Wastewater sources of priority contaminants in four Canadian Arctic Communities

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Abstract

The main goal of this thesis was the investigate the wastewater sources of pharmaceuticals, microplastics, and per- and poly-fluorinated alkyl substances (PFASs) in Canadian Arctic communities. Current literature on the local sources of these contaminants in this region are lacking. Thus, a novel study into these sources and occurrences was undertook to better understand the impact they may have on the aquatic ecosystem in Arctic communities.

Wastewater treatment plants (WWTPs) have been shown to be sources of all three contaminants studied here in more southern latitudes and in some Arctic cities as well. Given the relatively small populations of Canadian Arctic communities, wastewater systems are typically less sophisticated than those in more urbanized areas. This combined with the harsh Arctic climate can lead to different contaminant profiles and ecological stresses given the reduction of compound degradation prior to wastewater release. The organic diffusive gradients in thin-films (o-DGT) passive sampler was used for pharmaceutical sampling in four communities, a novel usage of this sampler in both a marine and Arctic setting. PFASs were sampled through simple grab sampling while microplastics utilized manta trawls which skim the surface of waters to retrieve floating plastics. Pharmaceutical concentrations (10 – 5000 ng/L) were measured at levels comparable to other studies conducted in the Norwegian and Greenland Arctic. WWTPs varied in both efficiency and detection of compounds leading to varying concentration profiles in communities. No current ecological risk is expected based on concentration in the receiving environment. PFASs were found to be three orders of magnitude higher during wastewater release compared to open ocean concentrations but dilution played a

large role in reducing these concentrations over time. Microplastics were unable to be accurately assessed given large field blank contaminations.

This thesis demonstrates that for both pharmaceuticals and PFASs, WWTPs can be a significant local source of contamination into aquatic Arctic systems, alongside long-range transport. The results presented here will contribute to both the scientific and regulatory community relating to Arctic contamination.

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List of Abbreviations

A – exposed surface area of sampler

AFFF – aqueous film-forming foam

AMAP – Arctic Monitoring and Assessment Program

ANOVA – analysis of variance

CHARS – Canadian High Arctic Research Station

C_{TWA} – time-weighted average water concentration

D – diffusion coefficient through the diffusive gel

DGT – diffusive gradients in thin-films

EC_{50} – effect concentration causing 50% of the population to exhibit the observed end-point

EtFOSA – N-ethyl perfluorooctanesulfonamide

EtFOSE – N-ethyl perfluorooctanesulfonamide ethanol

f_w – water associated fraction

HLB – hydrophilic-lipophilic balance

HQ – hazard quotients

K_d – solid-water partition coefficient

K_{ow} – octanol-water partition coefficient

LC – liquid chromatography

LC_{50} – lethal concentration required to kill 50% of the population

LC-MS/MS – liquid chromatography tandem mass spectrometry

LOD – limit of detection

LOQ – limit of quantification

MeFOSA – N-methyl perfluorooctanesulfonamide

MeFOSE – N-methyl perfluorooctanesulfonamide ethanol

M_{DGT} – mass analyte on DGT sampler

MS – mass spectrometry

MS/MS – tandem mass spectrometry

NSAID – nonsteroidal anti-inflammatory drug

o-DGT – organic-DGT

PCB – polychlorinated biphenyls

PFAA – perfluoroalkyl acid

PFAS – per- and polyfluoroalkyl substance

PFBS – perfluorobutanesulfonic acid

PFCA – perfluoroalkyl carboxylic acid

PFDA – perfluorodecanoic acid

PFNA – perfluorononanoic acid

PFOA – perfluorooctanoic acid

PFOS – perfluorooctanesulfonic acid

PFSA – perfluoroalkyl sulfonic acid

PFUnDA – perfluoroundecanoic acid

pKa – acid dissociation constant

POCIS – polar organic chemical integrative sampler

POP – persistent organic pollutant

SD – standard deviation

t – time

$t_{1/2}$ – half-life

TSS – total suspended solids

TWA – time-weighted average

UNEP – United Nations Environment Programme

WWTP – wastewater treatment plant

δ – phase thickness

CHAPTER 1

1. Introduction to Arctic Wastewater and Contaminants including Pharmaceuticals, Per- and polyfluorinated alkyl substances (PFAS) and Microplastics

Kevin M. Stroski

1.1 Objectives and Hypotheses

Objectives. The overall aim of this thesis is to evaluate the contamination of three classes of emerging contaminants in Canadian Arctic communities and the role of wastewater on those contamination profiles. The expected outcome of this work will contribute significantly to the knowledge regarding Arctic contamination of pharmaceuticals, per- and poly-fluorinated alkyl substances (PFASs), and microplastics. Further, as many of the local sources of these contaminants are not well studied in a Canadian context, the results gained will be of interest to both scientific and regulatory bodies going forward.

Hypotheses. Local wastewater inputs are a significant point-source of priority contaminants in Northern communities.

Structure of Thesis. This thesis focuses on the evaluation of three classes of contaminants; pharmaceuticals, PFASs, and microplastics originating from the wastewater releases in Canadian Arctic communities and is split into three chapters:

Chapter 1. This chapter summarizes much of the prior research relating to the work in this thesis, including information about wastewater treatment in general and within Arctic communities, specific information relating to the contaminants of interest including sources, fate and ecotoxicology and finally details on sampling and instrumental analyses of said compounds. Overall objectives and hypothesis of this thesis will also be outlined. Chapter 1 will lay the informational foundation for the results and discussions of the chapters following it.

Chapter 2. A standalone manuscript describing a one-year (2018) field study investigating the wastewater inputs of priority contaminants on four Canadian Arctic communities. The presence and distribution of pharmaceuticals in all four communities along with PFASs and microplastics in one was tested and reported. This chapter demonstrates the importance of local contamination sources in Arctic communities and will aid in the understanding of Arctic contamination in Canada.

Chapter 3. Summarizes the main findings of the research within this thesis, including implications and limitations of this work as well as future recommendations.

1.2 Wastewater Treatment

Wastewater management has been used throughout history to improve the standard of living for society. Recognizing the importance of clean water for public health, many empires (e.g. Roman, Egyptian) implemented drainage systems to remove waste from urban areas where large populations made it necessary (Angelakis and Rose, 2014). More recently, wastewater treatment plants (WWTPs) are responsible for handling the waste generated by humans in our cities and communities. Now more than ever, they are of great importance as water use worldwide increases, in conjunction with longer droughts and rising sea levels (Mullin and Rubado, 2017). The goal of impacting water as little as possible and potentially re-using water released in the environment is at the forefront of modern wastewater technologies (Giampietro, 2013). Therefore, many governments and cities have implemented wastewater release standards of which plants need to uphold (e.g. Wastewater Systems Effluent Regulations 2012 (Government of Canada, 2012)).

Conventional wastewater treatment is typically concerned with a few important features, mainly removing solids, reducing oxygen demand, and reducing nutrient levels before release (Government of Canada, 2012). Treatments are split into multiple sections of which a plant may have some or all, depending on the size, location, and financial ability of the community (Matamoros et al., 2016). Primary treatment, which removes the bulk solid material using filters or settling is the most basic and common step involved. Secondary treatment may then be used which can include extended aeration, bioreactors, and natural or constructed wetlands to better reach the goals stated before and even promote aerobic degradation of organic contaminants within the remaining sludge and water (Molinos-Senante et al., 2012). In recent years, larger facilities have added in tertiary and finishing steps such as UV-lamps and granular activated carbon to help degrade bacteria and contaminants prior to leaving the WWTP (Rahman et al., 2014). One important factor in wastewater treatment is the residence time within the facility. This can be thought of as the time it takes for a packet of water to travel through the entire system before being released into the open environment (Majewsky et al., 2011). While different facilities may employ a wide range of treatment options (Greses et al., 2018; Royaee and Sohrabi, 2012), increasing the residence time within a system will almost always lead to better results given that the system has more time to interact with the water and possibly break down or partition out the contaminants (Majewsky et al., 2011).

Small communities (<2000 people) are generally held to the same wastewater release guidelines as larger cities but lack the same tax base to support expensive tertiary and finishing steps (Molinos-Senante et al., 2012). As a result, the treatment

options are often less sophisticated, sometimes only employing primary treatment through a lagoon. However, given the smaller population of the community and thus the smaller volume of water, these WWTPs can hold their wastewater for longer periods than larger plants (Majewsky et al., 2011). By taking advantage of the increased residence time within the lagoon, it allows more time for degradation processes discussed below to occur and reduce nutrient and contaminant levels prior to release (MacLeod and Wong, 2010).

1.2.1 Degradation Processes

Many of these systems are not designed to deal with anthropogenic chemicals, but through the treatment process may remove or degrade them via specific mechanisms (Molinos-Senante et al., 2012). These processes can include hydrolysis (Liu et al., 2012), volatilization (Ning et al., 2015), oxidation (Xu et al., 2013), and conjugation (Hoque et al., 2014) but for the purposes of this thesis we will describe the three most relevant to the compounds studied: photolysis, sorption, and biodegradation.

1.2.1.1 Photolysis

Photolytic degradation can occur via two separate mechanisms. Direct photolysis involves contaminants absorbing natural sunlight (>290 nm) through functional groups, heteroatoms, and conjugated π-systems causing them to degrade (Challis et al., 2014). However, if compounds do not absorb light beyond the UV-C range (200-280 nm) this cannot occur (Boreen et al., 2003). In such cases, degradation through indirect photolysis may occur via a photosensitizer in the water. These materials (e.g. dissolved organic matter, nitrates, etc.) can transfer the energy gained from absorbing light to contaminants in the water via transient species such as hydroxy radicals (Challis et al.,

2014; Plumlee et al., 2009). Any surface waters exposed to light, including lagoons, can utilize these processes to help degrade chemical contaminants by holding wastewater open to the sun whereby these processes can occur over residence times which can be many months to even a year (Anderson et al., 2013; MacLeod and Wong, 2010).

1.2.1.2 Sorption

Sorption processes involve contaminants associating with solid material within the wastewater and thus causing them to settle out with the solids prior to release (Stasinakis, 2012). This process is extremely evident in WWTPs compared to open water given the much greater concentration of suspended solids within (Neudorf et al., 2017). The mechanisms of this process can include hydrophobic interactions, hydrogen bonding, and ion exchange pairs among contaminants and the solid material (Sassman and Lee, 2005; Tolls, 2001). The solid-water partition coefficient (K_d) is a simple way of representing a compound's tendency to sorb to solids and thus be removed through settling during the wastewater process (Narumiya et al., 2013). Given the high K_d values of some organic contaminants, sorption can be an important removal process for anthropogenic compounds.

1.2.1.3 Biodegradation

Biodegradation relies on bacterial and fungi communities in aquatic systems to degrade contaminants. These communities are quite prevalent in WWTPs given the high amounts of suspended solids along with high concentrations of nutrients in which they can grow (Stasinakis, 2012). Wastewater facilities can also promote these interactions through introducing activated sludge and anaerobic digestion processes which can promote bacterial growth (Greses et al., 2018). Biodegradation has been

shown to be an important removal process for pharmaceuticals, especially within lagoons and more external WWTPs (Anderson et al., 2013; Carlson et al., 2013).

1.2.2 Arctic Wastewater Treatment

Like small communities in more southern locations, Arctic communities are generally quite small and thus do not have the financial capacity to build and maintain a large sophisticated WWTPs (Krumhansl et al., 2015). Further, the harsh conditions and relative isolation of many of these communities from the developed world tend to make access to proper treatment significantly more difficult (Chouinard et al., 2014). Supplies and building costs for the introduction of WWTPs are prohibitively expensive and maintenance can also be a large cost, especially if they are operated inside where temperatures must be maintained even in the winter (Gunnarsdóttir et al., 2013). This leads many communities to rely on natural and constructed wetlands in which wastewater flows through after being held in isolated lagoons for up to a year (Alam, 2014; Chaves-Barquero et al., 2016). A study by Yates et al. (2012) investigated a newly implemented engineered wetland system in summer 2008 in the Kivalliq Region of Nunavut, Canada. Significant decreases in chemical oxygen demand and total suspended solids were seen in some communities while others saw little to no change due to the lagoons (Yates et al., 2012). They did not measure the presence or attenuation of anthropogenic contaminants. While long retention times within lagoons should promote degradation of organic contaminants, the harsh conditions can significantly reduce the effectiveness of the types of processes involved (Kallenborn et al., 2018). Light screening is an important factor when calculating photolysis rates as normally only the epilimnion of a water body will get the full strength of the sun (Challis

et al., 2014). During Arctic winters, ice and snow cover can completely block light from reaching the water below reducing photolysis rates and thus increasing contaminant concentrations in the local area (Challis et al., 2018b). Microbial communities have also been shown to operate at lower capacities in Arctic latitudes, further reducing the total removal of these contaminants (Gunnarsdóttir et al., 2013).

Understanding the extent of local contamination of priority contaminants in Arctic communities through WWTPs is imperative going forward. The Arctic has been said to be a good indicator of worldwide contamination due to long-range transport depositing many of the compounds of interest in the past (e.g., mercury, PCBs) whose local sources are minimal (AMAP, 2017). By understanding the local contamination of new priority contaminants, we can better understand their global distribution and potential for long-range transport. More importantly though, many of these communities rely heavily on a country food diet of fish, seals, and other aquatic creatures which may be impacted themselves or bioaccumulate these compounds up the food web, causing potential effects in the humans ingesting them (Curren et al., 2015). With populations in communities increasing along with tourism and the potential for more shipping routes (Statistics Canada, 2016), the human impact and thus the wastewater impact on the Arctic will only increase.

1.3 Contaminants in Aquatic Environments

Anthropogenic contaminants enter the environment through a great number of sources. The scale and impact of this contamination has been of great importance to scientists and governments for the past 50 years. This work has led to the creation and implementation of chemical regulation, like the Stockholm Convention in 2001 (UNEP,

2009), which aim to curb the usage of initially twelve of these pollutants but which has recently been expanded to include more compounds. Monitoring programs have also been implemented across the world and of most interest to this thesis, in the Arctic. For example, the Arctic Monitoring and Assessment Programme (AMAP) was established in 1991 by the eight Arctic nations and seeks to reliable and sufficient information to the status of and potential threat to the Arctic environment (AMAP, 2017). These threats can include many different things including ice and habitat loss due to climate change but also contamination of chemicals of emerging concern. In the last AMAP report in 2017, 17 different contaminants were listed of emerging Arctic concern including PFASs (Benskin et al., 2012; Kwok et al., 2013), brominated flame retardants (Howard and Muir, 2010), phthalates (Long and Bonefeld-Jørgensen, 2012), pharmaceuticals (Gunnarsdóttir et al., 2013; Krumhansl et al., 2015), polycyclic aromatic hydrocarbons (Wang et al., 2013), marine plastics and microplastics (Amélineau et al., 2016; Lusher et al., 2015), among others. This thesis will focus on 3 of these 17 families, namely pharmaceuticals, PFASs, and microplastics.

1.3.1 Pharmaceuticals

Studies on the prevalence and effects of pharmaceuticals in the aquatic environment have steadily increased since the 1990s due to their ubiquitous use and release as well as their potential for biotoxicity in non-target organisms (Brooks et al., 2009). These release patterns have even extended up into Arctic communities (Kallenborn et al., 2008) where due to the wide range of classes and structures, as seen in Table 1.1, the effects of such releases are widely unknown (Donaldson et al., 2010). The 27 pharmaceuticals studied in this thesis, detailed in Table 1.1 along with some

physiochemical properties, represent the following classes: β-blocker heart medicines (atenolol, metoprolol, propranolol), non-steroidal anti-inflammatory drugs (diclofenac, fenoprofen, ibuprofen, ketoprofen, naproxen), cholesterol-lowering drugs (clofibric acid, gemfibrozil), hormones (estrone, 17β-estradiol, 17α-ethynylestradiol), anti-seizure drugs (carbamazepine), anti-depressants (fluoxetine, paroxetine), and antibiotics (clarithromycin, enrofloxacin, erythromycin, roxithromycin, sulfachlorpyridazine, sulfadimethoxine, sulfamethazine, sulfamethoxazole, sulfapyridine, sulfisoxazole, trimethoprim). Many of the compounds studied in this thesis are indicative of both use and contamination patterns of pharmaceuticals worldwide and in the Arctic (Fabbri and Franzellitti, 2016; Huber et al., 2016; Kallenborn et al., 2018).

Table 1.1: Pharmaceuticals (27 total) studied in this thesis in alphabetical order. Physical-chemical properties are given for each compound. Adapted from Challis et al. 2016.

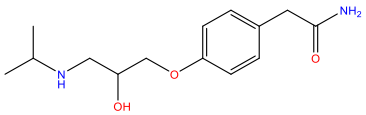
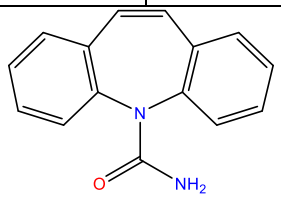
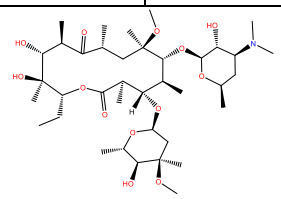
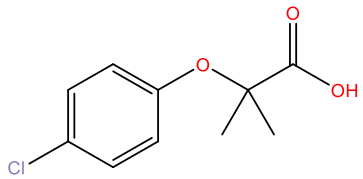
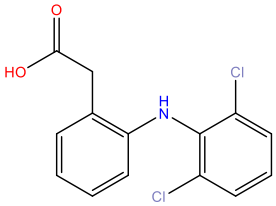
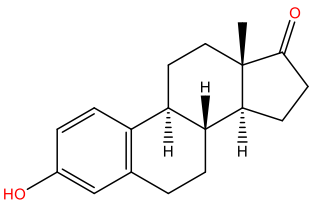
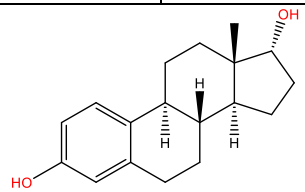
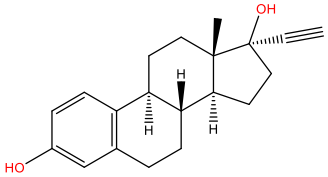
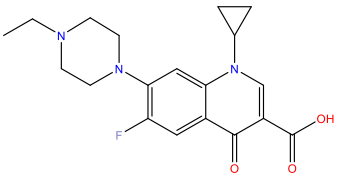
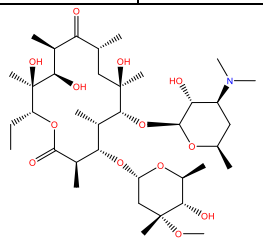
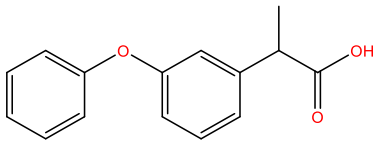
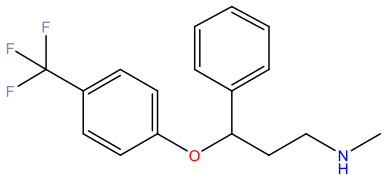
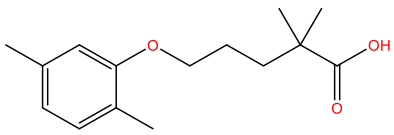
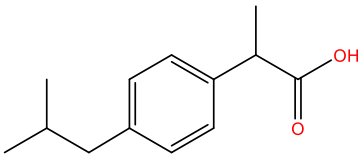
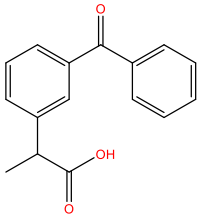
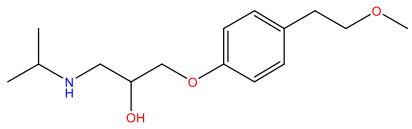
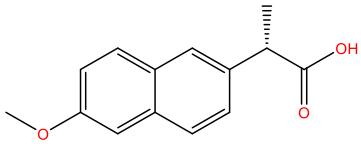
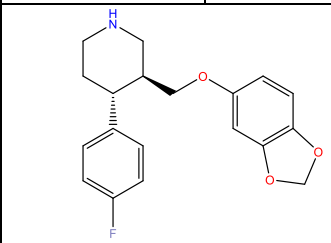
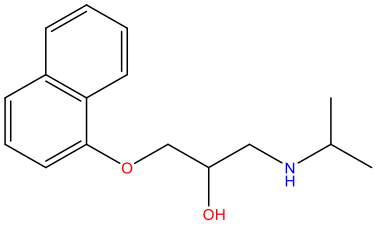
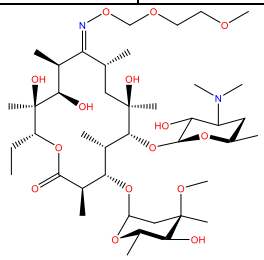
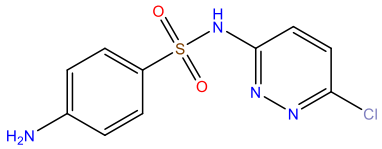
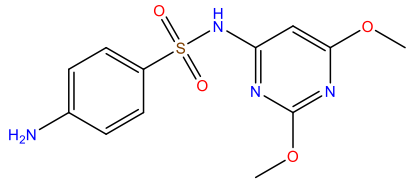
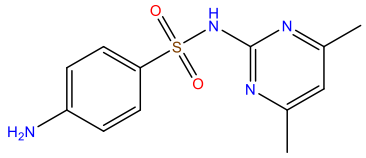
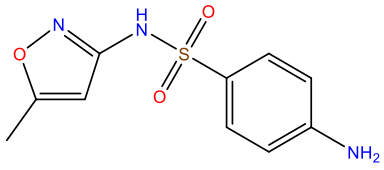
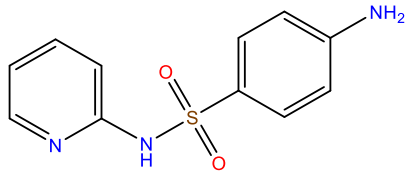
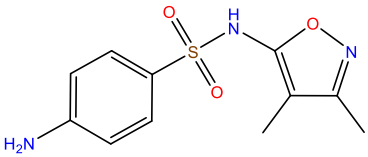
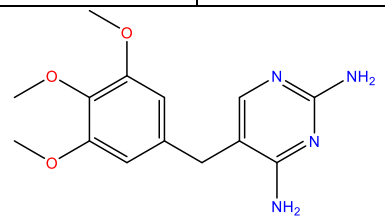
Atenolol		Carbamazepine		Clarithromycin	
$C_{14}H_{22}N_2O_3$	266.3 g/mol	$C_{14}H_{22}N_2O_3$	236.3 g/mol	$C_{14}H_{22}N_2O_3$	748.0 g/mol
$LogK_{ow}$ = 0.16	pK_a = 9.6	$LogK_{ow}$ = 2.45	pK_a = 13.9	$LogK_{ow}$ = 3.1	pK_a = 9.0
					
Clofibric Acid		**Diclofenac**		**Estrone**	
$C_{14}H_{22}N_2O_3$	214.6 g/mol	$C_{14}H_{22}N_2O_3$	296.1 g/mol	$C_{14}H_{22}N_2O_3$	270.4 g/mol
$LogK_{ow}$ = 2.6	pK_a = 3.2	$LogK_{ow}$ = 0.70	pK_a = 4.2	$LogK_{ow}$ = 3.1	pK_a = 10.5
					
17β-estradiol		**17α-ethynylestradiol**		**Enrofloxacin**	
$C_{14}H_{22}N_2O_3$	272.4 g/mol	$C_{14}H_{22}N_2O_3$	296.4 g/mol	$C_{14}H_{22}N_2O_3$	359.4 g/mol
$LogK_{ow}$ = 4.0	pK_a = 10.4	$LogK_{ow}$ = 3.7	pK_a = 10.5	$LogK_{ow}$ = 0.28	pK_a = 6.1
					
Erythromycin		**Fenoprofen**		**Fluoxetine**	
$C_{14}H_{22}N_2O_3$	733.9 g/mol	$C_{14}H_{22}N_2O_3$	242.3 g/mol	$C_{14}H_{22}N_2O_3$	309.3 g/mol
$LogK_{ow}$ = 3.1	pK_a = 8.8	$LogK_{ow}$ = 3.9	pK_a = 4.2	$LogK_{ow}$ = 3.8	pK_a = 10.1
					
Gemfibrozil		**Ibuprofen**		**Ketoprofen**	
$C_{14}H_{22}N_2O_3$	250.3 g/mol	$C_{14}H_{22}N_2O_3$	206.3 g/mol	$C_{14}H_{22}N_2O_3$	254.3 g/mol
$LogK_{ow}$ = 4.8	pK_a = 4.7	$LogK_{ow}$ = 4.0	pK_a = 4.9	$LogK_{ow}$ = 3.1	pK_a = 4.5
					

Table 1.1 cont.

Metoprolol		Naproxen		Paroxetine	
$C_{14}H_{22}N_2O_3$	267.4 g/mol	$C_{14}H_{22}N_2O_3$	230.3 g/mol	$C_{14}H_{22}N_2O_3$	329.4 g/mol
$LogK_{ow}$ = 1.7	pK_a = 9.7	$LogK_{ow}$ = 3.2	pK_a = 4.2	$LogK_{ow}$ = 4.0	pK_a = 10.3
					
Propranolol		**Roxithromycin**		**Sulfachloropyridazine**	
$C_{14}H_{22}N_2O_3$	259.3 g/mol	$C_{14}H_{22}N_2O_3$	837.0 g/mol	$C_{14}H_{22}N_2O_3$	284.7 g/mol
$LogK_{ow}$ = 3.5	pK_a = 9.4	$LogK_{ow}$ = 2.8	pK_a = 9.2	$LogK_{ow}$ = 0.89	pK_a = 2.0, 5.9
					
Sulfadimethoxine		**Sulfamethazine**		**Sulfamethoxazole**	
$C_{14}H_{22}N_2O_3$	310.3 g/mol	$C_{14}H_{22}N_2O_3$	278.3 g/mol	$C_{14}H_{22}N_2O_3$	253.3 g/mol
$LogK_{ow}$ = 1.5	pK_a = 1.9, 5.9	$LogK_{ow}$ = 0.80	pK_a = 2.3, 7.4	$LogK_{ow}$ = 0.89	pK_a = 2.1, 5.7
					
Sulfapyridine		**Sulfisoxazole**		**Trimethoprim**	
$C_{14}H_{22}N_2O_3$	249.3 g/mol	$C_{14}H_{22}N_2O_3$	267.3 g/mol	$C_{14}H_{22}N_2O_3$	290.3 g/mol
$LogK_{ow}$ = 0.35	pK_a = 2.2, 8.6	$LogK_{ow}$ = 0.05	pK_a = 1.5, 5.0	$LogK_{ow}$ = 0.91	pK_a = 4.0, 7.1
					

1.3.1.1 Sources and Occurrences

Long range transport of pharmaceuticals is unlikely due to their high rates of photolytic and microbial breakdown and low vapour pressures in the environment (Challis et al., 2014; MacLeod and Wong, 2010). As such, the major routes of pharmaceuticals into the Arctic, and in many cases the environment, is through WWTPs (Anderson et al., 2013; Carlson et al., 2013). Although many pharmaceuticals break down readily in receiving environments, there is still concern about the effects of the wastewater plume on the local flora and fauna (Burket et al., 2018). Removal of these compounds and their metabolites within conventional treatment plants has been shown to be inadequate for many compounds, including a large proportion of those studied in this thesis (Jarosova et al., 2012). Further, as discussed before, wastewater systems and performance in Arctic communities are expected to be less sophisticated and less efficient, leading to possibly different concentration profiles in the Arctic receiving environment, compared to lower latitudes (Gunnarsdóttir et al., 2013; Huber et al., 2016). Detections may also be based on usage within communities which, based on their geographical location or access to hospitals, can vary wildly (Fabbri and Franzellitti, 2016).

Average receiving water concentrations of pharmaceuticals around the world have typically been found to be in the ng/L range (Aus Der Beek et al., 2016). Dilution plays a major role in the reduction of concentrations from wastewater effluent into the environment, as concentrations within WWTPs can be found in the high µg/L range in some instances (Kallenborn et al., 2018; Weigel et al., 2004). Kallenborn et al. (2018) reviewed the pharmaceutical and personal care product contamination throughout the

Arctic and found a total of 110 different substances had been detected, with the majority (65%) being associated with sewage effluent. Like southern latitudes (Aus Der Beek et al., 2016), concentrations were much less in the freshwater and seawater samples compared to effluent ones, however certain compounds, such as naproxen and over-the-counter NSAIDs, were found more frequently and at higher concentrations in the Arctic (Huber et al., 2016; Kallenborn et al., 2018). These concentrations are imperative in understanding the potential toxicological effects they may have on the organisms in the plume. This thesis will utilize concentrations found in the environment to determine possible adverse effects to such organisms (Chapter 2) as well as determine the pharmaceutical load each community may be releasing yearly.

1.3.1.2 Environmental Fate

Pharmaceuticals can have many different structures based on the intended outcome of the drug in question, as seen in Table 1.1. This results in a wide range of different physical-chemical properties which can dictate the behavior and fate of the different drug classes in the environment (Brooks, 2018). Two important properties given in Table 1.1 can be used to help determine this fate. These are the octanol-water partitioning coefficient (K_{ow}), which describes a compound's propensity to partition between octanol (a liquid often used as a substitute for organic matter) and water, as well as the acid dissociation constant (pK_a) which indicates whether compounds will be neutral or ionic in environmental matrices. In general, contaminants with log K_{ow} values greater than 3 are considered to be potentially bioaccumulative (Howard and Muir, 2010). Of the 27 pharmaceuticals measured here, 14 of them fit this criterion. However, as mentioned before, pharmaceuticals are known to degrade quite quickly in the

environment through many of the processes described in the wastewater section. Photolysis, sorption, and biotransformation are generally considered to be the most important mechanisms of pharmaceutical fate (Challis et al., 2014; Lin and Reinhard, 2005; Narumiya et al., 2013; Stasinakis, 2012; Ternes et al., 2004) and given low volatilization and hydrolysis rates in the environment, these processes can largely be ignored (Daughton and Ternes, 1999).

All the pharmaceuticals studied in this thesis go through both direct and indirect photolysis to some extent and in most cases, photochemical transformation processes represent the major degradation pathway. The specific classes listed before can be grouped weakly into photo-labile (e.g. sulfonamides) and non-photo labile compounds (e.g. carbamazepine), however differences within groups can also be found (Challis et al., 2014). For example, within the group of over-the-counter NASIDs, different compounds exhibit very different rates of photolysis. Naproxen, the active ingredient within Aleve®, has been shown to undergo direct photolysis at a relatively rapid rate with a half life of only 1.9 hours alone and 1.4 hours in natural waters (Packer et al., 2003). Conversely, ibuprofen, another common over-the-counter drug, cannot absorb sunlight directly as it does not have any spectral overlap within the sunlight range (> 290 nm). Direct photolysis half lives of ibuprofen have thus been measured in excess of 200 hours whereas breakdown in natural waters was increased significantly to 15 hours, suggesting that photo-excited species are required to degrade ibuprofen through indirect photolysis (Lin and Reinhard, 2005).

Sorption is another important removal mechanism of certain pharmaceuticals, especially in the wastewater process (Bergheim et al., 2010). The relative

hydrophobicity of a compound, which can be represented by its log K_{ow}, has typically been used to describe this phenomenon, however studies have shown that this may be inaccurate for pharmaceuticals due to their range of binding mechanisms like hydrogen bonding and complexation (Brooks et al., 2009; Sassman and Lee, 2005; Ternes et al., 2004; Tolls, 2001). Calculated K_d values for pharmaceuticals can be used as an adequate representation of these compounds' propensity to sorb to solids in WWTPs based on the interactions listed. Narumiya et al. (2013) calculated such values in sludge derived from a WWTP utilizing activated sludge processes in Japan for many of the compounds in this thesis, including carbamazepine, ibuprofen, and some sulfonamide antibiotics. They found that majority of these contaminants had log K_d values smaller than 2, suggesting that less than 20% of these compounds would be associated with the solid phase during treatment (Narumiya et al., 2013).

Biodegradation of pharmaceuticals can be highly dependant on the specific conditions of either the WWTP or environment in which it may be occurring (Greskowiak et al., 2017). Differences in microbial communities, temperatures, pH values, and many other environmental conditions can result in half lives ranging from days to years. Arctic biodegradation is, to our knowledge, uncharacterized at this point but is expected to be on the slower end based on the harsh conditions and cold temperatures involved (Gunnarsdóttir et al., 2013).

1.3.1.3 Ecotoxicology

Many of the concerns related to pharmaceuticals are due to their design to be active in certain biochemical pathways within humans. Given this, responses of these chemicals to non-target organisms may produce unwanted effects and thus the

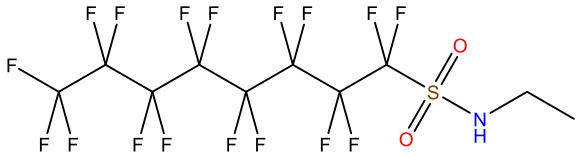
ecotoxicology has begun to be studied (Brooks, 2018; Jarosova et al., 2012). Currently studied endpoints for many of the pharmaceuticals listed (low mg/L levels) in Table 1.1 are orders of magnitude greater than current receiving water concentrations, both in the Arctic and around the world (low to high ng/L levels) (Arnold 2014). Many of these studies utilize standard toxicity methods which may not fully tell the story of potential chronic exposures to these contaminants (Rudd et al., 2014) and more importantly for this thesis, the knowledge regarding toxicity towards Arctic specific flora and fauna in unknown at this time (Kallenborn et al., 2018).

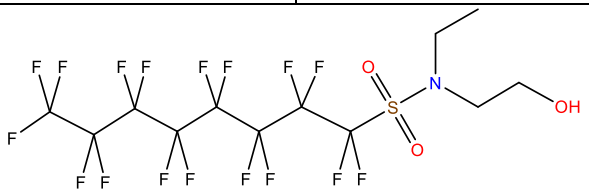
1.3.2 Per- and Poly-fluorinated alkyl Substances

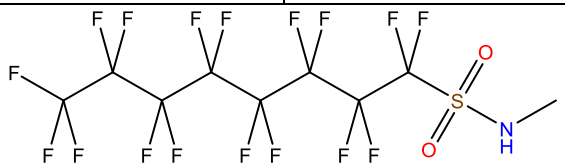
Since the 1950s, products utilizing PFASs have been produced and sold worldwide for both industrial and commercial uses (Kissa, 2001). These products take advantage of the relatively strong and stable C-F bond as well as the chemical and thermal stability of the compounds (Buck et al., 2011). However, in 2001 the widespread contamination of PFASs, and more specifically perfluorooctane sulfonate (or its acid perfluorooctane sulfonic acid) (PFOS) in both wildlife and human blood was demonstrated in two key articles (Giesy and Kannan, 2001; Hansen et al., 2001) leading to a rapid rate of increase regarding publications related to PFASs. Since then, dozens of other PFAS congeners have been detected in many different environmental media including food (Haug et al., 2010), drinking water (Cai et al., 2012), human-breast milk (Roosens et al., 2010), dust (D'hollander et al., 2010), and air (Chaemfa et al., 2010) all around the world and including in the Arctic. The relatively large number of studies related to PFAS sources, fate, and effects stem from their potential harmful effects to humans and high degree of public interest regarding these contaminants (Benson et al.,

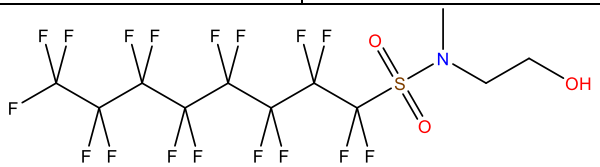
2017). PFOS and other C_8 sulfonate related compounds were also added under Annex B of the Stockholm Convention in 2009 restricting their use (UNEP, 2009). Other PFASs are also currently under review for addition to the convention owing to their persistence, bioaccumulation potential and toxicities. The 10 PFASs studied in this thesis have specific physio-chemical properties detailed in Table 1.x and are: *N*-ethyl perfluorooctanesulfonamide (EtFOSA), *N*-ethyl perfluorooctanesulfonamide ethanol (EtFOSE), *N*-methyl perfluorooctanesulfonamide (MeFOSA), *N*-methyl perfluorooctanesulfonamide ethanol (MeFOSE), perfluorobutane sulfonate (PFBS) and perfluorooctane sulfonate (PFOS), perfluorooctanoate (PFOA), perfluorononanoate (PFNA), perfluorodecanoate (PFDA), and perfluoroundecanoate (PFUnDA). This list of compounds represents the changing landscape of PFAS contamination including both long-chain legacy compounds (e.g. PFOS and PFOA) and short-chain replacements (e.g. PFBS) as well as some known airborne precursors (e.g. FOSAs and FOSEs) (Buck et al., 2011).

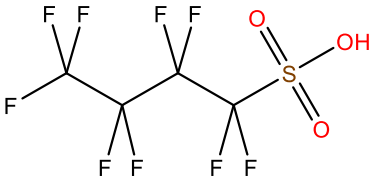
Table 1.2: Perfluorinated alkyl substances studied in this thesis. Selected physio-chemical properties are given for each target chemical and were gathered from (Rayne and Forest 2009).

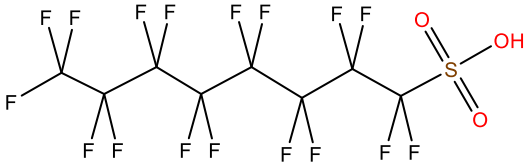
N-ethyl perfluorooctane sulfonamide (EtFOSA)	
$C_8F_{17}SO_2NH(C_2H_5)$	527.2 g/mol
$LogK_{ow}$ = 6.76	$t_{1/2\ (air)}$ = 1.2 day^{-1}
	

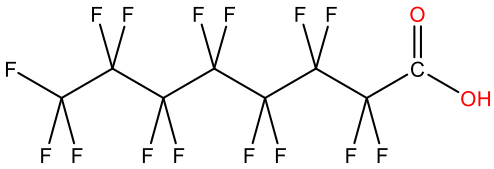
N-ethyl perfluorooctanesulfonamidoethanol (EtFOSE)	
$C_8F_{17}SO_2N(C_2H_5)CH_2CH_2OH$	571.3 g/mol
$LogK_{ow}$ = 6.0	$t_{1/2\ (air)}$ = 0.5 day^{-1}
	

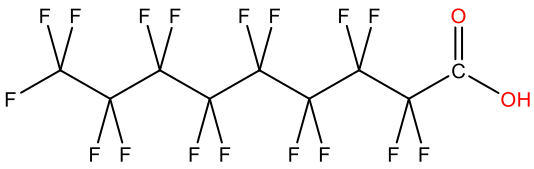
N-methyl perfluorooctane sulfonamide (MeFOSA)	
$C_8F_{17}SO_2NH(CH_3)$	513.2 g/mol
$LogK_{ow}$ = 6.27	$t_{1/2\ (air)}$ = 8.5 day^{-1}
	

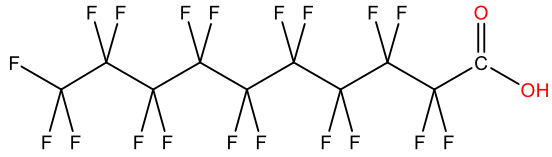
N-methyl perfluorooctanesulfonamidoethanol (MeFOSE)	
$C_8F_{17}SO_2N(CH_3)CH_2CH_2OH$	557.2 g/mol
$LogK_{ow}$ = 5.51	$t_{1/2\ (air)}$ = 0.7 day^{-1}
	

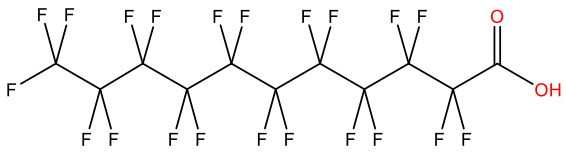
Perfluorobutane sulfonate (PFBS)	
$C_4F_9SO_3H$	300.1 g/mol
$LogK_{ow}$ = 1.82	$t_{1/2\ (air)}$ = 76 day^{-1}
	

Perfluorooctane sulfonate (PFOS)	
$C_8F_{15}SO_3H$	500.1 g/mol
$LogK_{ow}$ = 4.49	$t_{1/2\ (air)}$ = 76 day^{-1}
	

Perfluorooctanoate (PFOA)	
$C_7F_{15}COOH$	414.1 g/mol
$LogK_{ow}$ = 4.81	$t_{1/2\ (air)}$ = 21 day^{-1}
	

Perfluorononanoate (PFNA)	
$C_8F_{17}COOH$	464.1 g/mol
$LogK_{ow}$ = 5.48	$t_{1/2\ (air)}$ = 21 day^{-1}
	

Perfluorodecanoate (PFDA)	
$C_9F_{19}COOH$	514.1 g/mol
$LogK_{ow}$ = 6.15	$t_{1/2\ (air)}$ = 21 day^{-1}
	

Perfluoroundecanoate (PFUnDA)	
$C_{10}F_{21}COOH$	564.1 g/mol
$LogK_{ow}$ = 6.82	$t_{1/2\ (air)}$ = 21 day^{-1}
	

1.3.2.1 Sources and Occurrence

Environmental sources of PFASs contributing to such widespread contamination come from both the production and use of many different products. Polymer based applications such as clothing and textile stain repellent, grease proof cookware and food-contact paper such as microwavable popcorn bags can release compounds via leaching from or degradation off of the products themselves (Zabaleta et al., 2017). Conversely, surfactant based such as emulsifiers, foaming agents and dispersants apply PFASs directly into the environment depending on their application (Paul et al., 2009; Wang et al., 2014a). Production of PFASs and their precursors has been estimated to have been over 100,000 tonnes per year before the voluntary phase out of PFOS and PFOA by the major global manufacturer (3M) in 2000 to 2002 (3M Company, 2000a, 2000b; Prevedouros et al., 2006). This voluntary act along with the addition of PFOS to the Stockholm Convention in 2009 (UNEP, 2009) and many governments enacting strict regulations (e.g. Canada, Europe) has led to a reduction of longer-chain compound use in the western world (Environment Canada, 1999; European Union, 2008). However, countries like China, Russia, and India have yet to follow this act leading to continued inputs of long-chain PFASs into the environment (Jiang et al., 2015; Lindstrom et al., 2011). Further, products manufactured in western countries have generally taken to replacing the long-chain PFASs in their products to shorter versions leading to an increase of these short-chain compounds' prevalence in environmental media (Wang et al., 2014b).

Aquatic concentrations of PFASs can vary wildly depending on the likely sources of the contamination and the remoteness of the location (Ahrens, 2011). Ahrens (2011)

summarized much of the aquatic concentrations of PFOS and PFOA, two of the most prevalent congeners and found concentrations ranging from pg/L to mg/L. Total PFAS concentrations in the Arctic are generally much lower than more industrialized areas with average open water concentrations found ranging from 40 to 250 pg/L (Ahrens et al., 2010). Long-range transport is currently accepted as the major source of PFASs to the Arctic and other remote areas through two major pathways: atmospheric and oceanic transport (Cai et al., 2012; Muir et al., 2015; Yeung et al., 2017). Atmospheric transport occurs mainly through the release of volatile precursor compounds. These compounds are typically neutral in environmental conditions and thus more volatile compared to fluorinated acids (PFAAs) (Rayne and Forest, 2009). They can subsequently be degraded to form PFAAs (e.g. PFOA) and deposit into the Arctic through wet and dry deposition (Wong et al., 2018). On the other hand, PFAAs and PFSAs are typically ionic under environmental conditions as many of them are typically fully dissociated above pH 4 (Rayne and Forest, 2009). Oceanic transport through currents thus transports PFASs released in aquatic settings from more southernly locations and been shown to also contribute to the Arctic contamination of these compounds (Benskin et al., 2012).

While these processes are thought to contribute the majority of PFASs to the Arctic environment, point-sources within the Arctic itself are also important when considering the full breadth of contamination. Fire-fighting training sites have been identified in many locations as a significant source of these compounds due to the use of aqueous fire-fighting foams (AFFFs) on site (De Solla et al., 2012; Moody and Field, 1999). PFAAs are used as additives in AFFFs due to their ability to inhibit the

combustion of jet fuel and thus act as flame-retardants in fuel-based fires (Moody and Field, 2000). Groundwater, rivers, and streams contaminated with AFFF have been shown to have some of the largest concentrations found, sometimes exceeding 1 mg/L near air force bases and airports (Moody and Field 1999, Moody 2002) Contamination via AFFFs near airports has recently been shown to occur in the Arctic as well (Skaar et al., 2019), though it had been suspected in the past (Stock et al., 2007). Wastewater is another significant source of PFASs into the environment and is thought to be one of the major sources in more developed areas of the world alongside atmospheric deposition and discharge from industrial waste (Boulanger et al., 2005; Sinclair and Kannan, 2006). Arctic communities tend to be quite small (1000-8000 people) and thus impacts due to wastewater are assumed to be less significant, but important nonetheless. Chapter 2 of this thesis details measurements related to both potential local PFAS sources discussed (i.e. near airport AFFF use and wastewater), in an Arctic context.

1.3.2.2 Environmental Fate

As with other environmental contaminants, the fate and behavior of PFASs in aquatic systems is dictated mainly by their chemical structure. Unlike pharmaceuticals which contain many different structures and chemical groups, PFASs are much more uniform in structure (Table 1.2) with most of them containing a polar head (typically a sulfate or carboxylate) and an oleophobic tail (a fully fluorinated alkyl chain). In general, fully fluorinated compounds including PFOA and PFOS are considered extremely stable environmentally, resisting many degradation processes including hydrolysis, photolysis, oxidization, volatilization, and biodegradation (Prevedouros et al., 2006). The

compounds studied in this thesis can be split up into three groups based on their physio-chemical properties and structures. These groups are precursor compounds, long-chain PFASs and short-chain PFASs. The following section will describe some of the fate of these groups individually within the context of the Arctic and this thesis.

As discussed before, precursor compounds (e.g. FOSAs and FOSEs) are one of the major sources of PFASs into the environment. These compounds have shown to be susceptible to both abiotic (Plumlee et al., 2009) and biotic (Tomy et al., 2004) degradation processes in aquatic environments and are suspected to degrade into more persistent PFASs like PFOS (Benskin et al., 2013). Indirect photolysis of EtFOSE by hydroxyl radicals was observed by Plumlee et al. (2009) with PFOA suggested as the final degradation product of the reaction. On the other hand, direct photolysis was found to not be likely due to no absorbance above the UV range or into sunlight was found (Plumlee et al., 2009). This lack of direct photolysis is also found in the short and long-chain PFASs where indirect photolysis is also not expected (Rayne and Forest, 2009). One study investigated the photodegradation of PFOS by conventional UV-bulbs (254 nm) used in WWTPs and found that even under ideal conditions (pH = 4 so that compounds were neutral, not ionic) losses were less than 5% of starting concentrations (20 mg/L) were degraded (Yamamoto et al., 2007). Under environmentally relevant Arctic conditions these losses are expected to worsen, similar to pharmaceuticals (Gunnarsdóttir et al., 2013).

Sorption is not expected to be a significant removal pathway for PFASs even though log K_{ow} values may suggest otherwise (all but PFBS greater than 3). This is likely attributed to the ionic nature of these compounds in the environment causing them to be

associated with water much more than solids as it is assumed that only neutral contaminants will adsorb to solids (Narumiya et al., 2013; Rayne and Forest, 2009). Biodegradation is also unlikely for all PFASs studied in this thesis (Ahrens, 2011). Given the fully fluorinated alkyl chain on all the compounds, reductive defluorination would be the only real pathway in which they may be degraded by bacteria. However, these mechanisms typically require at least one available hydrogen on the carbon chain to initiate cleavage, which is not the case here (Rayne and Forest, 2009). The persistence of PFASs in the environment is of great concern to the scientific community as compounds may be biologically available for many years after their release (Houtz et al., 2016; Macinnis et al., 2019; Xiao, 2017).

1.3.2.3 Ecotoxicology

Toxicological effects of PFASs have been well studied on humans due to largely public outcry on the subject. In general, they are well absorbed orally into the body, do not metabolize within and have the potential for a number of serious health effects including but not limited to: endocrine disruption, immunotoxicity, neurotoxicity, and developmental disorders. Aquatic toxicities of PFASs have also been well studied and have been detected throughout the aquatic system including in invertebrates (Asher et al., 2012), fish (Sant et al., 2017), and all the way up polar bears (Sonne et al., 2012). The bioaccumulation potential for PFASs increases significantly with alkyl chain length with short-chain homologues (less than 7 carbons long) being considered non-bioaccumulative, while long-chain ones (>7 carbons) are considered potentially bioaccumulative (Ahrens and Bundschuh, 2014; Buck et al., 2011). Ding and Peijnenburg (2013) summarized the aquatic toxicities of many PFAS compounds and

precursors on aquatic life. They found that the majority of all standard toxicity endpoints tested on algae, invertebrates, and fish resulted in low to mid (1-100) mg/L acute toxicities (Ding and Peijnenburg, 2013). However, unlike many pharmaceuticals, concentrations near these endpoints have been measured in the environment near AFFF spills indicating the potential for acute effects on these communities (Moody and Field, 1999). Arctic concentrations have generally been found to be below this threshold (Skaar et al., 2019), though the potential for long-term chronic effects also exists. For example, Du et al. (2009) exposed zebrafish to PFOS over 70 days at varying µg/L levels to investigate such effects. They concluded that at concentrations as low as 50 µg/L could result in deformations of mortality to the offspring in females and accumulation and persistence of PFOS in the livers of males (Du et al., 2009). Like pharmaceuticals, toxicity towards Arctic communities is generally unknown so along with further chronic testing, effects towards more representative communities would better inform possible ecotoxicological results.

1.3.3 Microplastics

Globally, microplastics have become an important environmental contaminant. Plastic usage has been steadily increasing over the past few decades suggesting that contamination of microplastics will only increase in the future (Anderson et al., 2016). Defined as plastic particles measuring <5mm in diameter in any dimension, these microplastics have become ubiquitous in the world's temperate oceans (Andrady, 2011) and more recently are being found in freshwaters globally (Anderson et al., 2016, 2017). Additionally, the literature is beginning to show the potential threat of these microplastics to enter aquatic food webs (Andrady, 2011), and while bioaccumulation of

microplastics appears unlikely (Lohmann, 2017), their presence in all levels of the food web remains a concern (Au et al., 2017; Barboza et al., 2018). In response to the increasing concerns regarding plastic contamination, many governments including Canada, have either proposed or enacted legislation banning the use of primary microplastics in consumer products, a main source of them in the environment (Environment Canada, 2015; Mason et al., 2016). Chapter 2 of this thesis will investigate the presence and distributions of microplastics from wastewater in the Canadian Arctic, a topic which to our knowledge there are no published peer-reviewed reports on.

1.3.3.1 Sources and Occurrence

Primary microplastics are manufactured for both consumer and industrial products as microbeads. These products can include: facial cleansers, toothpastes, exfoliants, molding powders, and many others whose uses may utilize the beads as additives (Andrady, 2011). Through regular use and washing of these products, especially the personal care ones, these microbeads have the potential to enter WWTPs. Synthetic textiles (e.g. polyester, nylon, etc.) also have the potential to release microfibres into the environment through regular wear and washing (Hartline et al., 2016). Secondary microplastics arise when larger plastic debris are broken down through mechanical or photo-oxidative mechanisms (Barboza et al., 2018). Both primary and secondary plastics are contributing to the global contamination problem, however it will mainly be primary plastics which will be of interest on a local level.

Wastewater inputs have been identified as a major contributor to microplastics in impacted freshwaters (Anderson et al., 2016; Hartline et al., 2016; Mason et al., 2016).

Until very recently, it was assumed that remote regions such as the Arctic would have negligible levels of aquatic plastic, however, extensive Arctic sampling campaigns are suggesting that, similar to PFASs, ocean currents may deliver them to these locations (Cózar et al., 2017). The first report of microplastic occurrence in Arctic waters was by Lusher et al. (2015), who reported elevated levels of microfibers in surface samples taken from the south and southwest of Svalbard, Norway. Additionally, Obbard et al. (2014) and Bergmann et al. (2017) reported high levels of microplastics (>1000 microplastics/kg) in Arctic Sea ice and Arctic deep-sea sediments, respectively. Significant levels of microplastics have also been found in planktivorous diving seabirds off East Greenland, highlighting their potential for uptake into higher trophic organisms (Amélineau et al., 2016). Characterizing the presence and sources of microplastics is a crucial first step in understanding the risk these contaminants may be posing to Arctic ecosystems.

1.3.3.2 Environmental Fate

The fate of many plastics depends greatly on the density and shape. Low-density polyethylene plastics are expected to float on water surfaces while more dense compounds like polyvinylchloride will likely sink to lake, river, and sea beds (Anderson et al., 2016). These locations are not permanent though as turbulence may re-suspend settled plastics while floating ones may take on minerals or other particles, causing them to sink. Once in the aquatic environment, plastics can be subject to many different mechanisms of degradation including: photolysis, hydrolysis, biological, thermal, oxidative and mechanical (Mason et al., 2016; Obbard et al., 2014). Upon degradation,

microplastics can be potentially incorporated into biomasses or become even smaller, down to nano-scale sizes before complete mineralization (Andrady, 2011).

1.3.3.3 Ecotoxicology

The polymers and chains making up microplastics are, for the most part, not toxic by themselves as most aquatic species lack the appropriate enzymes to break down synthetic polymers. However, three potential modes of toxicity have still been proposed for these plastic debris: 1) stress due to ingestion, 2) desorption of chemical plastic additives (e.g. phthalates), and 3) as vectors for other organic contaminants. Anderson et al. (2016) reviewed the current knowledge surrounding these modes of toxicity in a Canadian context. They found that in many cases, ingestion of microplastics can occur in many aquatic organisms, including benthic and pelagic invertebrate species as well as potentials for larger fish contamination through diet (Anderson et al., 2016). While ingestion was found to be common, the physical effects caused by these plastics were limited. For example, Wegner et al. (2012) found reduced filtering activity in blue mussels (*Mytilus edulis*) in the presence of microbeads, which may have been a response to the low nutritional value of the plastic debris. However, no significant acute effects (e.g. mortality) were found due to the plastic ingestion (Wegner et al., 2012). Similar conclusions were found on lugworms (Wright et al., 2013), sea urchin (Kaposi et al., 2014), and sand hoppers (Farrell and Nelson, 2013). Effects due to leaching and release of plastic additives like phthalates are also a potential concern in aquatic organisms. These leachates can have much higher toxicities (ng/L to µg/L ranges) compared to microplastics, however their ability to be transferred to organisms is not well understood (Anderson et al., 2016). Plastics as vectors of other, hydrophobic

organic contaminants has also been suggested as a potential toxicological response. Laboratory experiments involving artificially contaminated plastics have shown the ability of legacy contaminants, like polybrominated diphenyl ethers, to accumulate in lugworms after plastic ingestion however the environmental relevance of these types of studies are unknown (Browne et al., 2013; Lohmann, 2017). While current studies seem to suggest that acute effects of microplastics are not significant, especially in environmentally relevant conditions, the potential for long-term chronic effects has largely gone un-studied and is unknown at this time.

1.4 Environmental Sampling

Successful environmental sampling is an important part of any environmental monitoring program. Samples must ideally be able to represent the sampling area, thus allowing conclusions to be drawn from the resulting data. In many cases, this may be difficult as environmental conditions of contaminants are known to fluctuate due to events such as rainfall, chemical spills, and especially WWTP releases (Miège et al., 2015). Many different sampling techniques have been developed and implemented to measure environmental concentrations, each of them with their own strengths and weaknesses. The four most popular are grab sampling, active sampling, passive sampling, and biomonitoring (Chen et al., 2013). Active sampling is not practical in Arctic environments due to the constant need for energy while biomonitoring does not allow us to identify chemical origins, an important goal of this thesis. The two techniques utilized in this thesis (i.e. grab and passive) will be introduced here followed by a brief introduction to the specific sampler used for a novel purpose in Chapter 2.

Grab sampling is the most basic type of aquatic environmental sampling as it involves retrieving a volume of water from a specific location, usually at a pre-determined depth below the surface, and then extracting the compounds of interest from the water (Alvarez et al., 2004). Also called spot sampling, this technique provides a simple, low cost way for laboratories to investigate any aquatic contaminants given proper extraction and analysis methods. However, given the snap-shot nature of the samples, contaminant events can be missed unless large numbers of samples are taken, leading to increased time and energy analyzing the samples. Passive sampling offers a solution to this problem by deploying simple, non-mechanical devices in aquatic systems for days to weeks which, due to the chemical potential gradient between the water and the sampler, continuously collect compounds over the sampling period (Miège et al., 2015). These samplers allow for fewer trips to the field and less samples to be extracted in lab, reducing costs through shipping and labour, a benefit especially in Arctic sampling. The concentrations derived from these devices are calculated as a time-weighted average (TWA) and can be more representative of the levels of contaminants organisms will be exposed to daily. There are trade-offs though as devices must be properly calibrated and sampling rates for all contaminants of interest measured in lab before field concentrations can be derived (MacLeod et al., 2007). Further, given the TWA nature of the calculations, high concentration events during deployment are not captured and abnormally high concentrations are missed, possibly missing acute effect concentrations towards organisms. Finally, sampling rates for certain passive sampling devices have been shown to vary under changing environmental conditions (e.g. temperature, pH) which may introduce more uncertainty

to the concentrations measured (Li et al., 2011, 2010). Given the low temperatures of Arctic aquatic systems as well as the prohibitive cost for shipping both people and samples to and from the Arctic, a device reducing the affects of these challenges on the overall study was required.

1.4.1 o-DGT Passive Sampler

The diffusive gradients in thin films (DGT) passive sampler has been around for a few decades for measuring metals availability in the aquatic environment (Li et al., 2005). In 2012, Chen et al (2012) pioneered a version designed to measure polar organic contaminants which has been furthered by many other researchers (Challis et al., 2018b, 2016; Stroski et al., 2018). Named the o-DGT (Chen et al., 2012), this sampler is built with two thin gels (0.75-1 mm) stacked upon one another with the bottom gel containing some concentration of sorbent known to interact with the contaminants of choice (Chen et al., 2013). A major advantage of this sampler, and likely one of the reasons it was adapted for organic contaminants, is the ability to ignore or account for significant environmental factors like flow rate and temperature within their sampling rates (Challis et al., 2016). Unlike many other passive samplers, the o-DGT has a large outer diffusive gel (0.75-1 mm) compared to the diffusive layer that is generated in the water as water flows around the sampler at almost any rate. This allows uptake into the sampler to be dictated entirely by diffusion through the outer gel layer which can be modelled based on temperature changes and thus allows sampling rates to be adjusted for changing temperatures (Challis et al., 2016). This adjustment is unique to the o-DGT as many other polar passive samplers are unable to properly model changes in temperature and sampling rates, causing TWA concentrations to

potentially be lower than true environmental concentrations due to improper sampling rates (Guibal et al., 2017; Li et al., 2010).

CHAPTER 2

2. Wastewater sources of per- and polyfluorinated alkyl substances (PFAS) and pharmaceuticals in four Canadian Arctic Communities

A version of this chapter has been submitted as:

Stroski K.; Luong K.; Challis J.; Chaves-Barquero, L.; Hanson, M.; Wong, C.S, **2019.** Wastewater sources of per- and polyfluorinated alkyl substances (PFAS) and pharmaceuticals in Canadian Arctic communities.

Submitted to Science of the Total Environment

Work completed by Kevin Stroski for this chapter includes: sample preparation and extraction, field work in Iqaluit, analytical extractions and instrumentation, data analysis, and writing.

2.1 Abstract

Effective removal of organic contaminants in wastewater effluent pose a challenge to small communities worldwide. Treatment in the Canadian Arctic is exceptionally challenging due to infrastructure demands and harsh climates. To better understand the efficacy of current treatment options and risks posed by pharmaceuticals on receiving waters in the Arctic, four representative communities within the Canadian territory of Nunavut were evaluated: Iqaluit, Baker Lake, Cambridge Bay, and Kugluktuk. Per- and poly-fluorinated alkyl substances (PFASs) and microplastics were also investigated in Cambridge Bay. These communities have treatment ranging from primary lagoons, engineered wetlands, and natural lakes. Pharmaceuticals were measured using the organic diffusive gradients in thin film (o-DGT) passive sampler in summer 2018. Of the 27 compounds studied, seven were found at least once: atenolol, carbamazepine, metoprolol, naproxen, sulfapyridine, sulfamethoxazole, and trimethoprim. Concentrations varied (10 – 5000 ng/L) between communities and treatment method showed no distinction in removal performance towards specific compounds. Iqaluit had the poorest overall performance while Baker Lake had the best. Measured pharmaceutical concentrations do not appear to pose a significant hazard to receiving waters at this time, based on known toxicological endpoints. PFAS concentrations were found to be over 100-fold greater in Cambridge Bay wastewater than previously reported Arctic seawater. Results suggest that wastewater may be an important point source of PFASs in Arctic communities. Microplastic contamination was unable to be assessed due to blank contamination in the field. The o-DGT passive samplers performed well in marine Arctic settings, a novel

usage. We recommend further testing of wastewater efficiencies in Arctic communities along with evaluations of seasonal variations.

2.2 Introduction

There have been significant efforts to understand sources, fate, and effects of contaminants in the Canadian Arctic (AMAP, 2017). However, nearly all such studies have focused on chemicals reaching the North via long-range transport from more temperate regions where these chemicals are produced or used (Butt et al., 2010; Donaldson et al., 2010; Letcher et al., 2017; Stow et al., 2017; Wong et al., 2018; Yeung et al., 2017). The issue of chemical contaminants from regional human activities has been given much less attention, likely due to the current sparse and relatively low populations of northern communities. Previous work in small non-arctic communities (e.g. Anderson et al., 2015; Carlson et al., 2013; Hoque et al., 2014; MacLeod and Wong, 2010; Vasskog et al., 2008), suggests that although wastewater contaminants are discharged at lower rates compared to larger population centers, they can still be present at concentrations that could pose potential ecotoxicological risks in receiving waters under chronic exposure scenarios. Given the similar population dynamics of these communities to those in the Canadian Arctic, these risks have the potential to threaten more northerly waters as well, particularly in light of the fragile ecosystems present in the Arctic.

Per- and polyfluorinated alkyl substances (PFAS) have been used as surfactants and polymers since the 1950s and are an important class of contaminant in the Arctic (AMAP, 2017; Buck et al., 2011). Several PFASs, like perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), have been measured in the Arctic and are shown to

be persistent and bioaccumulative in aquatic environments (De Solla et al., 2012; Howard and Muir, 2010; Letcher et al., 2017; Muir et al., 2015). Given northern communities reliance on more traditional food sources (i.e. fish, seals, whales, etc.), determining the impacts of these chemicals is of great importance. PFAS transport to the Arctic is generally thought to occur through two main processes: long-range atmospheric transport followed by deposition, and through oceanic currents from more southerly locations (Butt et al., 2010; Macinnis et al., 2019, 2017; Pickard et al., 2018; Yeung et al., 2017). While these processes are thought to contribute the majority of PFASs measured in the Arctic, other point-sources such as wastewaters and aqueous fire fighting foam (AFFF) have been shown to contribute to PFAS contamination of receiving waters in more populated regions (Chen et al., 2018; De Solla et al., 2012; Houtz et al., 2016). Stock et al., (2007) is a notable study as they investigated the PFAS contamination in air, water, and sediment of three Arctic lakes on Cornwallis Island, Nunavut, Canada. Resolute Lake was found to have significantly higher levels of PFOS and PFOA in the sediment and water compared to the other two lakes, even with similar inputs from the air. These elevated levels were suggested to have two possible sources: AFFF use from the nearby Resolute airport or wastewater and raw sewage dumping in the local area (Stock et al., 2007). A recent study in the Norwegian Arctic identified AFFF as a significant local source of PFASs to the soil, freshwater, and seawater of Svalbard, Norway (Skaar et al., 2019). However, overall these potentially important localized PFAS point-sources have not been well studied in Arctic communities.

Aqueous microplastic contamination has recently become a significant emerging contaminant of concern both globally and in the Arctic (AMAP, 2017; Andrady, 2011;

Environment Canada, 2015). Defined as plastic particles measuring <5mm in diameter in any dimension, they have been shown to have the potential for harmful effects both through ingestion and leaching of additives (Browne et al., 2013; Kaposi et al., 2014; Wegner et al., 2012). As plastic production increases by nearly 20 million tonnes a year from the already generated 300 million tonnes, the potential for harmful effects to aqueous life may also increase (Mason et al., 2016). While the Arctic region has been suggested as a final destination for some plastics floating in ocean currents (Cózar et al., 2017), the impacts of microplastics on this basin are not well studied (Amélineau et al., 2016; Bergmann et al., 2017; Lusher et al., 2015). Amélineau et al. (2016) investigated such contamination off the coast of Greenland and found that, similar to studies in other regions, locations closer to urbanized areas had higher concentrations of plastics compared to those more removed. Local contamination, especially through WWTPs has been linked to microplastic releases along with other local sources such as stormwater runoff and atmospheric fallout (Anderson et al., 2017; Mason et al., 2016). Thus an investigation into the impacts of WWTP sources in Arctic communities is important given these contaminants potential for both release and harm in such a fragile environment.

Pharmaceuticals are another class of compounds of global concern in both freshwater and marine ecosystems. The Arctic Monitoring and Assessment Programme (AMAP) classifies pharmaceuticals as contaminants of emerging concern to the Arctic and stresses the need for more comprehensive studies on the fate, environmental toxicology, and distribution profiles of pharmaceuticals in northern climatic conditions (AMAP, 2017). These compounds are designed to elicit specific biochemical responses

within the human body, but when released into the environment may cause unwanted effects on non-target organisms (Fabbri and Franzellitti, 2016; Kümmerer, 2009). The major source of human-use pharmaceuticals in the environment is wastewater effluent, as varying amounts of parent and metabolized pharmaceutical compound are excreted from the body and can end up in treatment plants, which, in many cases, are neither designed or optimized to deal with these types of contaminants (Gunnarsdóttir et al., 2013; Huber et al., 2016).

Removal of pharmaceuticals in treatment processes is compound-specific and typically limited even under ideal conditions, with many competing factors (e.g., hydraulic residence time, chemical concentration, temperature) controlling the rate of removal (Lishman et al., 2006). Treatment of wastewater in the Canadian Arctic is especially challenging for many reasons. Infrastructure is typically limited, given the small size and tax base of the communities, and the strains that the cold climate has on both construction and maintenance of infrastructure. Thus, many wastewater programs focused initially on disposal management techniques (i.e., lagoons and stabilization ponds) rather than the mechanical treatment systems typically found in southern Canadian communities (Chouinard et al., 2014). Low temperatures and harsh climatic conditions have also been shown to reduce removal of pharmaceuticals in the Arctic relative to lower latitudes (Bergheim et al., 2010). Ice cover can play a major role in this reduced removal as many systems rely on photolysis to attenuate pharmaceuticals over long residence times within lagoons. When covered with ice, aquatic photolysis rates are significantly reduced or eliminated resulting in greater concentrations under ice (Challis et al., 2018b; Kallenborn et al., 2018, 2008). Together with reduced microbial

processes at cold temperatures, the ability of lagoons to remove these contaminants is greatly impacted, resulting in greater persistence of contaminants over winter months (Gunnarsdóttir et al., 2013; Kallenborn et al., 2008).

Limited research on behaviour and removal of wastewater pharmaceutical contaminants in northern climates has been conducted (see Chaves-Barquero et al., 2016; Emnet et al., 2014; Gunnarsdóttir et al., 2013; Huber et al., 2016; Vasskog et al., 2008; Weigel et al., 2004), and only one such study has a Canadian context. Chaves-Barquero et al. (2016) reported on the release of wastewater contaminants into Cambridge Bay, Nunavut, in summer 2014. They detected a total of six pharmaceuticals out of twenty-eight screened in the wastewater effluent; however, none were found at detectable concentrations in receiving waters after release. As such, the authors concluded that the monitored pharmaceuticals being discharged did not pose a significant threat to aquatic organisms (Chaves-Barquero et al., 2016). However, given both harmonization efforts by the Canadian federal government towards more stringent wastewater treatment standards (e.g., Wastewater Systems Effluent Regulations of 2012 (Government of Canada, 2012)) and draft protection of aquatic life guidelines for pharmaceuticals (e.g., carbamazepine) (Canadian Council of Ministers of the Environment, 2018), evaluating factors in the Canadian North that affect wastewater presence and removal is crucial as anthropogenic influences increase. For example, greater resource exploitation in the Canadian North, coupled with increased access to the region from climate change, has resulted in an ever-increasing human footprint in the region itself. Nunavut, the largest of Canada's three northern territories, experienced an average population growth of 12.7% between 2011 and 2016, the largest in any

province or territory in Canada (Statistics Canada, 2016). This expanding human presence will result in greater stresses on northern infrastructure and ecosystems in the immediate region of communities from mines, tourism, and other areas of human activity. Consequently, it is crucial to understand current local and regional inputs of contaminants to these systems to better predict the impact of wastewater discharge from an increasing population. The new knowledge and tools developed from this work will help inform decision-making and efforts to minimize effects on northern ecosystems and human health.

In this study, we characterized the concentrations of select pharmaceuticals in wastewater releases from several communities in the Canadian Arctic. A total of four communities (Iqaluit, Baker Lake, Cambridge Bay, and Kugluktuk, Nunavut, Canada) with differing treatment systems and effluent release patterns were studied. These systems are primarily designed to remove nutrients and solids to meet Canadian wastewater guidelines and generally achieve this through long residence times within lagoons. Some also included polishing steps like natural and constructed wetlands to reduce impacts on receiving waters. The extent of PFAS contamination from AFFF use in Cambridge Bay was also studied given its history of use in the area. Wastewater was also sampled for PFAS contamination in Cambridge Bay alone. Microplastic contamination by WWTP was investigated in Cambridge Bay as well, both within the wastewater system as well as the marine setting. The main goals of this study were to; determine the concentrations of pharmaceuticals, PFASs, and microplastics in the effluent and receiving waters to inform exposure assessments and predict mass loadings, assess the relative efficiency of removal by these treatment systems under

northern conditions, and evaluate if there are any potential risks to non-target organisms in receiving environments.

2.3 Materials and Methods

2.3.1 Sampling Details

2.3.1.1 Pharmaceuticals

Complete details of development, optimization, assembly, and extraction of o-DGT are provided elsewhere (Challis et al., 2016; Stroski et al., 2018). Briefly, o-DGT samplers were constructed using two layered gels: a 0.75-mm, 25 mg Sepra-ZT (Phenomenex) binding gel made of 1.5% agarose (molecular biology grade, Sigma Aldrich, Oakville, ON) and a 0.9-mm polyacrylamide (15% acrylamide monomer and 0.1% cross linker) outer diffusive gel. The binding gel was placed on the standard DGT base (sorbent side up), then covered with the diffusive gel before being closed by the standard DGT cap (exposed area = 3.1 cm^2). Samplers were constructed in lab, then shipped to sites while hydrated in Milli-pore water (EMD Milli-Pore Synergy® System, Etobicoke, ON), and kept hydrated until deployment. Triplicate samplers were deployed in polar organic chemical integrative sampler (POCIS) cages with HOBO temperature loggers (Onset Computer Corporation, Bourne, MA) attached. Upon retrieval, samplers were shipped and stored frozen (-20°C) for 1-4 weeks until extraction, which did not result in any analyte loss (Challis et al., 2018a).

Using the mass of analyte on sampler (M_{DGT}), thickness of the diffusive gel layer (Δg), exposed area (A), deployment time (t), and analyte diffusion coefficient through the diffusive gel (D), o-DGT time-weighted average (TWA) water concentrations (C_{TWA}) were calculated using Equation 1. The boundary layer thickness is excluded from

Equation 1 because flow rate effects on o-DGT uptake are assumed to be negligible (Challis et al., 2016). Temperature specific diffusion coefficients were determined using D−T empirical relationships developed previously by Challis et al. for the same suite of target analytes (Challis et al., 2016). D was calculated based on the average in situ water temperature over each deployment.

$$C_{TWA} = \frac{M_{DGT}\Delta g}{DAt} \quad (1)$$

Laboratory and field blanks were extracted alongside each set of environmental samples. Field blanks were left open to the atmosphere during deployment and retrieval of passive samplers. Field blanks for the Iqaluit data set were contaminated due to technician error prior to deployment. All other field and lab blanks showed negligible levels of all analytes measured.

2.3.1.2 PFAS

Duplicate 500 mL grab samples utilizing high-density polyethylene bottles were taken at each site. Identical field blanks filled with approximately 500 mL of Milli-pore water were opened at each site during retrieval. Once retrieved, samples were kept cool (2 °C) until being shipped in sealed coolers for extraction. Extraction procedures followed a version of the method by Workman et al., 2019 adapted for water samples. Briefly, samples were dripped through OASIS HLB solid phase extraction cartridges before being eluted with 3 mL of methanol. Samples were then evaporated under nitrogen, reconstituted in 750 µL of methanol, and passed through a syringe filter before LC-MS/MS analysis. Lab blanks of Milli-pore water were also extracted alongside samples.

2.3.1.3 Microplastics

Depending on the site, microplastics sampling was either conducted using a manta trawl or a small zooplankton-like dip net (hereafter referred to as a mini-manta). The manta trawl (61 cm wide by 18 cm high) is equipped with a 3 m long, 333 µm mesh bag and 333 µm removable cod-end equipped with a detachable mechanical flow meter. The manta trawl, used for all open water sampling (throughout Cambridge Bay, marine and freshwater reference sites), was conducted in a similar fashion to Anderson et al. (2017). The trawl was be towed across the water's surface, alongside a boat at set speed for designated tow times (ca. 15 minutes). Given the logistical nature of trawl sampling for microplastics, triplicate samples are not the norm (Anderson et al., 2017). For the wastewater and wetland sampling sites that are not conducive to towing a large trawl, the mini-manta was used. This sampling device contains a smaller 333 µm net and cod-end that can be easily attached to a telescoping pole. Samples were taken at the outfall the lagoon and at the outfall into the bay, just downstream of the wetland where the flow was great enough to obtain sufficient sample in a reasonable time period. The wetland itself was not deep enough to do trawls. Once the nets were retrieved, all material were washed into the cod-end of the net, transferred to a glass sample jar, and preserved in 70% ethanol until processing in the laboratory. Samples were digested using a wet peroxide oxidation previously used in our lab (Anderson et al., 2017) and enumerated by microplastic type (fibre, film, foam, fragment, bead) under a microscope. Field and lab blanks will be prepared accordingly to control for microfiber contamination that may shed from clothing worn during sampling.

2.3.2 Sampling Sites

Four communities within the Canadian Arctic were monitored over the summer 2018 season (Figure 2.1) for pharmaceuticals. A brief description of each site and the sampling locations are provided below.

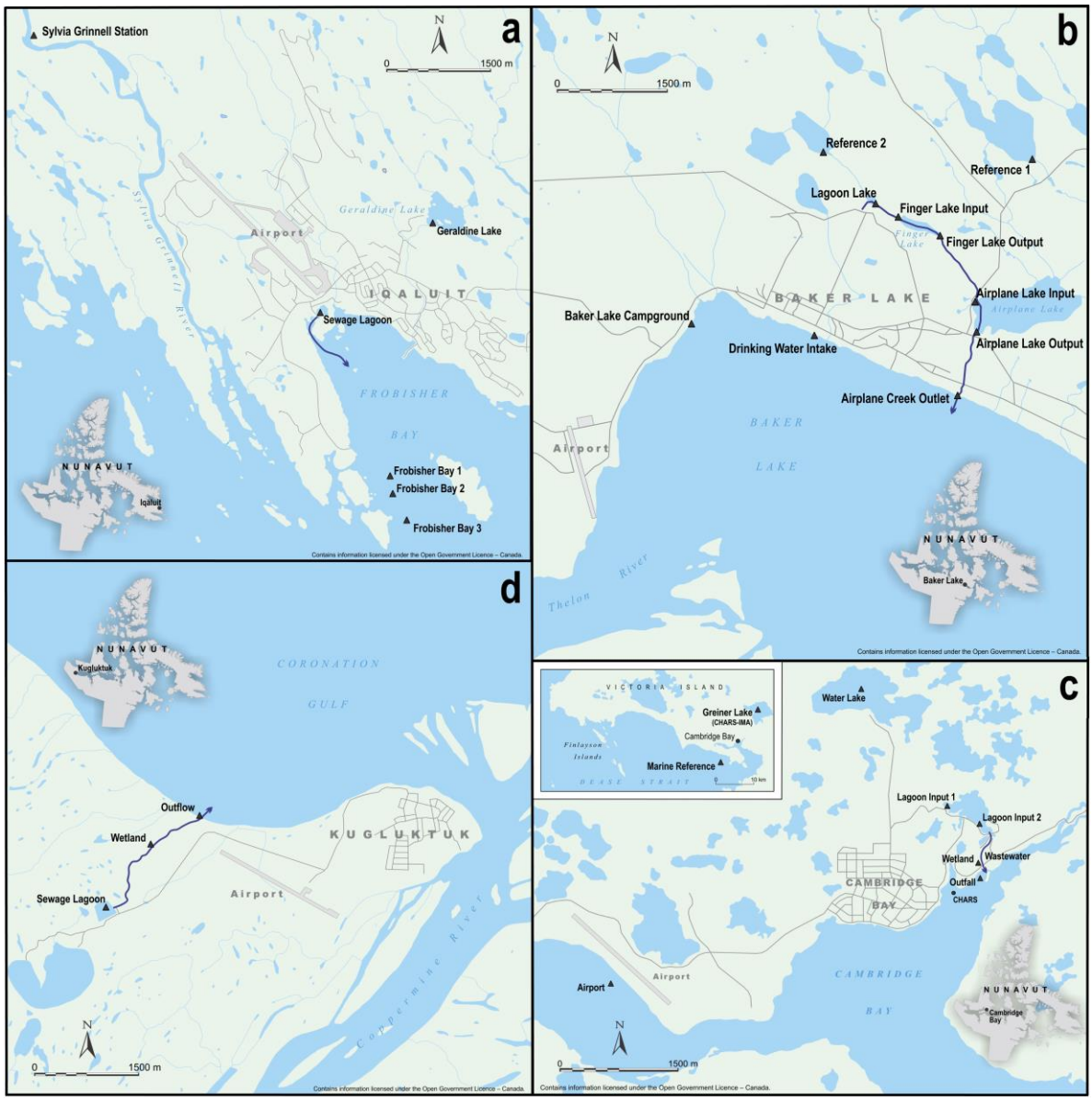


Figure 2.1: Sampling site locations within the communities (clockwise) of Iqaluit (a), Baker Lake (b), Cambridge Bay (c), and Kugluktuk (d), Nunavut, Canada. Blue arrows represent the flow of wastewater from the lagoon to the bay in each case.

2.3.2.1 Iqaluit

Iqaluit, located on Baffin Island, is the capital of Nunavut (Figure A1). It is the largest community in the territory and had a population of approximately 7,700 in 2016, a 15% increase since 2011 (Statistics Canada, 2016). The wastewater system in Iqaluit is comprised of a constructed wastewater lagoon which is continually discharged year-round through a Salsnes filter designed to remove solids before release into an open channel (i.e., directly into the marine environment). Approximately 7.2×10^8 L of wastewater is released per year (Neudorf et al., 2017). Municipal sewage from household sewage tanks is regularly transported to the lagoon by both sewage trucks and piped service. During the time of sampling, upgrades to the treatment plant were taking place with construction of both primary and secondary treatment systems to supplement the existing lagoon and accommodate the growing population.

A total of six sampling locations were identified based on local knowledge and interest (Figure 2.1a). Sites included inside the wastewater lagoon directly before release, three locations within Frobisher Bay to capture dilution patterns, and one location in an upstream river to be used as a clean reference site. Lake Geraldine was also studied as it is the drinking water source for the community. Samplers in Frobisher Bay were deployed in areas where they would be constantly submerged, even during changing tides, a requirement of this and many passive samplers (Challis et al., 2016). Sampling occurred between August 31st and September 19th, 2018. Sampler deployments in the Frobisher Bay sites averaged 15 days in water with an average temperature of 2 °C. Deployments in Sylvia Grinnell, Lake Geraldine, and the lagoon averaged 20 days in water with average temperatures of 5 °C, 6.5 °C and 7.5 °C

respectively. The discrepancy in deployment length can be attributed to deployments in the bay requiring a boat to be reached while other sites could be accessed more easily.

2.3.2.2 Baker Lake

Baker Lake is a freshwater tundra community impacted by mining activities on mainland Nunavut (Figure A1). It had a population of approximately 2,100 in 2016, a 10% increase since 2011 (Statistics Canada, 2016). The wastewater system monitored at Baker Lake is comprised of a constructed multi-celled holding lagoon system that performs primary treatment and seasonal discharges into a series of natural lakes and streams, which act as a wetland, before reaching Baker Lake with snow and ice melt, typically around June. Municipal sewage from household sewage tanks is regularly transported to the lagoon by sewage trucks year-round and based on populations can be approximated around 7.67×10^7 L per year.

A total of ten sites were monitored around the community based on local interest and concerns about wastewater impact on the surrounding lakes. Sampling sites (Figure 2.1b) followed the flow of wastewater from the lagoon (not sampled), directly into Lagoon Lake through Finger Lake (input and output) and Airplane Lake (input and output), and finally out Airplane Creek into Baker Lake. Two un-impacted reference sites, one upstream of the above hydrological system and another independent of it , were also sampled. A site near the campground was chosen to monitor direct dumping and as with Iqaluit, the drinking water source was also sampled. Sampling occurred from July 13th to July 22nd, 2018. Sites within Baker Lake (Airplane Creek, drinking water intake, and campground) experienced average water temperatures of 7.5 °C

while all other sites averaged water temperatures of around 15.5 °C over the sampling period.

2.3.2.3 Cambridge Bay

Cambridge Bay is located on Victoria Island in Nunavut (Figure A1). It had a population of approximately 1,800 in 2016, a 10% increase since 2011 and since the previous study data were collected (Statistics Canada, 2016). As per Chaves-Barquero et al. (2016), the wastewater system monitored at Cambridge Bay is comprised of a wastewater lagoon, formerly a series of natural lakes, that performs primary treatment and is discharged once annually, during the summer, into a small, hydrologically-isolated natural tundra wetland. The final effluent is released through an open channel into the marine environment, approximately 4.04×10^7 L in 2018. Municipal sewage from household sewage tanks is transported to the lagoon by sewage trucks year-round.

Four sites around the community and two more within the area were monitored using o-DGT samplers for pharmaceuticals. Sampling sites (Figure 2.1c) followed from the lagoon (Lagoon Input 2) into Cambridge Bay near the Canadian High Arctic Research Station (CHARS). Two reference sites outside the community, one upstream of the hydrological system and the other within the outflow of Cambridge Bay into the Northwest Passage, were also sampled. A marine reference site was added to see if any compounds could be detected as the bay emptied into the Northwest Passage. Sampling was performed both prior to and during the release of wastewater from the lagoon. Pre-release sampling was performed from July 5th to July 16th for inland locations, and July 4th to July 16th, 2018 for offshore locations. Wastewater release

occurred from July 23rd to August 24th, 2018 with samplers deployed during release from July 25th to August 22nd, 2018 for all sites. Temperatures ranged from 13.7 °C (Wetland, pre-release) to 4.4 °C (Marine, during release). Average temperatures for all sites at both sampling times can be found in Table A1. Many of the sampling sites chosen were done so based on the previous study (Chaves-Barquero et al., 2016) so that comparisons might be made over time.

Prior to the release of wastewater, PFAS grab sampling occurred at all sites (Figure 2.1c) except Lagoon 1 on July 4th and 5th, 2018. Lagoon, wetland and outflow sites were then sampled on July 25th, 2018, during the annual wastewater release. Lagoon, outflow and Water Lake sites were sampled again after release was completed on September 13th, 2018. The wetland site was not sampled at this time as it had dried.

Microplastic manta trawls were conducted at two time points; pre- (July 4th, 2018) and during-release (July 26th, 2018) and were taken at multiple points in the Bay to account for spatial heterogeneity. Mini-manta samples from the lagoon and bay outflows were taken in triplicate, pre- (July 4th, 2018) and during release (July 26th, 2018) to provide a good estimate of plastic loadings from the lagoon.

2.3.2.4 Kugluktuk

Kugluktuk is a tundra community on mainland Nunavut, Canada (Figure A1). It had a population of approximately 1500 in 2016, a 3% increase since 2011 (Statistics Canada, 2016). The wastewater system monitored at Kugluktuk is comprised of a constructed wastewater lagoon that performs primary treatment and is discharged once annually during the summer into an engineered constructed wetland, before reaching the Northwest Passage. Around 5.53×10^7 L of wastewater are released each year with

a reported residence time of 360 days within the lagoon prior to release (Alam, 2014). Municipal sewage from household sewage tanks is regularly transported to the lagoon by sewage trucks that perform dumping runs year-round.

A total of three sampling sites (Figure 2.1d) were selected that followed the flow of wastewater from the lagoon, through the wetland and finally the outflow into the Passage. Due to logistical limitations, only one trip to Kugluktuk was made. Sampling occurred from August 17th to August 24th, 2018 with average temperatures of 7.5 °C, 6.5 °C and 6 °C respectively from the lagoon outward.

2.3.3 Risk assessments for pharmaceuticals

Hazard quotients (HQs) were calculated for all detected compounds using standard tests and known endpoints gathered from the peer-reviewed literature to assess the potential risk of concentrations measured to primary producers, invertebrates, and fish (Białk-Bielińska et al., 2011; Cleuvers, 2005, 2003; Eguchi et al., 2004; Isidori et al., 2005; Kim et al., 2007; Küster et al., 2010; Li et al., 2016; van Den Brandhof and Montforts, 2010). Estimates for effect concentrations (EC50) or lethal concentrations (LC50) were obtained, with many coming from our previous study in Cambridge Bay (Chaves-Barquero et al., 2016). A conservative factor of 1000 was added to these estimates, as its typically done. The maximum concentration of each compound, at each location, was then divided by the lowest reported effect concentration to obtain a HQ. Hazard quotients greater then 1 were considered to have a significant potential to induce the effect considered, while those less than 1 were considered less likely to induce such effects (Hanson and Solomon, 2004).

2.3.4 Target Chemicals and Reagents

A total of 27 pharmaceuticals were analyzed in this work: 17-estradiol, 17-ethynylestradiol, atenolol, carbamazepine, clarithromycin, clofibric acid, diclofenac, enrofloxacin, erythromycin, estrone, fenoprofen, fluoxetine, gemfibrozil, ibuprofen, ketoprofen, metoprolol, naproxen, paroxetine, propranolol, roxithromycin, sulfamethazine, sulfamethoxazole, sulfapyridine, sulfisoxazole, sulphachloropyridazine, sulphadimethoxine, trimethoprim.

Ten PFASs were investigated and are named as per Buck et al., 2011. These included 4 precursor compounds: *N*-ethyl perfluorooctanesulfonamide (EtFOSA), *N*-ethyl perfluorooctanesulfonamide ethanol (EtFOSE), *N*-methyl perfluorooctanesulfonamide (MeFOSA), *N*-methyl perfluorooctanesulfonamide ethanol (MeFOSE); 2 sulfonates: perfluorobutane sulfonate (PFBS) and perfluorooctane sulfonate (PFOS); and 4 carboxylates: perfluorooctanoate (PFOA), perfluorononanoate (PFNA), perfluorodecanoate (PFDA), and perfluoroundecanoate (PFUnDA).

2.3.5 Instrumental Analysis

Analytes concentrations were determined by liquid chromatography tandem mass spectrometry (LC-MS/MS) using an Agilent 1200 Series LC pump and Agilent 6410B MS/MS (Agilent Technologies, Mississauga, ON) in electrospray ionization positive and negative mode. Details of chromatographic and MS/MS methods including LODs and LOQs can be found elsewhere (Challis et al., 2016; Workman et al., 2019).

2.3.6 Data Analysis

Prism v. 5.01 (GraphPad Software, La Jolla, CA) was used for statistical analyses. Statistical differences between sites were determined by two-way ANOVA

and Bonferroni post-hoc tests with an alpha value of 0.05. Errors in graphs and tables are presented as standard deviations of the mean, unless otherwise stated.

2.4 Results and Discussion

2.4.1 o-DGT Performance

This study represents a novel use of the recently developed o-DGT passive sampler in a marine setting. This sampler has been shown to better reflect continuous grab sampled water concentrations when compared to other passive samplers (e.g. POCIS) both in more temperate climates and in northern ones (Challis et al., 2018b, 2016). One of the benefits of this sampler is the ability to account for field temperatures with adjustable sampling rates based on diffusion through the outer gel. These relationships can, as an example, result in changes in o-DGT sampling rates of carbamazepine from 14.6 mL/day (23 °C) to 3.5 mL/day (4.5 °C), and are calculated based on diffusion-temperature relationships previously determined in lab (Challis et al., 2016). These large changes in sampling rates can result in potential underestimations of TWA concentrations if not considered. Further, the relative size and ease of transport make these samplers attractive for use in remote settings. Similar to POCIS, samplers could be shipped to sites, pre-made in lab, and could be kept frozen for weeks or months following retrieval without appreciable losses (Challis et al., 2018a). Small size and weight of samplers allowed for less expensive and obtrusive shipments than grab sample bottles filled with water, which are both heavy and large. Performance in both marine and freshwater systems, the ability to accommodate variable temperatures, and the ease of transport make the o-DGT sampler a useful tool for scientific and regulatory agencies conducting long term monitoring. Given recent interest (AMAP, 2017) for more

comprehensive studies of fate of pharmaceuticals in the Arctic, the success of this sampler offers an easy to use, robust sampler for such studies.

2.4.2 Pharmaceuticals

We will briefly compare our results to those of other published Arctic wastewater work before examining each site investigated in this study more in depth. Of the twenty-seven polar organic contaminants screened, only seven were detected above their LOQs at any of the sampling locations, in any of the communities. All detected compounds were pharmaceuticals: atenolol, carbamazepine, metoprolol, naproxen, sulfamethoxazole (not detected in Iqaluit), sulfapyridine, and trimethoprim. The greatest concentrations in each location were found in the lagoon sites for nearly all compounds. Baker Lake and Cambridge Bay treatment systems had the least total mass of pharmaceuticals leaving the lagoon per capita, while Iqaluit had the greatest. The greatest concentration of pharmaceuticals measured in receiving waters was in Kugluktuk. However, no significant hazards to aquatic life are expected, at this time, at any of the sites studied (Tables A6-9).

2.4.2.1 Arctic Comparison

There have been a small number of studies undertaken in the last few years to identify compounds and calculate concentrations of pharmaceuticals in the Arctic. Over 100 different compounds have been detected from classes including NSAIDs, anti-epileptics, antibiotics, β-blockers, anti depressants and hormones (Chaves-Barquero et al., 2016; Gunnarsdóttir et al., 2013; Huber et al., 2016; Kallenborn et al., 2018; Weigel et al., 2004). From these studies, we compare the concentrations of the four most commonly detected compounds from this study (Table 2.1).

Table 2.1: Concentration ranges of target pharmaceuticals in Iqaluit, Baker Lake, Cambridge Bay and Kugluktuk compared to different Arctic wastewater systems. Populations are given and represent the approximate number of persons the treatment system services. (NA: not analyzed, nd: below LOD)

Location	Atenolol (ng/L)	Carbamazepine (ng/L)	Metoprolol (ng/L)	Naproxen (ng/L)
Iqaluit, NU (7700)[a]	nd - 411	nd - 107	nd - 512	nd - 5210
Baker Lake, NU (2100)[a]	nd – 50.1	nd - 549	nd – 90.3	nd - 555
Cambridge Bay, NU (1800)[a]	nd – 89.5	nd - 2740	nd - 172	nd - 363
Kugluktuk, NU (1500)[a]	45.4 - 268	514 - 1810	52.5 - 398	422 - 1080
Cambridge Bay, NU 2014 (1600)[b]	nd - 97.4	1.2 - 428	nd	nd
Tromso, Norway (25,000)[c]	NA	nd - 270	nd - 340	NA
Klaksvic, Faroe Islands (5000)[d]	nd	NA	2.82	nd
Tórshavn, Faroe Islands (12,000)[d]	nd – 13.4	NA	nd - 653	nd - 1820
Akureyri, Iceland (18,000)[d]	501 - 711	NA	14.3 – 95.3	525 - 2340
Hveragerði, Iceland (2300)[d]	977 - 2230	NA	66.5 - 158	175 - 1920
Reykjavík, Iceland (125,000)[d]	1000 - 1650	NA	98.4 - 181	1210 - 2270

[a] This study
[b] (Chaves-Barquero et al., 2016)
[c] (Weigel et al., 2004)
[d] (Huber et al., 2016)

Many of the maximum concentrations in Table 2.1 represent the influent or lagoon concentrations of the various wastewater facilities studied. Naproxen was detected in almost all sites where it was studied, indicating its widespread use in the region. Atenolol appeared at higher concentrations in Icelandic communities compared

to Northern Canadian ones, whereas metoprolol, a similar drug (both β-blocker heart medication) was measured at similar levels in both places. Carbamazepine was quite ubiquitous within treatment systems where it was studied, likely due to its lack of photolytic and microbial degradation (Carballa et al., 2007).

Changes in pharmaceutical occurrences and concentrations between Arctic communities are due to many competing factors. Population demographics, local prescription levels, and regional restrictions on certain drugs will affect the types of compounds found in each location. Population densities in previous studies has been used to explain some of the concentration variation (Huber et al., 2016), however the data presented here suggest that other explanatory variables also require consideration. For example, Cambridge Bay and Kugluktuk generated by far the largest concentrations of carbamazepine while having the two smallest populations studied (Table 2.1), a clear indication that population even within a similar region may not always be the best descriptor of pharmaceutical occurrence. Treatment type may better help explain some of these differences, but variation will always be inherent due to changing climate, usage, and treatment.

2.4.2.2 Iqaluit

Six compounds were detected at least once in Iqaluit sites including: atenolol, carbamazepine, metoprolol, naproxen, sulfapyridine, and trimethoprim. During Iqaluit sampling, the field blank was contaminated by select compounds (e.g. atenolol, sulfapyridine, sulfamethoxazole) prior to deployment (Table A2). Corresponding lab blanks showed no contamination thus only samplers with masses at least 10 times greater than that of the field blank were accepted. All measurements near or below the

field blank were assumed to be non-detectable. As a result, the wastewater lagoon site was the only site where compounds were deemed to be above detectable concentrations. This is expected, as the lagoon receives continuous inputs from community wastewater. The absence of pharmaceuticals in both the upstream Sylvia Grinnell River and Lake Geraldine sites suggest that inputs from long range transport of pesticides and pharmaceuticals are not contributing significant amounts, if any. No analytes were detected at any sites within Frobisher Bay.

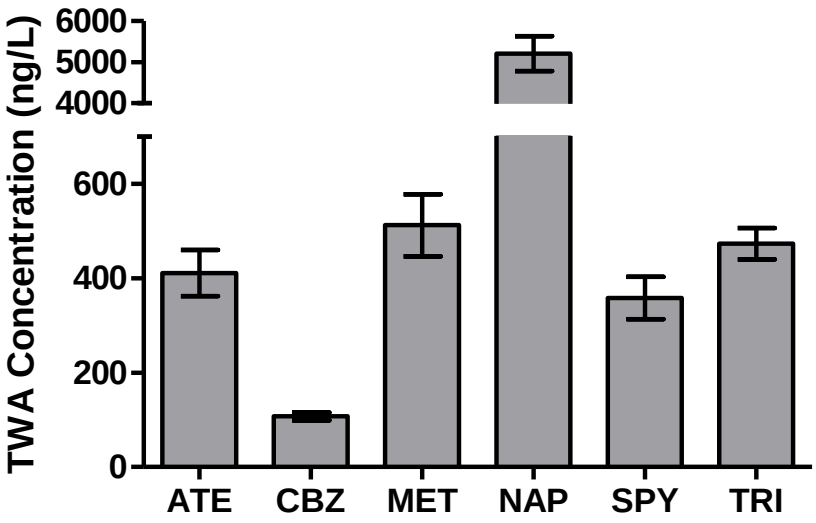


Figure 2.2: Mean (±SD, n=3) time-weighted-average (TWA) concentrations (ng/L) of pharmaceuticals in Iqaluit wastewater lagoon. No compounds were detected at any other sites in Iqaluit. Wastewater was sampled between August 31st and September 19th, 2018.

Mean TWA concentrations of the six compounds detected in the Iqaluit lagoon are shown in Figure 2.2. Naproxen had the greatest concentration of any compound detected within the lagoon at 5,210 ng/L, while carbamazepine had the least measured concentration at 107 ng/L (Figure 2.2, Table A2). The measured naproxen levels are likely due to its over-the-counter availability as it is one of the more common non-steroidal anti-inflammatory drugs (NSAIDs) on the market. It can be found in products

like Aleve® which, given the lack of a prescription needed to purchase, may be used more frequently in small and Northern communities (Samuelsen et al., 2015). Naproxen has been shown to be quite labile in sewage and is prone to high rates of anaerobic degradation in holding tanks (Carballa et al., 2007; Narumiya et al., 2013). These rates are expected to slow in Arctic communities due to lower temperatures, presumably less diverse microbial communities, and a lack of significant retention time in this treatment system; however, this process is still thought to contribute significantly to the removal of naproxen (Bergheim et al., 2010; Huber et al., 2016). This reduced rate of degradation was evident in the work by Challis et al. (2018b) to investigate the seasonal differences of wastewater influent and effluent in northern Manitoba. The treatment plant studied utilized three staging lagoons followed by a full-scale wastewater system including primary and secondary clarifiers, a much more sophisticated system than any of the ones in this study. Challis et al. (2018b) saw average increases of 2-12 times in both influent and effluent concentrations in the winter, including many of the compounds detected in this study. Naproxen saw the largest increase of almost three orders of magnitude from approximately 0.06 µg/L in summer 2015 (average temperature: 21 °C) to 35 µg/L in winter 2016 (average temperature: 0.5 °C) (Challis et al., 2018b). Such a drastic difference between naproxen and the other pharmaceuticals detected in that study suggest that degradation of this compound is greatly affected by temperature changes. This suggests that Arctic receiving waters may be more impacted by naproxen than similar southern communities. The large concentrations detected in this study seem to support this conclusion (Table 2.1), however without knowing specific usage patterns of the drugs in question, it is not possible to conclude that these elevated

concentrations are due solely to a change in degradation rate as NSAIDs may be used more in winter compared to summer for pain relief.

Dissipation of pharmaceuticals from the lagoon effluent into Frobisher Bay appear to be complete as no pharmaceuticals were measured in any sites downstream of the lagoon discharge (Table A2). However, the Frobisher Bay sites presented an interesting challenge as the Bay experiences over ten-meter-high changes in tides, twice per day. Neudorf et al., (2017) investigated the prevalence of antibiotic resistant genes in Iqaluit wastewater and within the study, conducted an experiment to determine the extent of tidal effects on these levels. Differences in gene totals during varying tides were observed in sites near the wastewater outflow. During low tide, the outflow creek from the lagoon discharges onto mainly sediment where it remains until high tides wash the discharge into the Bay (Neudorf et al., 2017). This could allow for compounds to be degraded more quickly by photolysis (e.g. naproxen $t_{1/2}$ = 1.5 hours) (Lin and Reinhard, 2005) as they would get more direct sunlight in the relatively shallow water or while sitting on sediment. However, it is also possible that the sediment could be acting as a sink for certain compounds during low tides, thus retaining the compounds and not allowing them to be diluted within the larger Bay. A simple way to represent an analytes propensity to interact with sediments is the distribution ratio K_d, which represents the equilibrium of pharmaceuticals between liquid and solid phases. Using this, we can then calculate the fraction of compounds in water (f_w) by comparing K_d to the total suspended solids (TSS) in the system, using Equation 2 (Ternes et al., 2004):

$$f_w = \frac{1}{1+K_d TSS} \quad (2)$$

Narumiya et al. (2013) calculated K_d values for a suite of pharmaceuticals in sewage sludge including many of the ones detected here. Using those values, as well as pH (7.9) and TSS (232 mg/L) values taken in the Iqaluit wastewater system from Neudorf et al. (2017) we found that even at low tides, where the TSS will be greatest, more than 95% of all compounds detected will be in the water. Using carbamazepine (K_d = 1.9 L/kg) as an example, the fraction in water under these conditions was greater than 99%. Further, rising tides are likely to resuspend and re-equilibrate some of the accumulated compounds into the water suggesting that sediments may not act as a significant sink for pharmaceuticals. We still recommend though, that in future expeditions, the effects of the tides on the pharmaceutical concentrations at discharge in Iqaluit be investigated.

2.4.2.3 Baker Lake

All seven of the compounds detected were found in at least one site at Baker Lake. Both reference lake sites showed no detectable compounds in any samples taken. Most of the offshore locations within Baker Lake itself had very low to negligible concentrations measured, with no detects at the drinking water intake (Table A3). Only metoprolol was detected at the campground site (9 ng/L), and carbamazepine (17 ng/L) and metoprolol (11 ng/L) detected in the creek outflow from Airplane Lake (Figure 2.3). Given that the wastewater lagoon is releasing sewage semi-continuously throughout the year, an estimation of 100 L/person per year was used to estimate the yearly release volume (Neudorf et al., 2017) at 7.67×10^7 L. Total concentrations of pharmaceuticals from wastewater within Baker Lake receiving waters were approximately 28 ng/L, resulting in a total mass loading of 2.15 g in 2018. Given the large dilution factor of the

lake, impacts from known ecotoxicological endpoints are expected to be insignificant as typical LC_{50} values for carbamazepine and metoprolol are greater than 10 mg/L (Tables A6-9) (Chaves-Barquero et al., 2016).

The greatest concentration of carbamazepine was found in Lagoon Lake (549 ng/L). As seen in Figure 2.3, concentrations of carbamazepine were significantly different between lakes ($p=0.05$) but were constant within the lakes themselves (i.e., intake concentration = outflow concentration) ($p=0.05$). Carbamazepine, an anti-convulsant, is known to be largely insensitive to both photodegradation and biodegradation (Carballa et al., 2007; Chaves-Barquero et al., 2016), as such, dilution is expected to be the main contributor to the attenuation through the system. As a baseline, carbamazepine showed a 2-fold dilution from Lagoon Lake to Finger Lake Input, no change within Finger Lake and then a 5-fold dilution from Finger Lake to Airplane Lake. Finally, there was a 3-fold dilution from Airplane Lake to the creek outflow into Baker Lake (Figure 2.4). We can assume that due to the relative stability of carbamazepine, such losses from dilution are typical of all pharmaceuticals released into this system. High usage patterns worldwide allowed Gasser et al. (2010, 2011) to use carbamazepine as a quantitative micropollutant tracer for determining wastewater contamination sources in Israel. Likewise, we used it to compare percent losses to other compounds in the aim of determining likely degradation pathways for the other pharmaceuticals detected.

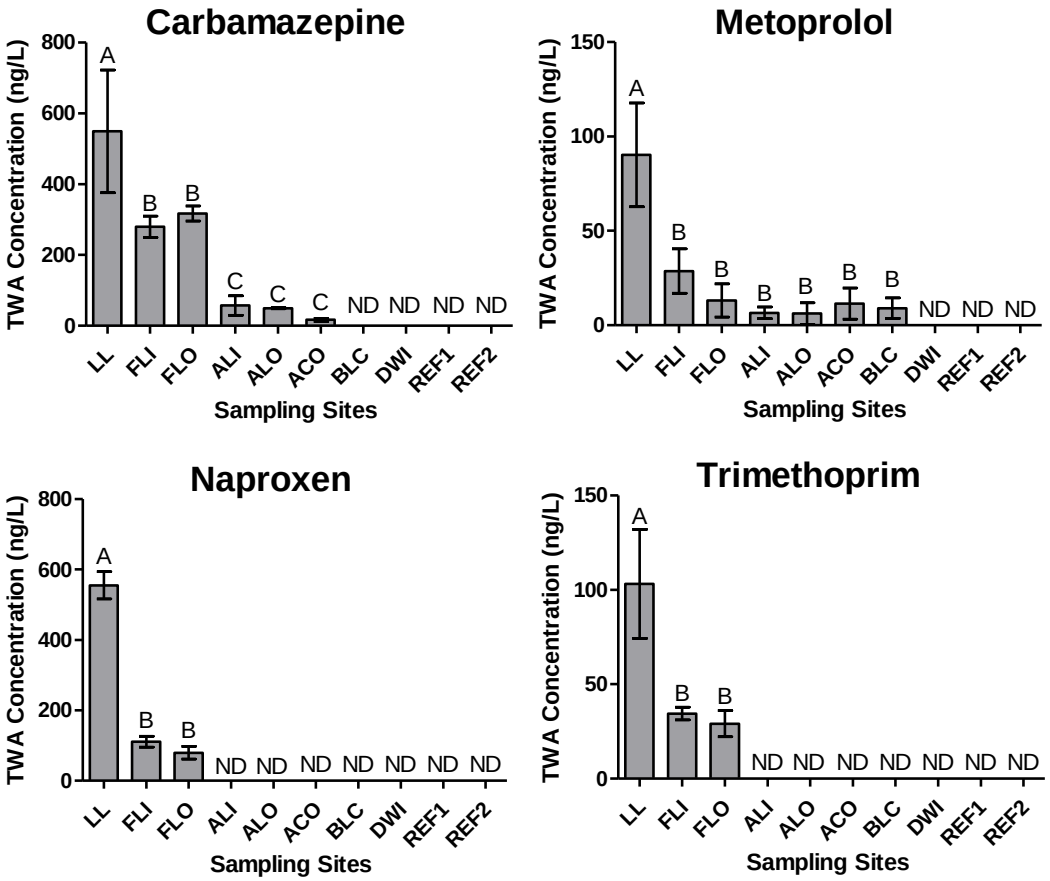


Figure 2.3: Mean (±SD, n=3) time-weighted-average (TWA) concentrations (ng/L) of pharmaceuticals through Baker Lake wastewater system. Note differing scales on y-axes. Sites follow from upstream, starting on left, to downstream, followed by reference sites and are: Lagoon Lake (LL), Finger Lake Input (FLI) and Outflow (FLO), Airplane Lake Input (ALI) and Outflow (ALO), Airplane Creek Outflow (ACO), Baker Lake Campground (BLC), Drinking Water Intake (DWI), and un-impacted Reference sites (REF1 and REF2). Wastewater was sampled between July 13th and July 22nd, 2018. Statistically significant ($p < 0.05$) differences between measurements were determined using 2-way ANOVA with Bonferroni post-hoc tests and are indicated by changing letters above bars. ND = below limit of detection (LOD).

Metoprolol, a β-blocker heart medicine, was detected at concentrations under 100 ng/L at all Baker Lake sites (Figure 2.3, Table A3). Significant attenuation occurred between Lagoon Lake and Finger Lake Input, which corresponded to a three-fold decrease (Figure 2.4). This change represents a 1.5 times larger loss compared to carbamazepine over the same time. While not statistically significant ($p=0.05$), it appears that a further two-fold dilution of metoprolol occurred within Finger Lake itself, which was not observed with carbamazepine. Losses to sediment and dissolved organic carbon are unlikely as metoprolol has been shown to interact minimally with solid phases before (Narumiya et al., 2013). Longer residence times within the lake (1-2 days), compared to the creeks between lakes (5-30 minutes), would allow more time for microbial and photolytic breakdown to occur. β-blockers are generally known to have long photolytic half-lives (on the order of 100 hours) (Challis et al., 2014), so losses to microbial degradation may better explain the trends seen in Figure 2.4.

Concentrations of naproxen in Lagoon Lake were the greatest of any compound detected in Baker Lake (555 ng/L). As discussed previously, naproxen is quite labile and readily degrades both anaerobically and photolytically. The loss of naproxen between Lagoon Lake and Finger Lake was 2.5 times greater than carbamazepine (Figure 2.4), which is consistent with the reported degradation literature for both compounds (Anderson et al., 2015; Lishman et al., 2006). A likely reason for this large loss between lakes is that while compounds flow through the creeks connecting lakes, they are more susceptible to photolysis due to the shallow, slow moving water. Upon reaching Airplane Lake, levels of naproxen were below the LOQ and beyond this point were undetectable.

Trimethoprim was detected at 103 ng/L in Lagoon Lake and showed a similar loss pattern to naproxen. Finally, sulfamethoxazole and sulfapyridine, two sulfonamide antibiotics, were detected within the system below 100 ng/L (Figure 2.3, Table A3). Both compounds were found in Finger and Airplane Lake but not downstream in Baker Lake, which is consistent with the other compounds observed.

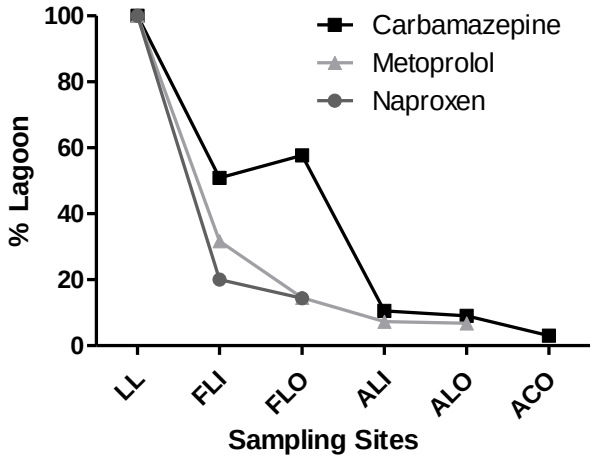


Figure 2.4: Percent losses of metoprolol and naproxen compared to carbamazepine at downstream sites relative to Lagoon Lake (LL) in Baker Lake, NU. Other sites include: Finger Lake Input (FLI) and Outflow (FLO), Airplane Lake Input (ALI) and Outflow (ALO), and Airplane Creek Outflow (ACO).

2.4.2.4 Cambridge Bay

Data gathered in this section will be compared directly with that of Chaves-Barquero et al. (2016) to identify potential trends in contaminant residues as well as concentrations between the initial study in 2014 and the one performed here in 2018. Of the six pharmaceuticals detected in 2014, five were also detected in 2018 (atenolol, carbamazepine, metoprolol, sulfamethoxazole, trimethoprim). The antibiotic clarithromycin was the only compound not detected in the current study, but two previously unseen compounds, a sulfonamide antibiotic (sulfapyridine) and a NSAID

(naproxen), were above their respective LODs in this current study (Chaves-Barquero et al., 2016). As with the previous study, most locations offshore showed considerable dilution resulting in much lower concentrations or non-detects at Outfall, Greiner Lake, Water Lake, and Marine Reference (Figure 2.5, Table A4). It should be noted that along with a different sampling duration (14 days in 2014, 12 days pre-release and 28 days during release in 2018), Chaves-Barquero et al. (2016) utilized POCIS to measure pharmaceuticals, while we used the more recently developed o-DGT passive sampler. Comparisons of these samplers and their relative performance can be found elsewhere (Challis et al., 2018b).

In 2014, a maximum concentration of 97 ng/L of atenolol was detected in the lagoon during release (Chaves-Barquero et al., 2016). A similar concentration was seen in 2018 during release (89 ng/L); however, a much greater concentration of 212 ng/L was measured in the lagoon prior to release (Figure 2.5). The reason for the large difference between these two values is unknown, but, as was seen in 2014, different sampling times within the same lagoon site can result in nearly a three-fold difference in concentration. It may be that samplers were deployed in a more concentrated area prior to release and that when the discharge began, this area was mixed. Lagoon and wetland measurements do show a significant reduction of atenolol concentrations (around 50%) during release, almost identical to the 2014 reduction of 45% (Chaves-Barquero et al., 2016). No sites offshore showed detectable levels of atenolol in 2018, where as in 2014 the outfall showed very low concentrations of < 10 ng/L. The general agreement between 2014 and 2018 data for atenolol is promising as it shows that the o-DGT passive sampler can generate similar trends to those determined using the

POCIS. Interestingly, detectable levels of atenolol (45 ng/L) were found in the wetland prior to release (Figure 2.5). A similar phenomenon was observed for carbamazepine, a less labile compound than atenolol, in 2014 (Chaves-Barquero et al., 2016). Nevertheless, as the wetland is hydrologically isolated from the surroundings, it suggests that the lagoon may be leaking water and thus contaminants into the wetland outside of the release. Another explanation could be that due to winter conditions leading to low or no microbial and photolytic degradation, some compounds are able to survive the Arctic winter in frozen surface waters.

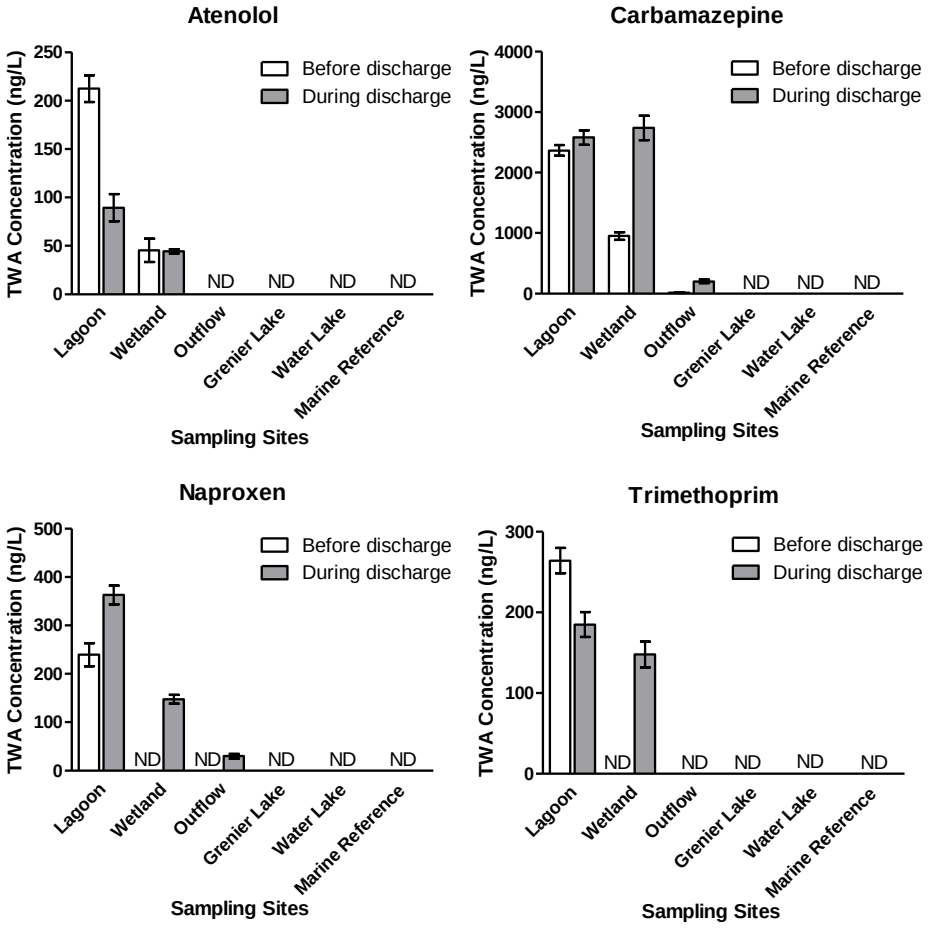


Figure 2.5: Mean (±SD, n=3) time-weighted-average (TWA) concentrations (ng/L) of pharmaceuticals in Cambridge Bay wastewater system, before and during the wastewater discharge process. Wastewater was sampled from July 4 to July 16 and from July 24 to August 22, 2018. Wastewater was released from July 23 to August 24, 2018. ND: below limit of detection (LOD).

Carbamazepine trends were similar to 2014, but concentrations were much greater in 2018 (Table 2.1). No apparent removal was seen between the lagoon and wetland during release (Figure 2.5), which was not unexpected given that carbamazepine is quite insensitive to degradation and there is very little dilution within the wetland (Carballa et al., 2007; Challis et al., 2014). Furthermore, as seen in 2014, some carbamazepine was detected in the wetland prior to release suggesting that some may leaked in or remained from the previous discharge. However, the concentration (951 ng/L) was almost nine times greater than in 2014 (116 ng/L), and this was also the case for the concentrations during release (Chaves-Barquero et al., 2016). The relatively high levels of analyte detected prior to any wastewater release in the wetland (i.e., nearly 1 µg/L of carbamazepine remaining) may be concerning as it suggests that the wetland may be concentrating some analytes prior to discharge which may wash them into the bay at greater concentrations than expected. The result of this in 2018 (Figure 2.5) was a detectable amount of carbamazepine entering the lake at Outflow both prior to release (16 ng/L) and during release (202 ng/L), which was not seen in 2014. Furthermore, while the levels were below the limit of quantification (5.7 ng/L), characteristic MS peaks for carbamazepine were seen in the Marine Reference samples during discharge that were above the limit of detection (1.7 ng/L), indicating that there may be some analyte on the sampler (Table A4). At such a far location from the original point of release, these findings are unexpected and suggest either improper disposal of these compounds in the local area or perhaps that the wastewater release can reach into the bay. No peaks were seen for either reference lakes. We advise that these Marine Reference values we interpreted with caution.

A maximum carbamazepine concentration of approximately 425 ng/L was seen in the lagoon in 2014, while in 2018 we measured a concentration of 2,580 ng/L, over five times greater in the lagoon and nine times in the wetland during release (Table 2.1). There have been developments in Cambridge Bay since the previous study that may account for some of the increased levels. Namely, the opening and subsequent use of the CHARS facility, which has drawn more permanent residents to the town (12% growth since 2011) (Statistics Canada, 2016), and could have contributed to the increase. The greater concentrations in 2018 may also be due, at least in part, to the change in sampler used. POCIS sampling rates in 2014 were calibrated for room temperature but utilized in water well below that (< 10 °C) (Chaves-Barquero et al., 2016). Sampling rates have been shown to decrease around two times for carbamazepine from 23 °C to 5°C in o-DGT passive samplers (Challis et al., 2016). Assuming similar trends for POCIS, this would reduce the difference between years to 2.5-fold, accounting for nearly half of the difference seen suggesting possible under-estimations of concentrations in 2014. Given that o-DGT rates are adjustable by temperature and may better represent the true in-situ sampling rates seen in the field, they may lead to more accurate concentrations in such cold climates.

Trimethoprim and naproxen also showed greater 2018 concentrations, compared to 2014 (Table 2.1, Table A4) (Chaves-Barquero et al., 2016). Like carbamazepine, trimethoprim experienced a nearly nine times increase in lagoon concentration during release (26 ng/L in 2014, 185 ng/L in 2018) while naproxen was not detected in 2014 (Chaves-Barquero et al., 2016), but was detected in the lagoon in 2018 during release at 363 ng/L. Naproxen experienced a 10-fold loss before reaching the outflow and was

measured at 30 ng/L entering the Bay (Figure 2.5). In general, sulfamethoxazole concentrations were much lower in 2018, with measured concentrations less than 50 ng/L. This contrasts with 2014 when concentrations exceeded 150 ng/L in the lagoon and wetland. This drop may be due to changing use patterns in the community however no data is available to support this claim. Sulfapyridine was detected at concentrations < 30 ng/L in the wetland and lagoon, and metoprolol was mostly found at similar levels. Both lake sites and the marine reference showed no measurable levels of any of these five compounds (Figure 2.5, Table A4).

Total mass loadings were calculated based on data received from the Municipality of Cambridge Bay. An average sewage flow rate of 2,000 L/minute was discharged from the lagoon from July 23 to August 24, 2018. With the valve being closed periodically to improve flow, and on weekends, a total decanting period of 336.7 hours was estimated. Due to sampling starting one day after release and stopping 2 days prior to the end, a period of 300 hours was used for calculations. Only one compound was detected in the outflow during the release period: carbamazepine at 202 ng/L (Figure 2.5). Approximately 36 million litres were decanted during the sampling period, equating to a total mass loading of 7.27 g into Cambridge Bay. Similar results were seen during a wastewater release event in a southern Manitoba community lagoon into Dead Horse Creek. During the discharge of the lagoon that services both Winkler and Morden, Manitoba (combined population of 18,000), approximately 70 g of carbamazepine was released (Carlson et al., 2013). Given the difference in population (Cambridge Bay approx. 1,800), the release of 7.3 g of carbamazepine (4.0 mg/person)

into receiving waters in Cambridge Bay is consistent with that of the similar primary lagoon treatment in southern Manitoba discussed above (3.9 mg/person).

2.4.2.5 Kugluktuk

The seven compounds detected in this study were found throughout the Kugluktuk wastewater system. All compounds were measured at all three sampling sites, including the outflow of the wetland into the Northwest Passage (Figure 2.6, Table A5). Kugluktuk and Cambridge Bay share similar community sizes, but Kugluktuk has a constructed wetland whereas Cambridge Bay has a natural wetland. For these reasons we will compare the efficiencies and outflows of both here.

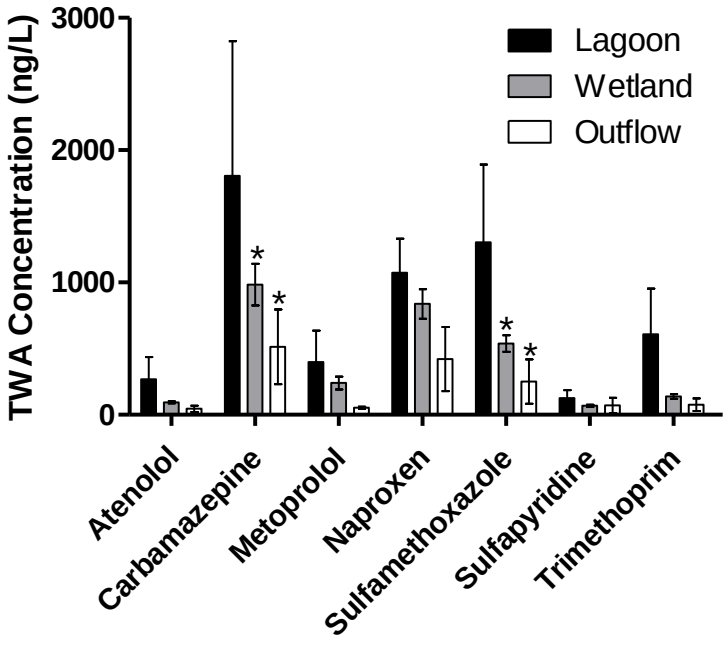


Figure 2.6: Mean (±SD, n=3) time-weighted-average (TWA) concentrations (ng/L) of pharmaceuticals in Kugluktuk wastewater system. Wastewater was sampled between August 17th and August 24th, 2018. * indicates statistical difference from lagoon concentration using two-way ANOVA and Bonferroni post-hoc tests (p < 0.05).

Only two compounds showed statistically significant reductions between the lagoon and wetland sites ($p=0.05$). Interestingly, one of these compounds was carbamazepine, which showed a 46% reduction from lagoon to wetland and 71% overall reduction to the outflow. Compared to the Cambridge Bay wetland, which has shown no attenuation of carbamazepine in two separate studies (here and Chaves-Barquero et al., 2016), the engineered wetland of Kugluktuk appears to remove it more effectively. Likewise, sulfamethoxazole had a 59% decrease in the Kugluktuk lagoon and 81% total at the outflow. While the concentrations were much lower in Cambridge Bay, very little attenuation was seen and thus sulfamethoxazole remained constant throughout the system during release (Figure 2.5). In fact, all the compounds detected within the Kugluktuk system showed decent reductions, ranging from 46% (sulfapyridine) to 87% (metoprolol, trimethoprim) with an average removal rate of 74% (Figure 2.6). Outflow concentrations ranged from 45 ng/L (atenolol) up to 514 ng/L (carbamazepine) for a total pharmaceutical concentration of 1,430 ng/L leaving the wastewater system, larger than any other site (Table A5). This results in a total mass loading of pharmaceuticals into the Passage of 79.2 g, over ten times higher than Cambridge Bay. Notably, Kugluktuk was the only site to have all seven analytes detected in the outflow and to have all seven > 100 ng/L within the lagoon. Kugluktuk is the smallest of the communities in this study (1,500 people) and yet the incident rates of all compounds detected in the lagoon is higher than both Baker Lake and Cambridge Bay. Reasons for the higher measured concentrations are unknown at this time but may relate to factors such as population usage and lagoon degradation. Because Kugluktuk discharges into the Northwest Passage, and subsequently into the Arctic Ocean,

dilution will contribute significantly to the dissipation of these compounds. Further research to understand the high rates of pharmaceuticals in this treatment system is recommended, as well as continued measurement of the levels entering and leaving it.

2.4.2.6 Risk Assessment

Hazard quotients (HQ) were calculated for all organic contaminants detected based on toxicity data reported in the peer-reviewed literature for primary producers, invertebrates, and fish (Tables A6-9). Most compounds, at most locations, had HQ values ranging from 10^{-4} to 10^{-1}. Only sulfamethoxazole in Kugluktuk showed a HQ greater than 1 for the alga *Pseudokirchneriella subcapitata.* This indicates that there is potential for growth inhibition of algal species at sulfamethoxazole concentrations within both the lagoon and wetland of Kugluktuk. However, concentrations measured in the receiving waters had HQs of less than 1, indicating no apparent risk of inhibition. While HQs greater than 1 were found, the 1000-fold uncertainty factor adds a high degree of conservatism to the calculations and given the lack of risk observed for receiving waters, we can conclude that the risk is minimal in Kugluktuk. We can also conclude that there is no discernible ecological risk to aquatic life for any other compounds and locations based on the concentrations measured. We did not use Arctic or marine-specific effect concentrations, which would better represent the locations studied. Investigations into these values for Arctic organisms are therefore recommended.

2.4.2.7 General Remarks

The data gathered here, in most cases, is based on one sampling period during summer 2018. While passive sampling provides a more manageable way to understand contaminant concentrations in systems compared to simple grab sampling, the

presence or absence of pharmaceuticals and their corresponding concentrations are quite variable, as demonstrated by the Cambridge Bay data (Chaves-Barquero et al., 2016). This variability can be due to factors external to the treatment system (e.g., usage patterns in the community) as well as within it (e.g., residence times, changes in temperature, ice cover, cloud cover, etc.) (Bergheim et al., 2010; Chouinard et al., 2014; Huber et al., 2016). Nonetheless, patterns did emerge from this data set and are discussed below.

Table 2.2: Mass loadings per person (mg/person) over a full year of wastewater release from lagoons in Iqaluit, Baker Lake, Cambridge Bay and Kugluktuk. Compounds detected are atenolol (ATE), carbamazepine (CBZ), metoprolol (MET), naproxen (NAP), sulfamethoxazole (SMX), sulfapyridine (SPY) and trimethoprim (TRI). Σ column represents the total pharmaceuticals released at each location. Populations are given in brackets.

Location	ATE	CBZ	MET	NAP	SMX	SPY	TRI	Σ
Iqaluit (7700)	38.4	10.0	47.9	487	-	33.5	44.2	621
Baker Lake (2100)	1.83	20.0	3.30	20.3	2.63	0.76	3.76	52.6
Cambridge Bay (1800)	2.01	57.9	0.69	8.15	0.43	0.40	4.15	73.7
Kugluktuk (1500)	9.88	66.7	14.7	39.6	48.0	4.64	22.4	206

The four treatment systems varied quite a lot in their removal efficiencies. Table 2.2 represents the amount of material released from lagoons over a full year using the concentrations calculated here, adjusting for population size. As can be seen in the sum pharmaceutical column, the Iqaluit lagoon performed worst with regards to pharmaceutical removal, releasing over 600 mg/person per year directly into Frobisher Bay, while Baker Lake's lagoon performed best at only 53 mg/person per year. The poor performance of Iqaluit's lagoon is not surprising as at the time of sampling, the wastewater was continually flowing out of the lagoon with only a Salsnes filter installed

to remove nutrients and solids. The short residence times within the lagoon did not allow for any meaningful degradation to occur before release, allowing many of the compounds to enter receiving waters. While this was occurring though, a new treatment plant involving both primary and secondary treatment systems was being installed along with repairs to the existing infrastructure. These upgrades should reduce the extent to which pharmaceuticals are released into receiving waters in Iqaluit.

With similar wastewater systems (i.e. lagoon, short wetland, release), Cambridge Bay had nearly three times less sum pharmaceuticals released from the lagoon than Kugluktuk (Table 2.2). Average lagoon temperatures were similar in both sites during sampling times and given that both release their wastewater once per year, residence times within lagoons can be assumed to be similar. However, the large difference in release amounts between sites may suggest that the Cambridge Bay lagoon better attenuates pharmaceuticals than Kugluktuk. Baker Lake performed the best out of any site, releasing only 53 mg/person per year indicating that the constructed, multi-celled lagoon used there is successful in removing some pharmaceutical residues.

Many of these sites have wetlands which are hydrologically isolated and continue to perform treatment before wastewater reaches watersheds. While not relevant for Iqaluit given its current lack of wetlands, the remaining sites all include these and can then be further compared by outflow masses which better indicate how much compound may be reaching the receiving environment. Cambridge Bay and Kugluktuk showed sum pharmaceutical outflow totals of 4.0 and 52.8 mg/person per year, respectively while Baker Lake, had a sum pharmaceutical at outflow of 1.0 mg/person per year. Both Cambridge Bay and Baker Lake had nearly complete attenuation when released into

receiving waters from their respective wetland systems, while Kugluktuk appeared to produce only a 4-fold change after wetland release (Figure 2.6, Table A5). Cambridge Bay has a previously reported wetland residence time of approximately 1 – 2 days and given the similar style of treatment, Kugluktuk can be assumed to have the same (Chaves-Barquero et al., 2016). While true residence times at Baker Lake are unknown, the nature of its path (i.e. through three separate natural lakes and streams) allows for more opportunities for the compounds to be degraded before release, likely by photolysis and microbial means. By utilizing the natural lakes around the community, Baker Lake was able to reduce the mass of compound leaving the system without the need for a constructed treatment plant, unlike Kugluktuk (Figures 2.3 and 2.6). These observations highlight the variability in treatment styles due to availability of resources inherent within Arctic wastewater strategies. We recommend further studies within these sites to monitor the changing pharmaceutical concentrations and specifically within Kugluktuk to better understand why its constructed lagoon and wetland appears to perform worse compared to the natural ones used in Cambridge Bay and Baker Lake.

2.4.3 Per- and Polyfluorinated Alkyl Substances

Of the ten PFASs tested for, only five were detected in any samples in Cambridge Bay, NU. They include three long chain perfluoroalkyl carboxylates (PFCAs) PFOA, PFNA and PFDA; one of the most prominently studied substances in PFOS and a short-chain replacement compound in PFBS. None of the four pre-cursor compounds tested were found in any of the samples however given their volatility this is not unexpected (Buck et al., 2011; Pickard et al., 2018; Stock et al., 2007). PFASs were observed only in samples related to the wastewater system (i.e. lagoon, wetland,

outflow) as seen in Figure 2.7. The contamination profiles remained consistent throughout the wastewater release with the short-chain PFBS being the most prevalent (14.7 – 85.1 ng/L), followed by significant amounts of PFOA (9.92 – 80.4 ng/L) and PFOS (4.20 – 70.6 ng/L). Small amounts of PFNA (2.33 – 11.7 ng/L) and PFDA (0.44 – 4.67 ng/L) were also detected (Table A10). This profile is consistent with current use of PFASs worldwide given the voluntary phase-out of many of the long-chain PFCAs and PFOS by North American producers in the early 2000s along with the addition of PFOS to the Stockholm Convention under Annex B (Buck et al., 2011). A recent study into PFAS contamination of seawater at Svalbard, Norway found perfluorobutanoic acid (PFBA), a degradation product of short-chain PFASs, to be a dominant compound detected in ice cores and snow sampling (Kwok et al., 2013). PFBA was also found to be a major compound detected in the Barrow Strait of the Canadian Arctic in 2015, however PFBS has also been widely detected through Arctic samples (Ahrens et al., 2010; Cai et al., 2012; Kwok et al., 2013; Muir et al., 2015). High ratios of PFOA (36%) and PFOS (19%) in the samples taken in this study suggest that this transition to commercial products utilizing short-chain PFASs may not be fully complete in Cambridge Bay. It is also possible though, that these longer-chain compounds may be added during snow melts, which has been shown to be a significant source in previous studies (Skaar et al., 2019; Vincent and Muir, 2015).

Concentrations measured in the wastewater system (Figure 2.7, Table A10) were found to be 10- to 1000-fold greater than those reported in surrounding seawater. Reported seawater values have been found in the 10 to 300 pg/L range for individual PFASs with sum PFAS totals generally ranging around 500 to 1000 pg/L (Benskin et al.,

2012; Cai et al., 2012; Kwok et al., 2013; Muir et al., 2015; Stock et al., 2007). As Figure 2.7 shows, sum PFAS levels in the wastewater system are over 200 ng/L before release and greater than 75 ng/L in Cambridge Bay during the wastewater release. Total mass of PFAS entering the Bay for 2018 is estimated at 3.38 g which, while much less than the amounts entering the Arctic through long-range transport systems (Wong et al., 2018; Xiao, 2017; Yeung et al., 2017) is still a significant amount, especially to the local area. No degradation is seen within the system given the relative strength of the C-F bonds within these compounds (Buck et al., 2011). Concentrations after release in the Bay were below detection limits, however we do not expect them to be completely gone. Similar to other studies done in Canadian Arctic seawater, we would expect both the Cambridge Bay and Marine Reference sites to show pg/L levels of sum PFAS however given our current method and detection limits (0.1 – 0.33 ng/L) we do not have the capacity to measure these concentrations.

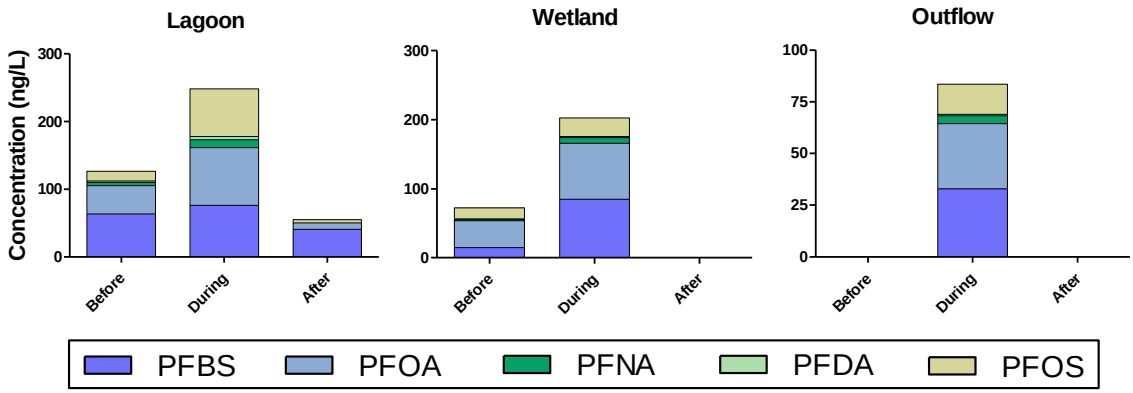


Figure 2.7: Concentrations (ng/L) of PFASs in lagoon, wetland and outflow sites of Cambridge Bay, NU wastewater system in summer 2018. Duplicate samples were taken before, during and after the annual release which took place from July 23rd to August 24th. No compounds were detected at Airport, Water Lake, Greiner Lake or Marine Reference sites.

Interestingly, samples taken near the airport showed no PFAS contamination even though previous use of AFFF on-site would suggest leakage into the Bay could occur (De Solla et al., 2012; Houtz et al., 2016). Recently, Skaar et al. (2019) investigated the contamination profile of PFASs due to AFFF use at fire-fighting training locations in the Norwegian Arctic. They found that these sites were a significant local source of PFASs to the surrounding area, primarily PFOS and the six carbon long cousin perfluorohexane sulfonate, which are the main components of AFFF (Skaar et al., 2019). Given similar use at the Cambridge Bay airport, we expected to see similar contamination, but this was not found. This may be due to the remediation program that was implemented in Cambridge Bay for this site (Fisher, 2015), however without proper soil samples we cannot fully conclude that the area is clean. Given the similar concentrations released by AFFF contaminated sites in other studies (i.e. hundreds of ng/L), we can conclude that wastewater, like fire-fighting training sites, can be a significant point source of PFASs in Arctic communities. We recommend that PFAS contamination of wastewater be further studied in more Arctic communities to determine its true impact both locally and in the greater Arctic area.

2.4.4 Microplastics

Microplastic particles were found in all samples collected, including blanks. Of the five microplastic types investigated (fibre, film, foam, fragment, bead), fibres accounted for most of all plastics found (98.6%) with only one film, one fragment, and three foams detected across all 368 measured plastics. No microbeads were detected in any samples. There was no significant difference found in samples obtained in

various field locations compared to those gathered as field blanks. Field blanks utilized a pouring method whereby samples were poured on site into clean jars to account for possible contamination by user clothing. Given that many of the same types (fibres) and amounts of plastic found in said blanks matched those found in all other samples, we cannot draw any meaningful conclusions from the data presented here. One potential candidate for the contamination source could be the clothing worn by users during sampling. Previous studies have shown that synthetic textiles, including jackets and sweaters, can release microplastic fibres (Hartline et al., 2016) which may account for the similarity between plastics across all samples taken. We recommend further studies on the microplastic contamination of Arctic lakes given that the results gathered here are inconclusive on the role of wastewater as a source of them to the Arctic environment.

Table 2.3. Total microplastic fibre counts in Cambridge Bay wastewater facility, before (July 4th) and during (July 26th) the wastewater discharge process. Blank samples were poured on site.

Number of Plastics\ Sites	Field Blank	Lagoon	Wetland	Outflow	Water Lake	Greiner Lake	Marine Ref
Pre-release	26	27	41	67	1	18	23
During release	53	47	21	11	-	-	-

2.5 Conclusions

The study presented here identified for the first time the presence of pharmaceuticals in the wastewater systems and surrounding waters of three Canadian Arctic communities: Iqaluit, Baker Lake, and Kugluktuk. Cambridge Bay, while having been previously studied in 2014, was again monitored to see if pharmaceutical signatures and concentrations had changed over time. Of the 27 pharmaceuticals tested for, only seven were detected, with six of them being detected in all four

communities. Variations between communities and through time in Cambridge Bay were observed. Treatment type could be used to explain some of the variation within, but no clear trends were observed beyond this. Our data suggests that attenuation of many of the pharmaceuticals found does occur in each of the four treatment systems and especially in the natural lake system of Baker Lake. Concentrations of pharmaceuticals leaving both Iqaluit and Baker Lake were minimal to negligible and are not thought to pose any ecological risk to the surrounding waters. Concentrations in Cambridge Bay and Kugluktuk were greater due to the nature of their treatment systems (single release in a year), however, dilution is expected to play a major role in reducing pharmaceuticals concentrations to negligible levels in the Northwest Passage. Further studies into the seasonal variation within these communities, along with more in-depth testing of the wastewater treatment efficiencies, are recommended to further the base of knowledge provided here.

A novel investigation of per- and poly-fluorinated alkyl substances in a Canadian Arctic wastewater system was also done. Ten PFASs were investigated in Cambridge Bay to assess local contamination sources. Five compounds were detected including one short-chain replacement compound as well as four long-chain homologues. While no contamination was seen near the airport where expected, results suggest that wastewater may be an important source of local contamination of PFASs in the Arctic and that concentrations seen previously may not be just due to long-range transport of these chemicals through the air and ocean currents. Given the novel nature of this work, more studies into the fate and effects of PFASs in Arctic wastewater are suggested.

The potential release of microplastics through the Cambridge Bay WWTP was also investigated for both type and number of plastics. The majority of plastics detected were in the form of fibres. Unfortunately, wastewater sources were unable to be determined due to field blank contamination during the study. Conclusions were therefore unable to be made and thus further research is recommended.

CHAPTER 3

3. Overall Synthesis

Kevin M. Stroski

3.1 Summary of Novelty of Research Findings

Understanding the sources, occurrence, and fate of contaminants in the environment is key to assessing their potential impact. Arctic monitoring studies have been heavily focused on the long-range sources of many contaminants, yet local sources can also have significant impacts on aquatic concentrations. The understanding of local sources, especially those through WWTPs in the Canadian Arctic is lacking, leading to potential challenges for both regulators and communities who aim to maintain or improve water quality in the area. This thesis describes a preliminary study into the potential wastewater sources and impacts of pharmaceuticals on four Canadian Arctic communities as well as the impacts of PFASs and microplastics on one of those four communities.

The research conducted here, as laid out in Chapter 2, utilized o-DGT passive samplers to determine pharmaceutical contamination within the Iqaluit, Baker Lake, Cambridge Bay, and Kugluktuk WWTPs and surrounding areas. Seven different drugs were found to be released in total, with concentrations varying both by community and through the WWTPs themselves. Kugluktuk appeared to have the largest total pharmaceutical mass release of any community studied here, with carbamazepine, naproxen, and sulfamethoxazole being the top three contributors. Naproxen concentrations were found to be the greatest in most WWTPs studied (low µg/L levels), a potential consequence of reduced degradation processes available in Arctic climates. Risk assessments showed that given the reduction of concentration through wastewater systems, there appears to be no current ecological risk on aquatic organisms at this time. PFASs were also detected in the Cambridge Bay WWTP indicating that local

sources may an important factor for Arctic contamination, alongside the long-range transport of these compounds which has been more heavily studied. Microplastic contamination was investigated however no conclusions could be drawn at this time due to blank contamination during sampling.

Overall this research supports the hypothesis that WWTPs can be local sources of contamination for both pharmaceuticals and PFASs in Canadian Arctic communities. However, the current impacts of these releases appear to be negligible on the receiving environment with many concentrations being below measured levels for organism responses in nearly all cases.

3.2 Challenges and Future Directions

There were a few challenges encountered in this thesis that can inform future directions for Arctic contamination work. Simple logistical problems which occurred could have been solved given more time and resources, however given the scope of a MSc program not all problems could be addressed. Thus a few questions regarding distribution and occurrence of these contaminants remain.

Iqaluit sampling was one of the major issues that came up during this project. o-DGT samplers were sent up with diffusive and binding gels reversed which caused on the fly fixes to be made. During this, contamination of samplers may have occurred leading to the large field blank detections seen in the results. This may have contributed to the non-detects of pharmaceuticals outside of the lagoon including within Frobisher Bay itself. Another possible oversight was the flow of water within the Bay. Looking at Figure 2.1a we can see that the sites within Frobisher Bay were all west of Long Island,

the lone land mass in the harbour near Iqaluit. These sites were chosen primarily for convenience as there were already deployed construction buoys which the cages were easily attached to for the duration of sampling. However, after consulting with local elders in a recent Department of Fisheries and Oceans meeting in Iqaluit, they suggested that the water flow may in fact flow east around the island, indicating that our sampling locations may not have been ideal. It is possible that some pharmaceuticals may be detected in this area of the Bay, assuming that the flow is as described. Further, as discussed in Chapter 2, the large tidal effects in the Bay make sampling near the lagoon outflow difficult. Given what we now know, many of these problems can be addressed with more representative sampling sites chosen along with the potential for tidal effects to be incorporated through perhaps buckets filled with samplers entrenched near the outflow. This information should be incorporated into future sampling in the Iqaluit harbour to further support the work presented here.

While outside of the scope of this thesis, the lack of proper toxicity end points for Arctic organisms towards the contaminants screened for is unfortunate. Estimates using typical lab species like *Daphnia magna* allowed for approximations but testing on Arctic specific species would better allow ecological assessments to be accurate to the area studied. These endpoints are thus recommended to be investigated.

Microplastics and PFASs were only screened in one community in this study, largely due to logistical reasons. As with pharmaceuticals, further years of study along with expanding to the other communities would better allow conclusions to be drawn about the potential impact local sources may have on these contaminants. Microplastics

especially will need more consistent and careful preparatory work to mitigate the field blank issue seen in the results gathered here.

The potential persistence of certain compounds through winter months in both wetlands and outflow locations was observed in Cambridge Bay. While this may be due to a leak of the lagoon, it also brings up a question unable to be answered by the current data set. Namely what the concentration profiles look like during the winter months under ice and how they may be contributing to the overall levels seen in this study. Winter sampling may be difficult in Arctic terrain however results would be of interest to the scientific community to better understand the persistence and possible toxicity of these contaminants during the winter months.

The thesis focused on a novel study into the impact that WWTPs have on Canadian Arctic communities for pharmaceuticals, PFASs, and microplastics. The occurrence and fate of these compounds are likely to only increase as populations increase, indicating a need for both consistent monitoring and treatment going forward. The work represents a significant contribution to this effort relating both WWTP efficiencies and effluent concentrations to four representative communities in the Nunavut province. These results, paired with many of the suggestions presented here would very likely aid both regulators and communities in their water quality and treatment goals moving forward.

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5. Appendix

Additional Information for Chapter 2

Summary

This section contains additional information for Chapter 2 including maps, temperature data, raw contaminant data, and calculated hazard quotients in the forms of figures and tables.

Figure A1: Sampling communities across the territory of Nunavut, Canada.

Table A1. Average water temperatures (°C) of Cambridge Bay sites prior to wastewater release and during wastewater release sampling times (n=3).

Temperature\Sites	Lagoon	Wetland	Outflow	Water Lake	Greiner Lake	Marine
Pre-release	12.8	13.7	6.8	6.6	10.9	4.5
During release	8.8	7.9	6.4	9.2	8.5	4.4

Table A2. Mean concentrations (ng/L) of detected organic micropollutants in the Iqaluit wastewater treatment facility and receiving waters in 2018. All other compounds were below their limits of detection. LOQs and LODs (ng/L) are indicated below each compound's name. Standard deviations (n=3) are denoted in parentheses.

Compound	Site						
	Lagoon	Frobisher 1	Frobisher 2	Frobisher 3	Lake Geraldine	Sylvia Grinnell	Field Blank
Atenolol (LOQ: 1.0, LOD: 0.3)	411 (49)	ND	ND	ND	ND	ND	23.3
Carbamazepine (LOQ: 5.7, LOD: 1.7)	107 (8)	ND	ND	ND	ND	ND	ND
Metoprolol (LOQ: 2.1, LOD: 0.6)	512 (66)	ND	ND	ND	ND	ND	ND
Naproxen (LOQ: 120, LOD: 35)	5210 (427)	ND	ND	ND	ND	ND	ND
Sulfapyridine (LOQ: 1.9, LOD: 0.6)	358 (45)	ND	ND	ND	ND	ND	28.7
Trimethoprim (LOQ: 12, LOD: 3.6)	473 (33)	ND	ND	ND	ND	ND	ND

Table A3. Mean concentrations (ng/L) of detected organic micropollutants in the Baker Lake wastewater treatment facility and receiving waters in 2018. All other compounds were below their limits of detection. LOQs and LODs (ng/L) are indicated below each compound's name. Standard deviations (n=3) are denoted in parentheses.

Compound	Site									
	Lagoon Lake	Finger Lake In	Finger Lake Out	Airplane Lake In	Airplane Lake Out	Airplane Creek Out	Drinking Water Intake	Camp-ground	Reference 1	Reference 2
Atenolol (LOQ: 1.0, LOD: 0.3)	50 (20)	8.1 (2.7)	6.4 (2.8)	ND	ND	ND	ND	ND	ND	ND
Carbamazepine (LOQ: 5.7, LOD: 1.7)	549 (173)	280 (30)	317 (21)	57 (28)	50 (2)	17 (4)	ND	ND	ND	ND
Metoprolol (LOQ: 2.1, LOD: 0.6)	90 (27)	29 (12)	13 (9)	6.6 (3.1)	6.1 (5.8)	11 (8)	ND	9.0 (5.5)	ND	ND
Naproxen (LOQ: 120, LOD: 35)	555 (39)	111 (15)	80 (18)	< 120	< 120	ND	ND	ND	ND	ND
Sulfamethoxazole (LOQ: 66, LOD: 20)	72 (4)	41 (9)	< 66	< 66	ND	ND	ND	ND	ND	ND
Sulfapyridine (LOQ: 1.9, LOD: 0.6)	21 (7)	8.2 (3.2)	6.1 (1.7)	ND	ND	ND	ND	ND	ND	ND
Trimethoprim (LOQ: 12, LOD: 3.6)	103 (29)	34 (3)	29 (7)	< 12	< 12	ND	ND	ND	ND	ND

Table A4. Mean concentrations (ng/L) of detected organic micropollutants in the Cambridge Bay wastewater treatment facility and receiving waters in 2018. All other compounds were below their limits of detection. LOQs and LODs (ng/L) are indicated below each compound's name. Standard deviations (n=3) are denoted in parentheses.

Compound	Site						
	Time frame (Discharge)	Lagoon	Wetland	Outflow	Grenier Lake	Water Lake	Marine Ref.
Atenolol (LOQ: 1.0, LOD: 0.3)	Before	212 (14)	45 (12)	ND	ND	ND	ND
	During	89 (14)	44 (2)	ND	ND	ND	ND
Carbamazepine (LOQ: 5.7, LOD: 1.7)	Before	2366 (88)	951 (62)	16 (7)	ND	ND	ND
	During	2580 (120)	2740 (202)	202 (29)	ND	ND	< 5.7
Metoprolol (LOQ: 2.1, LOD: 0.6)	Before	172 (16)	< 2.1	ND	ND	ND	ND
	During	31 (13)	14 (19)	ND	ND	ND	ND
Naproxen (LOQ: 120, LOD: 35)	Before	240 (24)	ND	ND	ND	ND	ND
	During	363 (19)	148 (9)	< 120	ND	ND	ND
Sulfamethoxazole (LOQ: 66, LOD: 20)	Before	209 (17)	ND	ND	ND	ND	ND
	During	< 66	< 66	< 66	ND	ND	ND
Sulfapyridine (LOQ: 1.9, LOD: 0.6)	Before	26 (2)	4.2 (1)	ND	ND	ND	ND
	During	18 (3)	4.7 (0.2)	ND	ND	ND	ND
Trimethoprim (LOQ: 12, LOD: 3.6)	Before	264 (16)	ND	ND	ND	ND	ND
	During	185 (16)	148 (16)	ND	ND	ND	ND

Table A5. Mean concentrations (ng/L) of detected organic micropollutants in the Kugluktuk wastewater treatment facility and receiving waters in 2018. All other compounds were below their limits of detection. LOQs and LODs (ng/L) are indicated below each compound's name. Standard deviations (n=3) are denoted in parentheses.

Compound	Site		
	Lagoon	Wetland	Outflow
Atenolol (LOQ: 1.0, LOD: 0.3)	268 (169)	94 (8)	45 (23)
Carbamazepine (LOQ: 5.7, LOD: 1.7)	1807 (1016)	984 (158)	514 (283)
Metoprolol (LOQ: 2.1, LOD: 0.6)	398 (237)	240 (49)	53 (10)
Naproxen (LOQ: 120, LOD: 35)	1075 (257)	838 (112)	422 (243)
Sulfamethoxazole (LOQ: 66, LOD: 20)	1303 (588)	539 (63)	251 (168)
Sulfapyridine (LOQ: 1.9, LOD: 0.6)	126 (59)	68 (8)	71 (58)
Trimethoprim (LOQ: 12, LOD: 3.6)	609 (346)	139 (18)	76 (47)

Table A6. Calculated hazard quotients for organic micropollutants detected by o-DGT samplers in the Iqaluit wastewater treatment facility and receiving waters from August 17 to August 24, 2018. Only most concentrated values tested unless value > 1 found. Full data set of measured concentrations available in Table A2.

Compound	Site type	Species	Toxicity endpoint	Toxicity value (mg/L)	MEC (mg/L)	HQ	Reference
Atenolol	Lagoon	*Lemna spp.*	EC50 - 7 day growth inhibition	> 320	4.11×10^{-4}	1.28×10^{-3}	(Cleuvers, 2005)
		Daphnia magna	EC50 - 48 h immobilization	313	4.11×10^{-4}	1.31×10^{-3}	(Cleuvers, 2005)
		Pimephales promelas	NOEC - 32 day growth inhibition	3.2	4.11×10^{-4}	1.28×10^{-1}	(Küster et al., 2010)
Carbamazepine	Lagoon	*Lemna minor*	EC50 - 7 day growth inhibition	22.5	1.07×10^{-4}	4.77×10^{-3}	(Cleuvers, 2003)
		Daphnia magna	EC50 - 48 h immobilization	> 100	1.07×10^{-4}	1.07×10^{-3}	(Cleuvers, 2003)
		Oryzias latipes	LC50 - 28 day exposure	35.4	1.07×10^{-4}	3.03×10^{-3}	(Kim et al., 2007)
Metoprolol	Lagoon	*Lemna spp.*	EC50 - 7 day growth inhibition	> 320	5.12×10^{-4}	1.60×10^{-3}	(Cleuvers, 2005)
		Daphnia magna	EC50 - 48 h immobilization	438	5.12×10^{-4}	1.17×10^{-3}	(Cleuvers, 2005)
		Danio rerio	EC50 – 72 h embryo exposure	12.6	5.12×10^{-4}	4.06×10^{-2}	(van den Brandhof and Montforts, 2010)
Naproxen	Lagoon	*Lemna minor*	EC50 - 7 day growth inhibition	24.2	5.21×10^{-3}	2.15×10^{-1}	(Cleuvers, 2005)
		Daphnia magna	EC50 - 48 h immobilization	174	5.21×10^{-3}	2.99×10^{-2}	(Cleuvers, 2005)
		Danio rerio	LC50 – 96 h embryo exposure	115.2	5.21×10^{-3}	4.52×10^{-2}	(Li et al., 2016)
Sulfapyridine	Lagoon	*Scenedesmus vacuolatus*	EC50 - 24 h growth inhibition	5.28	3.58×10^{-4}	6.78×10^{-2}	(Bialk-Bielinska et al., 2011)
		Lemna minor	EC50 - 72 h growth inhibition	0.46	3.58×10^{-4}	7.78×10^{-1}	(Bialk-Bielinska et al., 2011)
Trimethoprim	Lagoon	*Selenastrum capricornutum*	EC50 - 72 h growth inhibition	80.3	4.73×10^{-4}	5.89×10^{-3}	(Eguchi et al., 2004)
		Daphnia magna	EC50 - 48 h immobilization	120.7	4.73×10^{-4}	3.92×10^{-3}	(Kim et al., 2007)
		Oryzias latipes	LC50 - 48 h exposure	> 100	4.73×10^{-4}	4.73×10^{-3}	(Kim et al., 2007)

Table A7. Calculated hazard quotients for organic micropollutants detected by o-DGT samplers in the Baker Lake wastewater treatment facility and receiving waters from August 17 to August 24, 2018. Only most concentrated values tested unless value > 1 found. Full data set of measured concentrations available in Table A3.

Compound	Site type	Species	Toxicity endpoint	Toxicity value (mg/L)	MEC (mg/L)	HQ	Reference
Atenolol	Lagoon	*Lemna spp.*	EC50 - 7 day growth inhibition	> 320	5.01×10^{-5}	1.57×10^{-4}	(Cleuvers, 2005)
		Daphnia magna	EC50 - 48 h immobilization	313	5.01×10^{-5}	1.60×10^{-4}	(Cleuvers, 2005)
		Pimephales promelas	NOEC - 32 day growth inhibition	3.2	5.01×10^{-5}	1.57×10^{-2}	(Küster et al., 2010)
Carbamazepine	Lagoon	*Lemna minor*	EC50 - 7 day growth inhibition	22.5	5.49×10^{-4}	2.44×10^{-2}	(Cleuvers, 2003)
		Daphnia magna	EC50 - 48 h immobilization	> 100	5.49×10^{-4}	5.49×10^{-3}	(Cleuvers, 2003)
		Oryzias latipes	LC50 - 28 day exposure	35.4	5.49×10^{-4}	1.55×10^{-2}	(Kim et al., 2007)
Metoprolol	Lagoon	*Lemna spp.*	EC50 - 7 day growth inhibition	> 320	9.03×10^{-5}	2.82×10^{-4}	(Cleuvers, 2005)
		Daphnia magna	EC50 - 48 h immobilization	438	9.03×10^{-5}	2.06×10^{-4}	(Cleuvers, 2005)
		Danio rerio	EC50 – 72 h embryo exposure	12.6	9.03×10^{-5}	7.17×10^{-3}	(van den Brandhof and Montforts, 2010)
Naproxen	Lagoon	*Lemna minor*	EC50 - 7 day growth inhibition	24.2	5.55×10^{-4}	2.29×10^{-2}	(Cleuvers, 2005)
		Daphnia magna	EC50 - 48 h immobilization	174	5.55×10^{-4}	3.19×10^{-3}	(Cleuvers, 2005)
		Danio rerio	LC50 – 96 h embryo exposure	115.2	5.55×10^{-4}	4.82×10^{-3}	(Li et al., 2016)
Sulfamethoxazole	Lagoon	*Pseudokirchneriella subcapitata*	EC50 - 72 h growth inhibition	0.52	7.21×10^{-5}	1.39×10^{-1}	(Isidori et al., 2005)
		Daphnia magna	EC50 - 48 h immobilization	25.2	7.21×10^{-5}	2.86×10^{-3}	(Isidori et al., 2005)
		Oryzias latipes	LC50 - 48 h exposure	562.5	7.21×10^{-5}	1.28×10^{-4}	(Kim et al., 2007)
Sulfapyridine	Lagoon	*Scenedesmus vacuolatus*	EC50 - 24 h growth inhibition	5.28	2.07×10^{-5}	3.92×10^{-3}	(Bialk-Bielinska et al., 2011)
		Lemna minor	EC50 - 72 h growth inhibition	0.46	2.07×10^{-5}	4.50×10^{-2}	(Bialk-Bielinska et al., 2011)
Trimethoprim	Lagoon	*Selenastrum capricornutum*	EC50 - 72 h growth inhibition	80.3	1.03×10^{-4}	1.28×10^{-3}	(Eguchi et al., 2004)
		Daphnia magna	EC50 - 48 h immobilization	120.7	1.03×10^{-4}	8.54×10^{-4}	(Kim et al., 2007)
		Oryzias latipes	LC50 - 48 h exposure	> 100	1.03×10^{-4}	1.03×10^{-3}	(Kim et al., 2007)

Table A8. Calculated hazard quotients for organic micropollutants detected by o-DGT samplers in the Cambridge Bay wastewater treatment facility and receiving waters from August 17 to August 24, 2018. Only most concentrated values tested unless value > 1 found. Full data set of measured concentrations available in Table A4.

Compound	Site type	Species	Toxicity endpoint	Toxicity value (mg/L)	MEC (mg/L)	HQ	Reference
Atenolol	Lagoon	*Lemna spp.*	EC50 - 7 day growth inhibition	> 320	2.12×10^{-4}	6.63×10^{-4}	(Cleuvers, 2005)
		Daphnia magna	EC50 - 48 h immobilization	313	2.12×10^{-4}	6.77×10^{-4}	(Cleuvers, 2005)
		Pimephales promelas	NOEC - 32 day growth inhibition	3.2	2.12×10^{-4}	6.63×10^{-2}	(Küster et al., 2010)
Carbamazepine	Lagoon	*Lemna minor*	EC50 - 7 day growth inhibition	22.5	2.74×10^{-3}	1.22×10^{-1}	(Cleuvers, 2003)
		Daphnia magna	EC50 - 48 h immobilization	> 100	2.74×10^{-3}	2.74×10^{-2}	(Cleuvers, 2003)
		Oryzias latipes	LC50 - 28 day exposure	35.4	2.74×10^{-3}	7.74×10^{-2}	(Kim et al., 2007)
Metoprolol	Lagoon	*Lemna spp.*	EC50 - 7 day growth inhibition	> 320	1.72×10^{-4}	5.38×10^{-4}	(Cleuvers, 2005)
		Daphnia magna	EC50 - 48 h immobilization	438	1.72×10^{-4}	3.93×10^{-4}	(Cleuvers, 2005)
		Danio rerio	EC50 – 72 h embryo exposure	12.6	1.72×10^{-4}	1.37×10^{-2}	(van den Brandhof and Montforts, 2010)
Naproxen	Lagoon	*Lemna minor*	EC50 - 7 day growth inhibition	24.2	3.63×10^{-4}	1.50×10^{-2}	(Cleuvers, 2005)
		Daphnia magna	EC50 - 48 h immobilization	174	3.63×10^{-4}	2.09×10^{-3}	(Cleuvers, 2005)
		Danio rerio	LC50 – 96 h embryo exposure	115.2	3.63×10^{-4}	3.15×10^{-3}	(Li et al., 2016)
Sulfamethoxazole	Lagoon	*Pseudokirchneriella subcapitata*	EC50 - 72 h growth inhibition	0.52	2.09×10^{-4}	4.02×10^{-1}	(Isidori et al., 2005)
		Daphnia magna	EC50 - 48 h immobilization	25.2	2.09×10^{-4}	8.29×10^{-3}	(Isidori et al., 2005)
		Oryzias latipes	LC50 - 48 h exposure	562.5	2.09×10^{-4}	3.72×10^{-4}	(Kim et al., 2007)
Sulfapyridine	Lagoon	*Scenedesmus vacuolatus*	EC50 - 24 h growth inhibition	5.28	2.58×10^{-5}	4.89×10^{-3}	(Bialk-Bielinska et al., 2011)
		Lemna minor	EC50 - 72 h growth inhibition	0.46	2.58×10^{-5}	5.61×10^{-2}	(Bialk-Bielinska et al., 2011)
Trimethoprim	Lagoon	*Selenastrum capricornutum*	EC50 - 72 h growth inhibition	80.3	2.64×10^{-4}	3.29×10^{-3}	(Eguchi et al., 2004)
		Daphnia magna	EC50 - 48 h immobilization	120.7	2.64×10^{-4}	2.19×10^{-3}	(Kim et al., 2007)
		Oryzias latipes	LC50 - 48 h exposure	> 100	2.64×10^{-4}	2.64×10^{-3}	(Kim et al., 2007)

Table A9. Calculated hazard quotients for organic micropollutants detected by o-DGT samplers in the Kugluktuk wastewater treatment facility and receiving waters from August 17 to August 24, 2018. Only most concentrated values tested unless value > 1 found. Full data set of measured concentrations available in Table A5.

Compound	Site type	Species	Toxicity endpoint	Toxicity value (mg/L)	MEC (mg/L)	HQ	Reference
Atenolol	Lagoon	*Lemna spp.*	EC50 - 7 day growth inhibition	> 320	2.64×10^{-4}	8.38×10^{-4}	(Cleuvers, 2005)
		Daphnia magna	EC50 - 48 h immobilization	313	2.64×10^{-4}	8.56×10^{-4}	(Cleuvers, 2005)
		Pimephales promelas	NOEC - 32 day growth inhibition	3.2	2.64×10^{-4}	8.38×10^{-2}	(Küster et al., 2010)
Carbamazepine	Lagoon	*Lemna minor*	EC50 - 7 day growth inhibition	22.5	1.81×10^{-3}	8.03×10^{-2}	(Cleuvers, 2003)
		Daphnia magna	EC50 - 48 h immobilization	> 100	1.81×10^{-3}	1.81×10^{-2}	(Cleuvers, 2003)
		Oryzias latipes	LC50 - 28 day exposure	35.4	1.81×10^{-3}	5.10×10^{-2}	(Kim et al., 2007)
Metoprolol	Lagoon	*Lemna spp.*	EC50 - 7 day growth inhibition	> 320	3.98×10^{-4}	1.24×10^{-3}	(Cleuvers, 2005)
		Daphnia magna	EC50 - 48 h immobilization	438	3.98×10^{-4}	9.09×10^{-4}	(Cleuvers, 2005)
		Danio rerio	EC50 – 72 h embryo exposure	12.6	3.98×10^{-4}	3.16×10^{-2}	(van den Brandhof and Montforts, 2010)
Naproxen	Lagoon	*Lemna minor*	EC50 - 7 day growth inhibition	24.2	1.08×10^{-3}	4.44×10^{-2}	(Cleuvers, 2005)
		Daphnia magna	EC50 - 48 h immobilization	174	1.08×10^{-3}	6.18×10^{-3}	(Cleuvers, 2005)
		Danio rerio	LC50 – 96 h embryo exposure	115.2	1.08×10^{-3}	9.33×10^{-3}	(Li et al., 2016)
Sulfamethoxazole	Lagoon	*Pseudokirchneriella subcapitata*	EC50 - 72 h growth inhibition	0.52	1.30×10^{-3}	2.51	(Isidori et al., 2005)
		Daphnia magna	EC50 - 48 h immobilization	25.2	1.30×10^{-3}	5.17×10^{-2}	(Isidori et al., 2005)
		Oryzias latipes	LC50 - 48 h exposure	562.5	1.30×10^{-3}	2.32×10^{-3}	(Kim et al., 2007)
	Wetland	*Pseudokirchneriella subcapitata*	EC50 - 72 h growth inhibition	0.52	5.39×10^{-4}	1.04	(Isidori et al., 2005)
		Daphnia magna	EC50 - 48 h immobilization	25.2	5.39×10^{-4}	2.14×10^{-2}	(Isidori et al., 2005)
		Oryzias latipes	LC50 - 48 h exposure	562.5	5.39×10^{-4}	9.58×10^{-4}	(Kim et al., 2007)
	Outflow	*Pseudokirchneriella subcapitata*	EC50 - 72 h growth inhibition	0.52	2.51×10^{-4}	4.83×10^{-1}	(Isidori et al., 2005)
		Daphnia magna	EC50 - 48 h immobilization	25.2	2.51×10^{-4}	9.96×10^{-3}	(Isidori et al., 2005)
		Oryzias latipes	LC50 - 48 h exposure	562.5	2.51×10^{-4}	4.46×10^{-4}	(Kim et al., 2007)
Sulfapyridine	Lagoon	*Scenedesmus vacuolatus*	EC50 - 24 h growth inhibition	5.28	1.26×10^{-4}	2.39×10^{-2}	(Bialk-Bielinska et al., 2011)
		Lemna minor	EC50 - 72 h growth inhibition	0.46	1.26×10^{-4}	2.74×10^{-1}	(Bialk-Bielinska et al., 2011)
Trimethoprim	Lagoon	*Selenastrum capricornutum*	EC50 - 72 h growth inhibition	80.3	6.09×10^{-4}	7.58×10^{-3}	(Eguchi et al., 2004)
		Daphnia magna	EC50 - 48 h immobilization	120.7	6.09×10^{-4}	5.05×10^{-3}	(Kim et al., 2007)
		Oryzias latipes	LC50 - 48 h exposure	> 100	6.09×10^{-4}	6.09×10^{-3}	(Kim et al., 2007)

Table A10: Mean concentrations (ng/L) of detected PFASs in Cambridge Bay, NU. All other PFASs were below limits of detection. Standard deviations (n=2) are given in parenthesis.

Site	Compound						
	Time frame (Discharge)	PFBS	PFNA	PFDA	PFOA	PFOS	Sum PFAS
Lagoon	Before	63.6 (49.6)	5.12 (2.12)	1.72 (0.62)	41.6 (21.2)	14.6 (7.4)	127 (54.5)
	During	76.2 (41.3)	11.7 (3.76)	4.67 (2.16)	85.2 (29.5)	70.6 (36.3)	248 (62.6)
	After	40.6 (11.5)	ND	ND	9.92 (3.79)	4.20 (0.08)	54.7 (12.1)
Wetland	Before	14.7 (2.1)	2.33 (0.01)	0.44 (0.33)	38.9 (6.6)	16.4 (5.4)	72.7 (8.8)
	During	85.1 (92.6)	8.36 (5.17)	1.67 (0.84)	80.4 (44.2)	27.0 (24.0)	203 (106)
	After	-	-	-	-	-	-
Outflow	Before	ND	ND	ND	ND	ND	ND
	During	32.9 (16.2)	3.82 (1.00)	0.70 (0.17)	31.5 (9.3)	14.6 (6.4)	83.5 (19.7)
	After	ND	ND	ND	ND	ND	ND