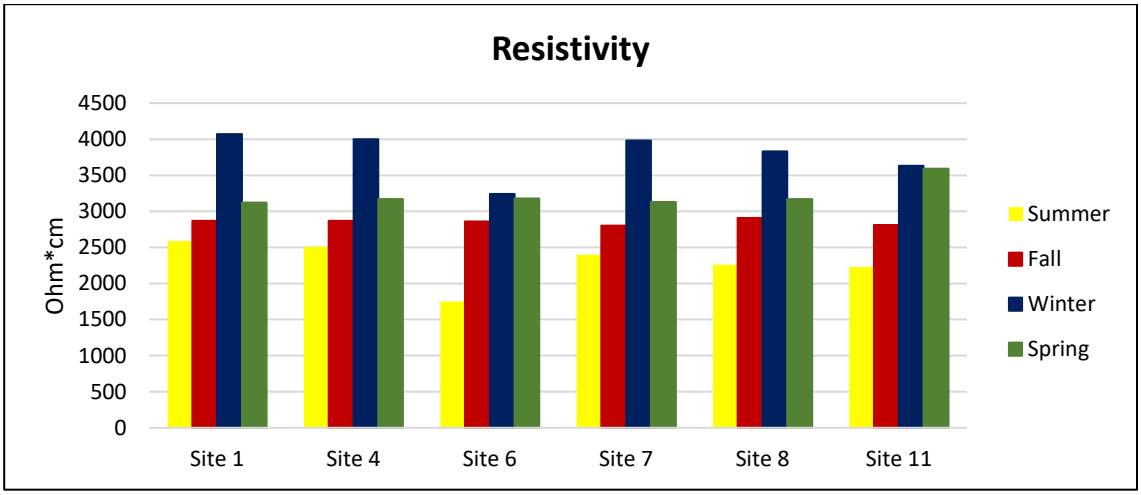

Figure D 4. Resistivity values for every site and season.

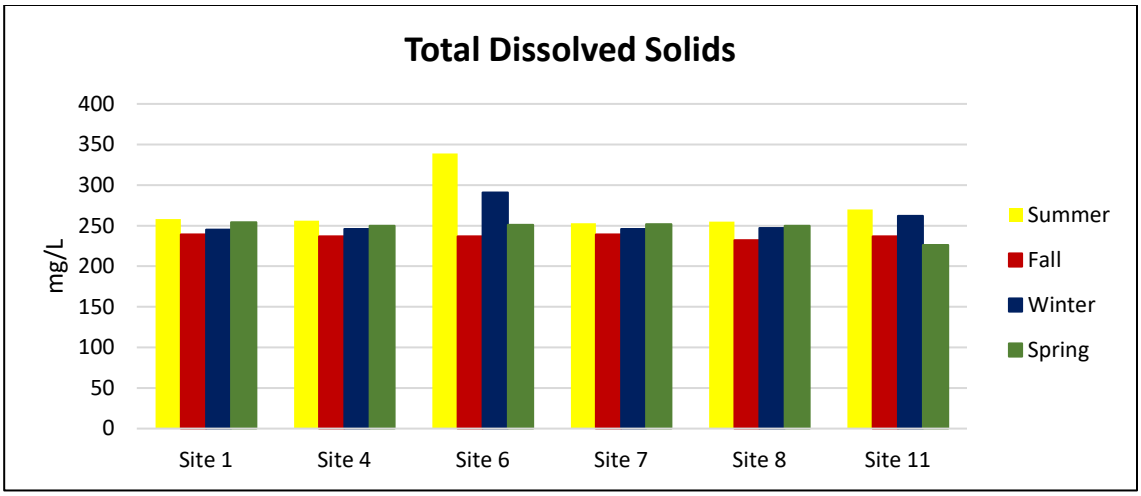

Figure D 5. Total dissolved solids values for every site and season.

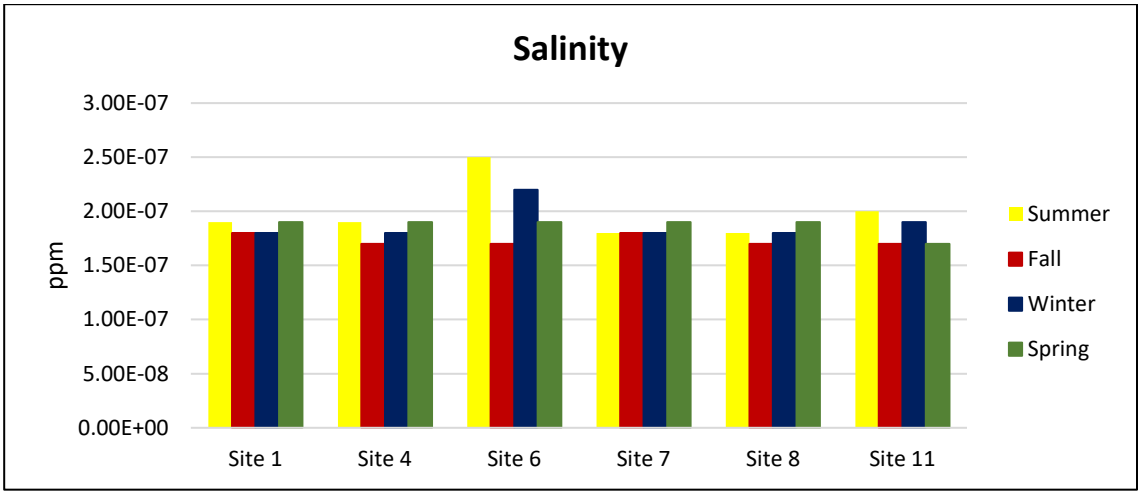

Figure D 6. Salinity values for every site and season.

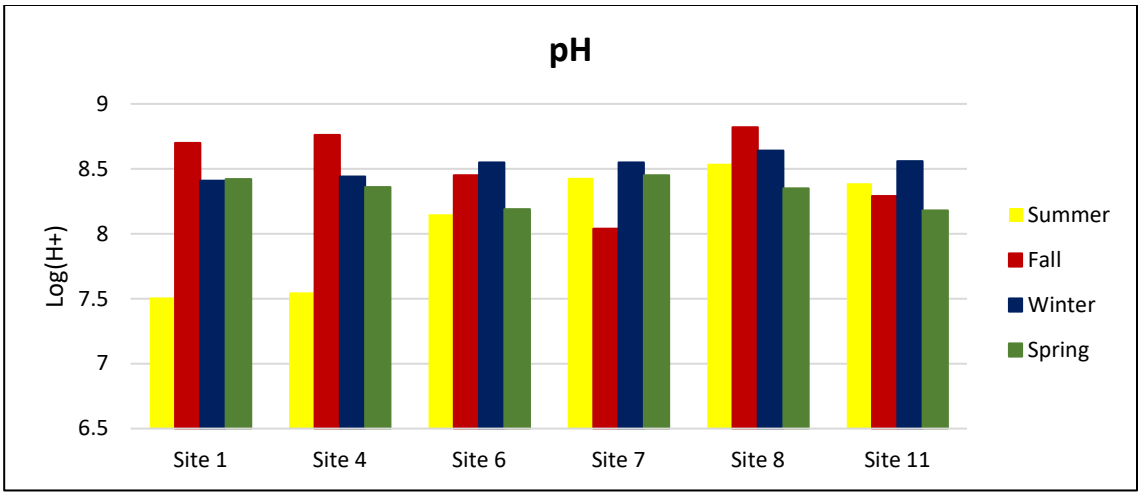

Figure D 7. pH values for every site and season.

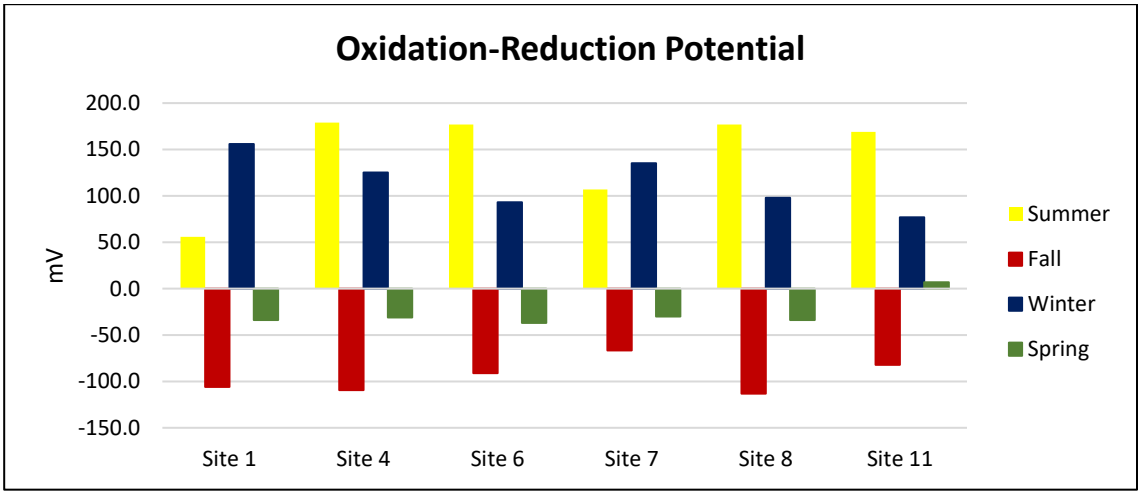

Figure D 8. Oxidation-reduction potential values for every site and season.

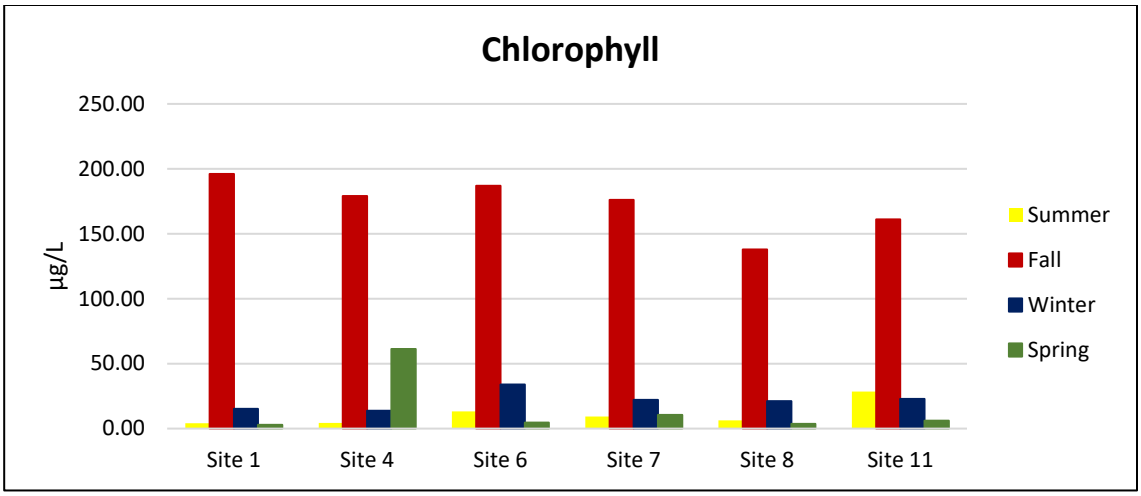

Figure D 9. Chlorophyll (concentration) values for every site and season.

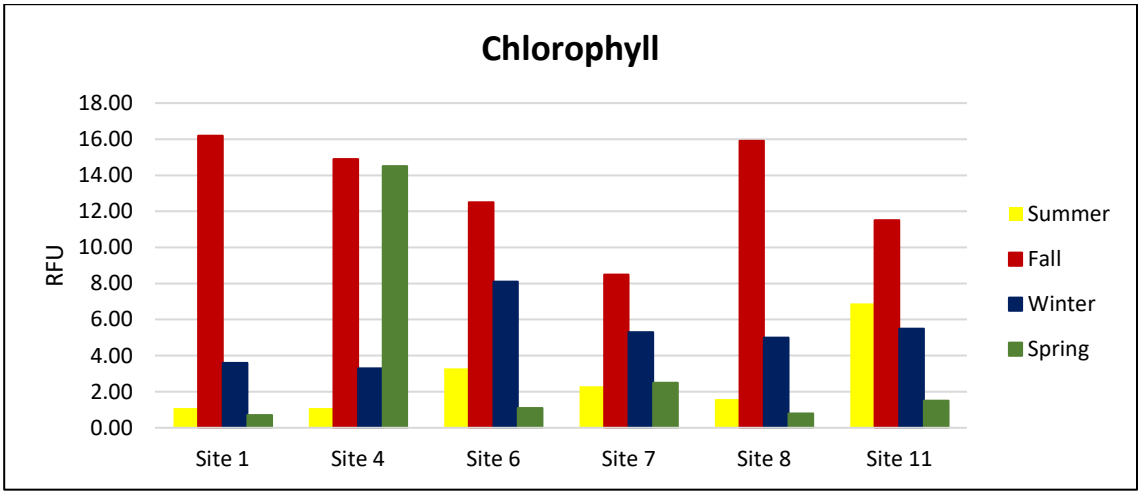

Figure D 10. Chlorophyll (RFU) values for every site and season.

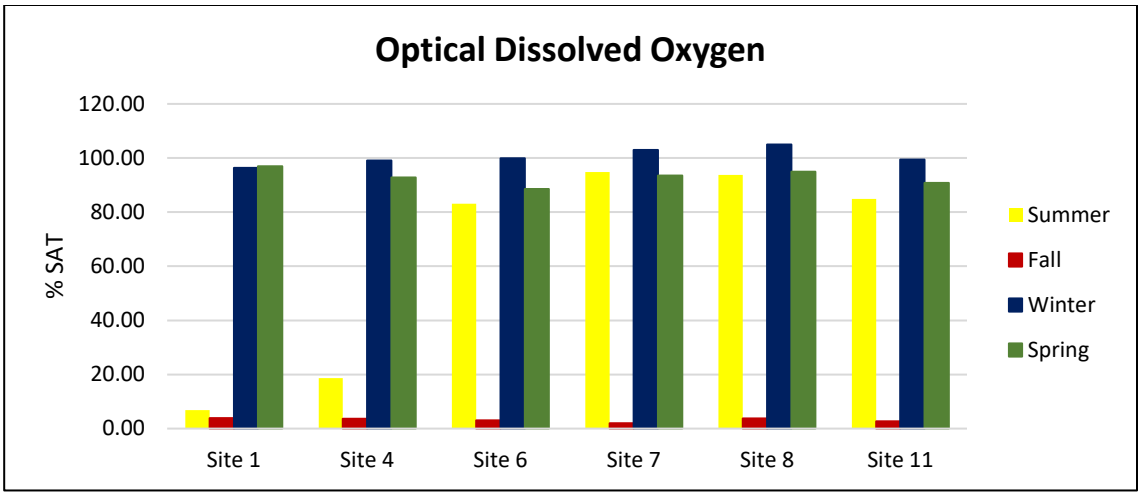

Figure D 11. Optical dissolved oxygen (% SAT) values for every site and season.

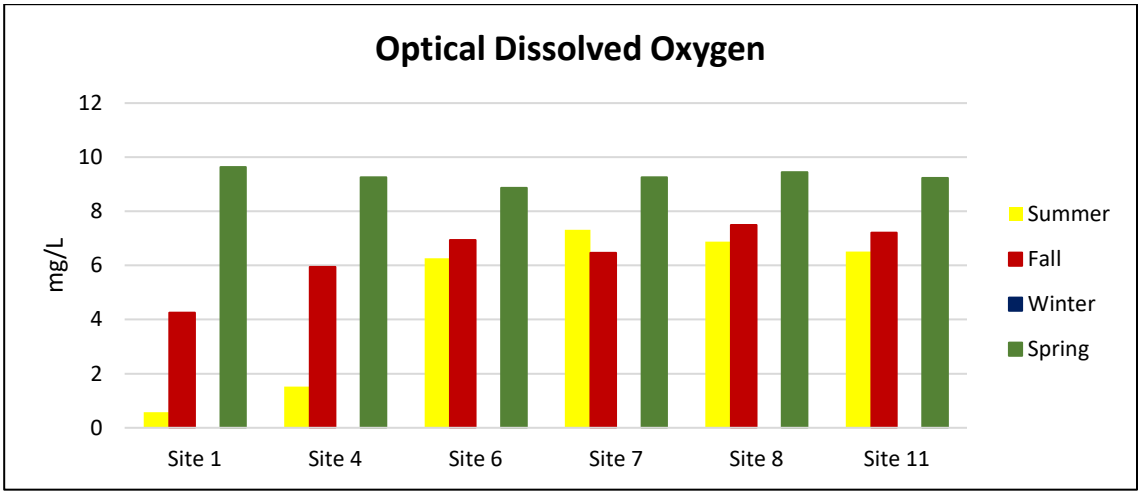

Figure D 12. Optical dissolved oxygen (as a concentration) values for every site and season.

Appendix E: Graphs for Loading Factor Evaluation

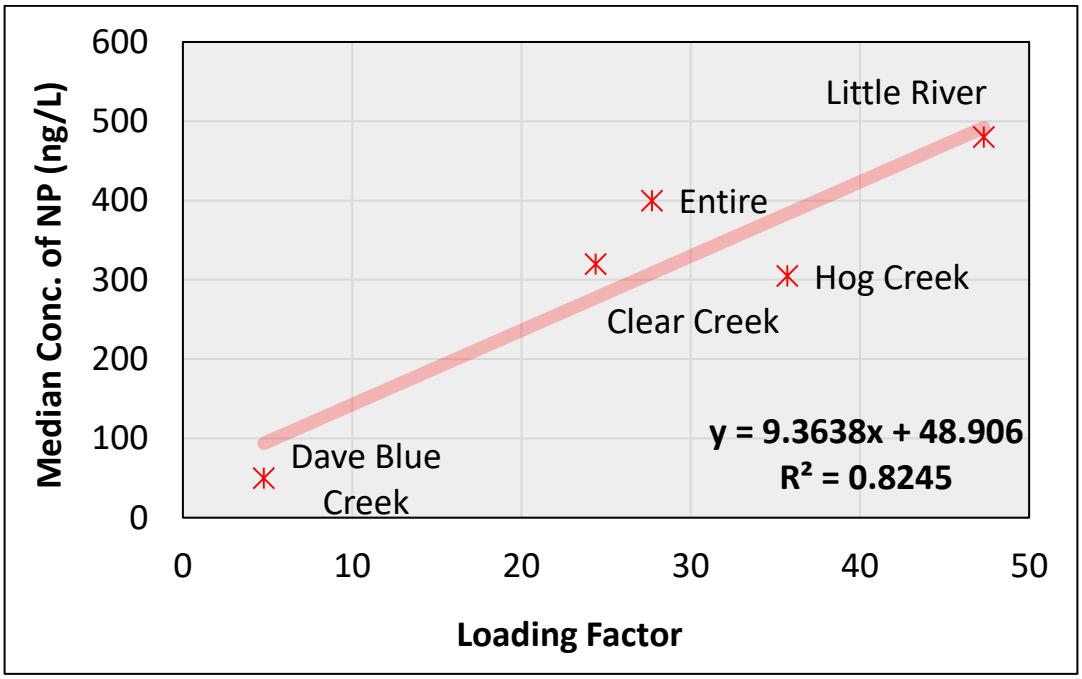

Figure E 1. Median concentrations of the benchmark industrial compound NP (ng/L) that correspond to a site/sub-watershed plotted against the loading factor.

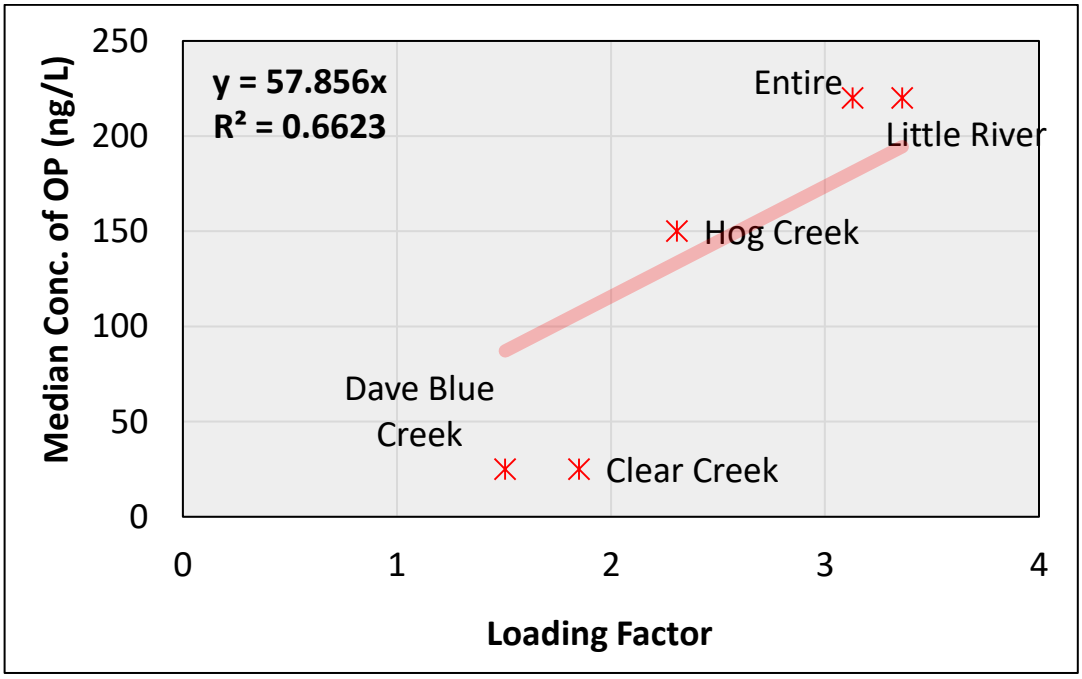

Figure E 2. Median concentrations of the benchmark industrial compound OP (ng/L) that correspond to a site/sub-watershed plotted against the loading factor.

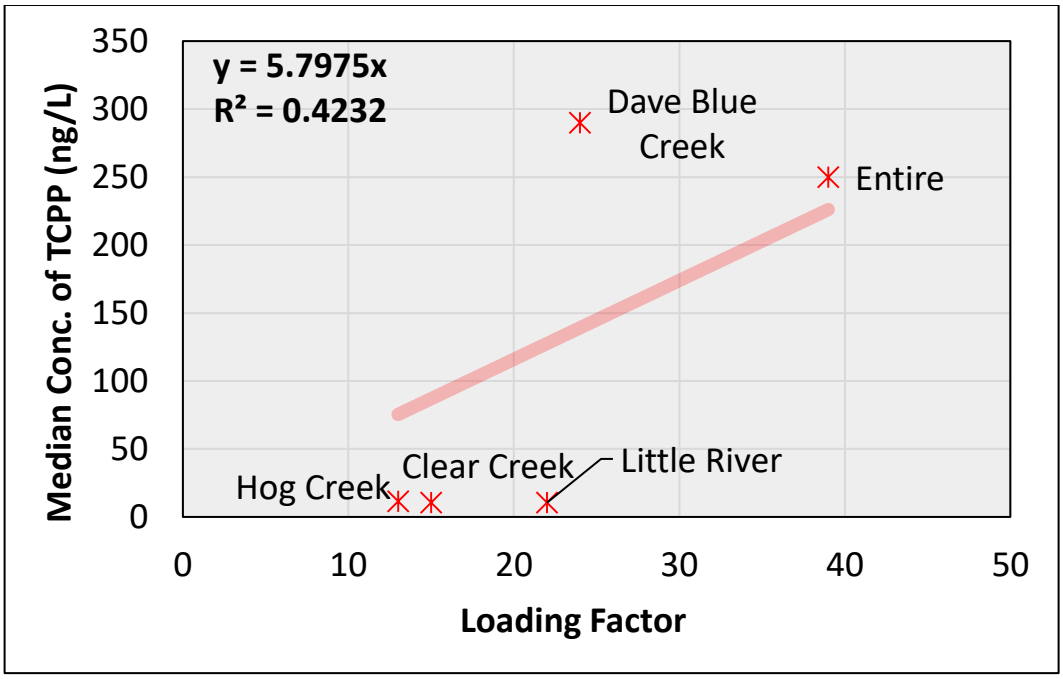

Figure E 3. Median concentrations of the benchmark industrial compound TCPP (ng/L) that correspond to a site/sub-watershed plotted against the loading factor.

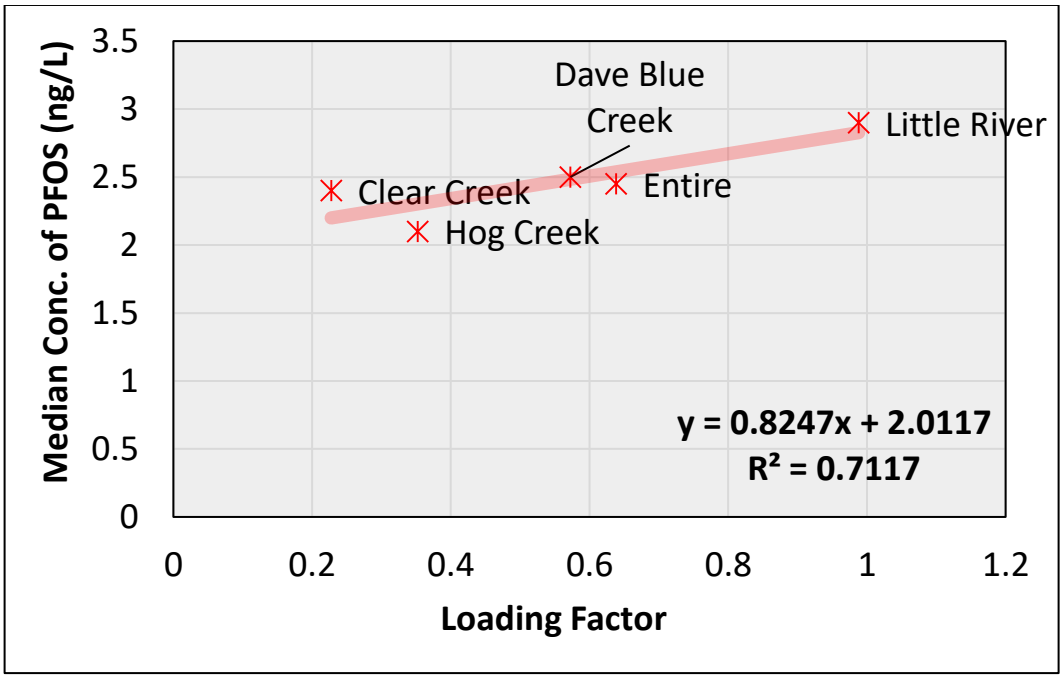

Figure E 4. Median concentrations of the benchmark industrial compound PFOS (ng/L) that correspond to a site/sub-watershed plotted against the loading factor.

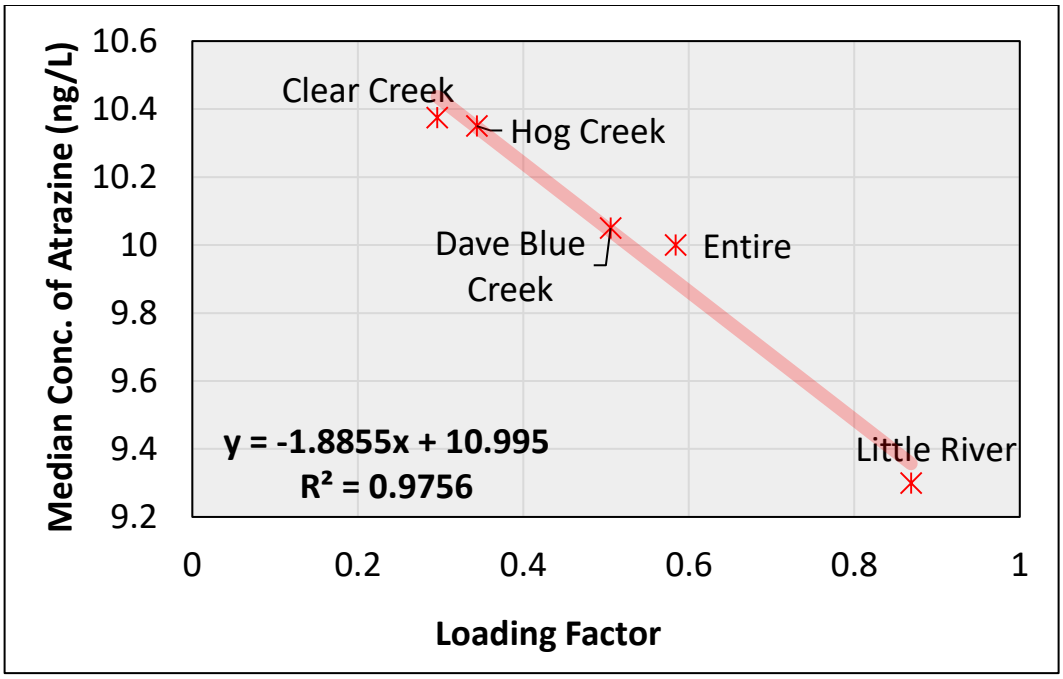

Figure E 5. Median concentrations of the benchmark pesticide compound atrazine (ng/L) that correspond to a site/sub-watershed plotted against the loading factor.

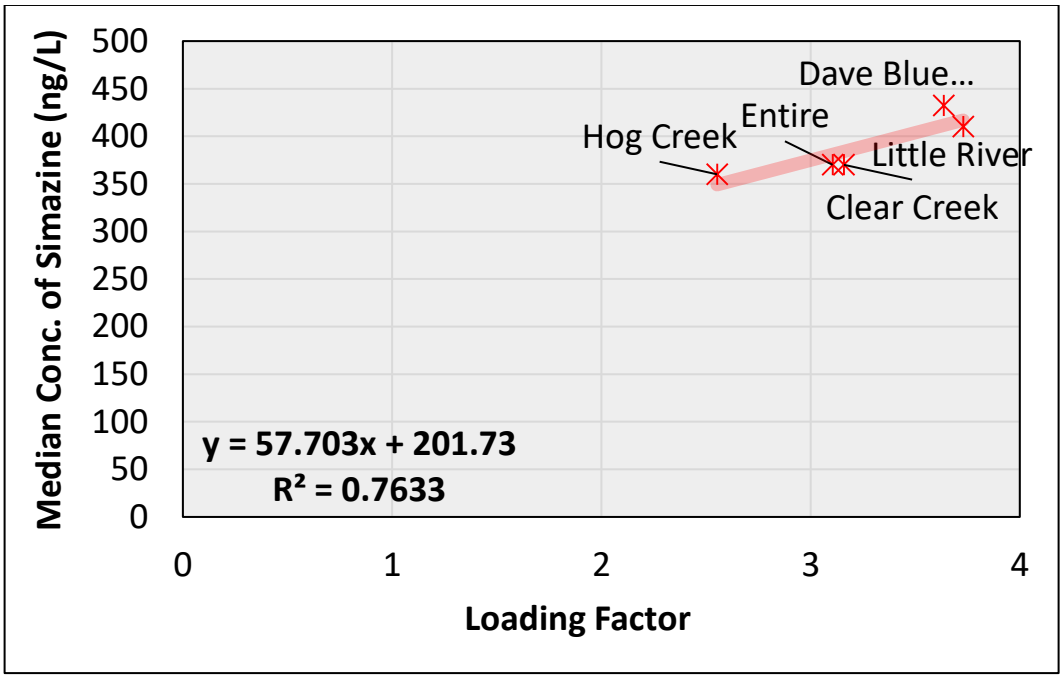

Figure E 6. Median concentrations of the benchmark pesticide compound simazine (ng/L) that correspond to a site/sub-watershed plotted against the loading factor.

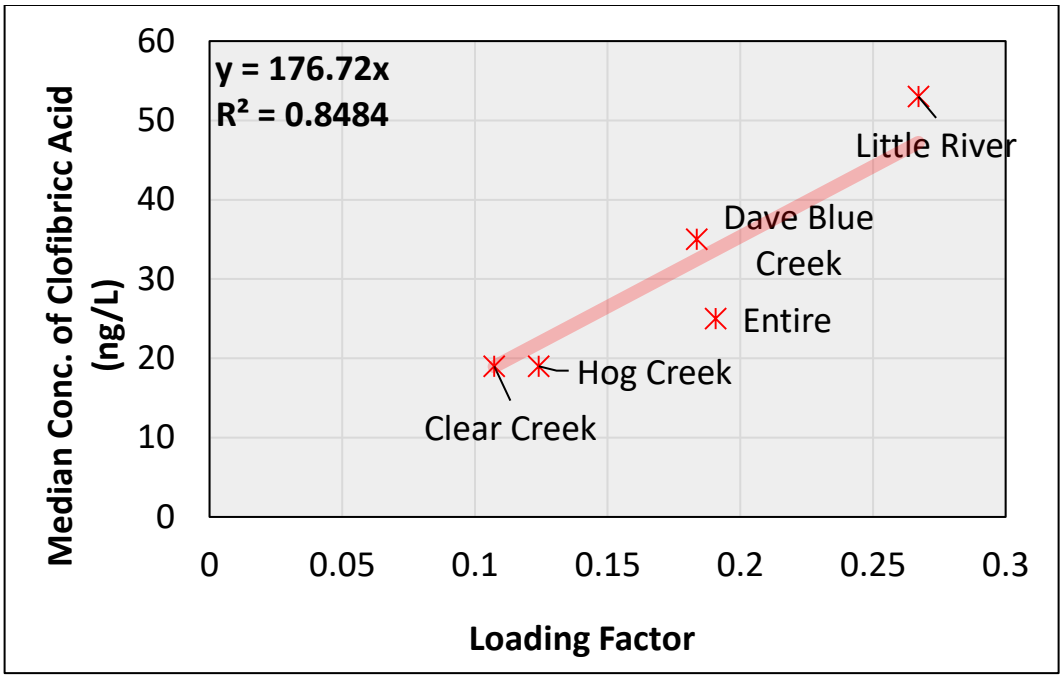

Figure E 7. Median concentrations of the benchmark PPCP compound clofibric acid (ng/L) that correspond to a site/sub-watershed plotted against the loading factor.

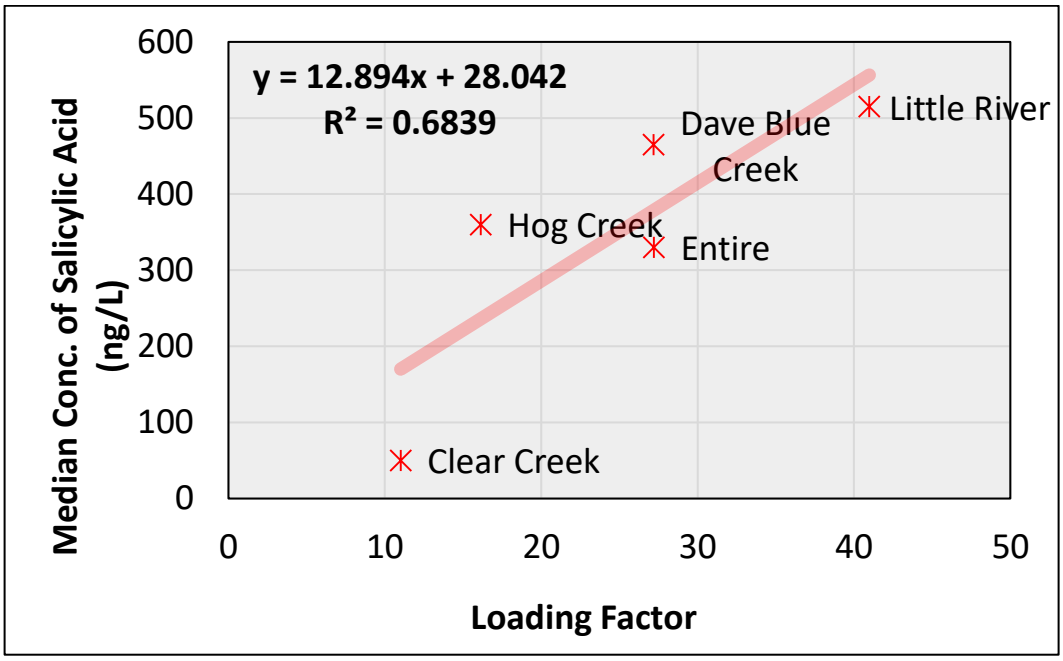

Figure E 8. Median concentrations of the benchmark PPCP compound salicylic acid (ng/L) that correspond to a site/sub-watershed plotted against the loading factor.

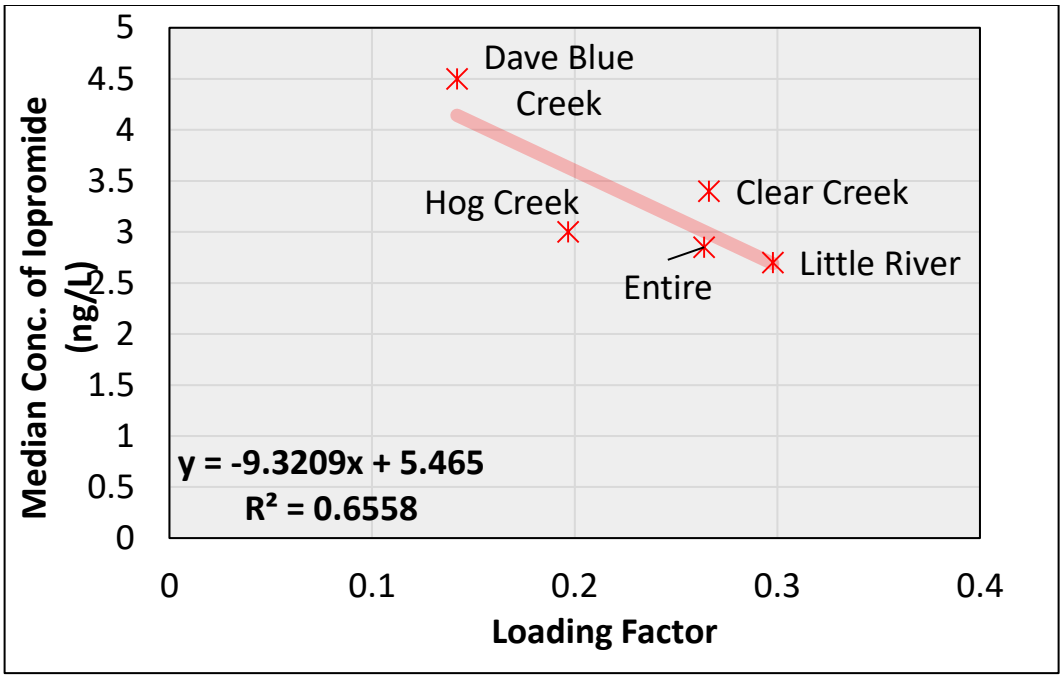

Figure E 9. Median concentrations of the benchmark PPCP compound iopromide (ng/L) that correspond to a site/sub-watershed plotted against the loading factor.

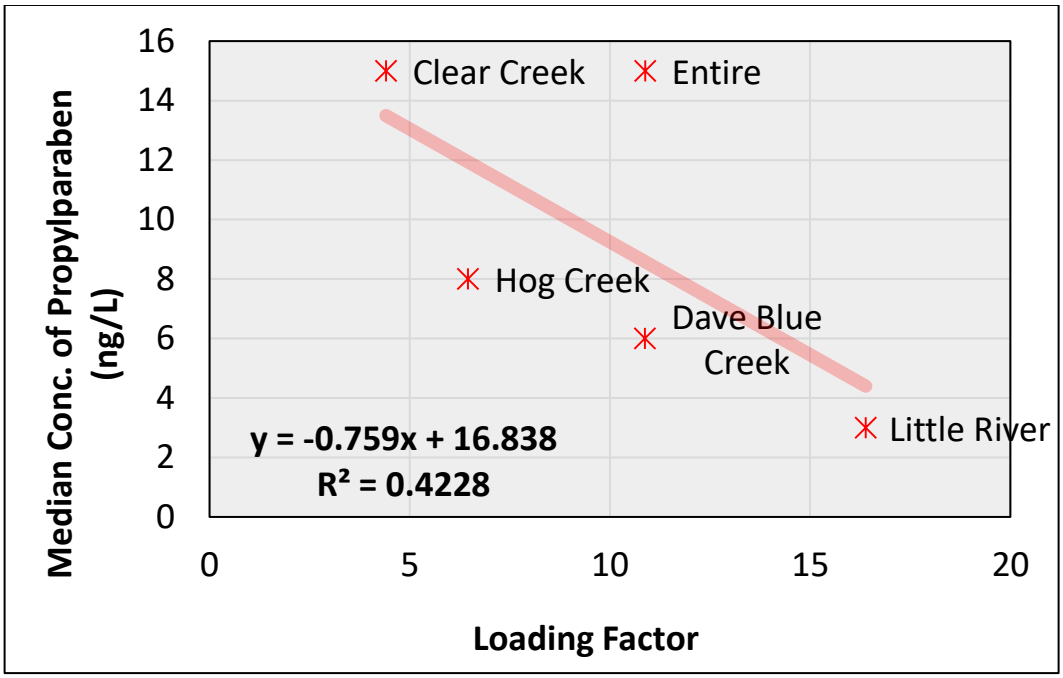

Figure E 10. Median concentrations of the benchmark PPCP compound propylparaben (ng/L) that correspond to a site/sub-watershed plotted against the loading factor.

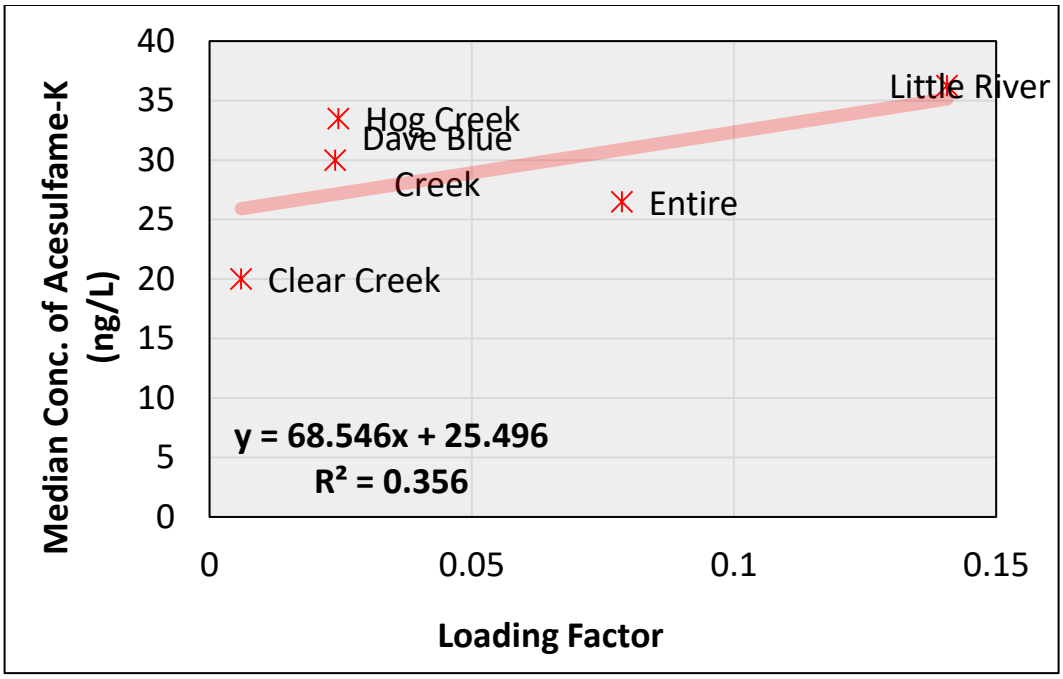

Figure E 11. Median concentrations of the benchmark other compound acesulfame-K (ng/L) that correspond to a site/sub-watershed plotted against the loading factor.

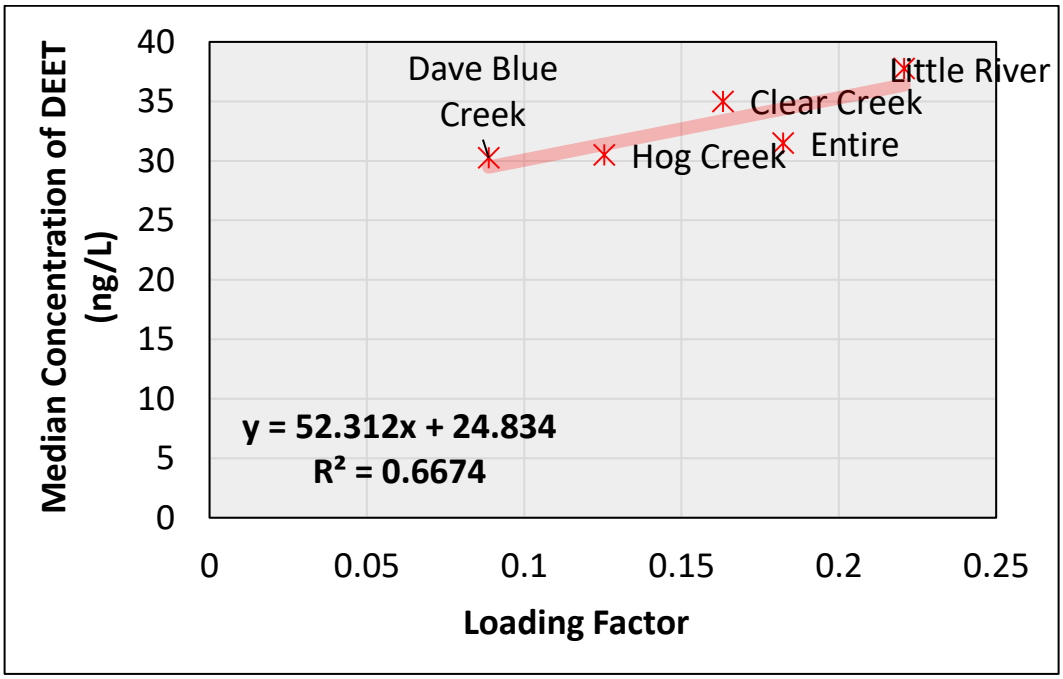

Figure E 12. Median concentrations of the benchmark other compound DEET (ng/L) that correspond to a site/sub-watershed plotted against the loading factor.