Advanced Wastewater Treatment and a Holistic Approach Recommended to Mitigate the Effects of Endocrine Disrupting Chemicals on the Aquatic Environment - A Case Study: Alberta, Canada

For Decision Makers and for the Public Interest



A project submitted to meet the requirements of the Master of Land and Water Systems (MLWS) program at the University of British Columbia.

Ву

Jenna Szuch Submitted: August 2019

EXECUTIVE SUMMARY

Emerging contaminants are frequently detected in the aquatic environment. The term "emerging contaminants" is used to describe pollutants that are not currently regulated or may be in the process of regulation. Among these emerging contaminants, endocrine disrupting chemicals (EDCs), which are often found in pharmaceuticals and personal care products (PPCPs) are a concern. EDCs disrupt how the endocrine system would respond to normal events, and as a result, can cause adverse effects (physiological or developmental) in wildlife and people. EDCs and PPCPs have been detected in soils, edible tissues of plants, surface water, groundwater, treated wastewater, treated drinking water, and in aquatic life. EDCs are typically found in surface waters, groundwater, wastewater, and drinking water at concentrations of part-per-billion to part-per-trillion. However, EDCs can exert their effects on wildlife at these low concentrations. There are approximately 80,000 known chemicals in the environment, and currently 1000 chemicals have been classified as EDCs (Schug et al., 2016). As well, there are thousands of new chemicals released into the environment every year with limited and sometimes no testing, and a lack of understanding about the future impacts (Schug et al., 2016; Thomas Zoeller et al., 2012).

This paper evaluates evidence regarding the adverse effects EDCs and PPCPs have on aquatic life and people, and highlights the potential risk that exists for humans from exposure to EDCs in the aquatic environment. EDCs are introduced into the environment through a variety of urban, rural and industrial sources. Treated wastewater is a major source of EDCs and PPCPs entering the aquatic environment. Municipal wastewater treatment plants were designed to control a variety of substances, such as nutrients and pathogens, which are (typically) successfully removed. However, this is not the case for a wide range of emerging contaminants, such as EDCs and PPCPs that are present in low concentrations and possess unique characteristics.

Mitigating the effects of wastewater disposal into the environment will continue to be a challenge, especially as the number of emerging contaminants detected in the aquatic environment continues to increase (Holeton, Chambers, & Grace, 2011; Schug et al., 2016). New federal wastewater effluent regulations (WSER; SOR/2012-139) in Canada indicate a minimum of secondary treatment, or an equivalent treatment. Municipalities that do not meet this standard are required to upgrade their treatment facilities. Wastewater facilities will be investing in technologies that will used for decades to come. Yet evidence demonstrates that secondary treatment is only partially able to remove EDCs and PPCPs. Advanced treatment methods provide an opportunity to achieve greater removal efficiencies of emerging contaminants and should be considered. This places Canada in a unique position as it allows municipalities to be proactive about the concerns of today, but also the emerging concerns of the future. Municipalities that choose to implement more advanced treatment options have the opportunity to achieve results far greater than current minimum requirements. In addition, it is likely that in the future, wastewater effluent regulations will become more stringent as research progresses.

This paper also discusses the efficacy of several advanced oxidation processes (AOPs), and the need for a holistic approach to successfully identify the best available technology. There are a variety of advanced wastewater treatments, but if AOPs are being considered the following must be taken into account:

- A combination of AOPs has proven to be more effective, rather than a single AOP when removing EDCs and their by-products.
- Ozonation should not be adopted unless it is combined with an effective method to prevent the formation of toxic by-products (Stalter, Magdeburg, Weil, Knacker, & Oehlmann, 2010).
- Adaptive wastewater management is needed, and advanced wastewater options should be considered to mitigate the effects of EDCs on the aquatic environment and the unknown long-term effects on human health.

The presence of EDCs and PPCPs in the environment is a complex land and water issue, which requires a holistic approach. It is important to recognize that depending on how the issue of EDCs is framed, different conclusions can be reached. It is essential to include the frameworks from a variety of disciplines. This can help eliminate a disciplinary bias, while recognizing the interconnectedness of land and water.

TABLE OF CONTENTS

EXECUTIVE SUMMARY	2
TABLE OF CONTENTS	3
1. INTRODUCTION	
2. PROJECT OBJECTIVES	
3. OUTLINE OF APPROACH 3.1 SCOPE OF PROJECT	
4. OVERVIEW: THE ENDOCRINE SYSTEM AND EDCS	8
5. SOURCES AND PATHWAYS OF EDCS	9
6.THE EFFECTS OF EDCS ON AQUATIC ORGANISMS AND PEOPLE 6.1 EDCs and Aquatic Organisms. 6.2 EDCs and Human Health	10 11
7. DOMESTIC WASTEWATER AND TREATMENT PROCESSES 7.1 WASTEWATER TREATMENT PROCESSES	
8. OVERVIEW: WASTEWATER EFFLUENT AS A SOURCE OF PPCPS AND EDCS IN SURFACE W 8.1 WASTEWATER SLUDGE	15
9. WASTEWATER EFFLUENT REGULATIONS IN CANADA	
10. PINE CREEK WWTP LOCATED IN CALGARY, ALBERTA 10.1 THE BOW RIVER	16 18
11. EFFICACY OF WASTEWATER TREATMENT	22 24
12. DISCUSSION	28
13. CONCLUDING REMARKS	
ACKNOWLEDGEMENTS	32
REFERENCES	32

1. INTRODUCTION

Emerging contaminants have been detected in the aguatic environment around the world. The term "emerging contaminants" is used because the vast majority of these chemicals are unregulated, or are in the process of regulation (Barceló, 2003; Esplugas, Bila, Krause, & Dezotti, 2007). However, many of these contaminants have harmful effects on people, wildlife, and the environment (Esplugas et al., 2007). Among these emerging contaminants, endocrine disrupting chemicals (EDCs) are a major concern. EDCs interact and display characteristics similar to hormones (Kabir, Rahman, & Rahman, 2015; Schug et al., 2016). As a result, EDCs can alter how the endocrine system would normally function, which can cause adverse effects (e.g. developmental or physiological) in wildlife and people (Boxall et al., 2012; Kabir et al., 2015; Roig et al., 2013; Schug et al., 2016; Thomas Zoeller et al., 2012; Zoeller et al., 2014). EDCs have been defined as: "an exogenous chemical, or mixture of chemicals, that can interfere with any aspect of hormone action" (Schug et al., 2016; Thomas Zoeller et al., 2012; Zoeller et al., 2014).

TABLE 1. EXAMPLES OF EDCs

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Contaminant	Description			
BPA	Plastic Component			
DEHP	Plasticizers; Also a			
	component in a variety of			
	consumer products			
DBP	Plasticizers; Also found in			
	carpets, paints, insect			
	repellents, hair spray			
Nonylphenol	Surfactants, Detergents			
Butylated Hydroxyanisole	Food Preservative			
DDT	Pesticide			
Atrazine	Pesticide			
17 β-estradiol	Natural Hormone			
17 α-ethinylestradiol	Synthetic Hormone			
Fluoxetine	Antidepressant			
Mercury	Heavy Metal			
Lead	Heavy Metal			
Musk Ketone	Fragrance			
Fluoxetine	Antidepressant			
Methyl/Ethyl/Propyl/	Preservative in most			
Butylparabens	cosmetics and PCPs*			
Hexabromocyclododecane	Flame Retardant			

*PCPs: personal care products Adapted from: Ebele, Abou-Elwafa Abdallah, & Harrad, 2017; Esplugas, Bila, Krause, & Dezotti, 2007; Fast, 2015; Sosiak & Hebben, 2005

Some examples of commonly used products containing EDCs are human and animal medicines or pharmaceuticals, personal care products (e.g.

fragrances, cosmetics, sunscreen agents), plastics (e.g. Bisphenol A), and pesticides (TABLE 1) (Montes-Grajales, Fennix-Agudelo, & Miranda-Castro, 2017; Raghav, Eden, Mitchell, & Witte, 2013; Roig et al., 2013). EDCs can enter surface waters through a variety of urban, industrial, and rural sources (M. Chen et al., 2006). Kabir e al. states: "It is observed from different studies that endocrine disruptors are present in the air that we breathe, the water that we drink and even in the soil in which our food is cultivated." (Kabir et al., 2015; p. 244). Therefore, endocrine disruption is not only a concern for endocrinologists and toxicologists, but it is also a complex land and water issue involving the public, environmental scientists, ecologists, biologists. academics, and many researchers. To tackle the complex problems that arise from EDCs, it is clear that a multidisciplinary systems approach is needed (Schug et al., 2016).

A major source of EDCs entering surface water is from wastewater effluent due to inefficient removal of pharmaceuticals and personal care products (PPCPs) during the wastewater treatment process (Boxall et al., 2012; M. Chen et al., 2006; Jeffries, Jackson, Ikonomou, & Habibi, 2010; Montes-Grajales et al., 2017; Yang, Yong, Kim, & Tsang, 2017). EDCs can also enter surface waters from agricultural runoff (Ebele, Abou-Elwafa Abdallah, & Harrad, 2017; Schug et al., 2016), runoff from urban grass fields, aquaculture facilities, improper disposal of PPCPs, and emissions from manufacturing sites (Boxall et al., 2012). A single source is not responsible for the introduction of EDCs into surface waters; rather it is a combination of multiple sources (Roig et al., 2013). From a geographical perspective, certain sources and exposure pathways of EDCs may play a more important role than others (Padhye, Yao, Kung'u, & Huang, 2014). However, point sources such as wastewater effluent from wastewater treatment plants (WWTPs) can be directly managed.

If these contaminants persist in surface waters, there is the potential for EDCs to appear in drinking water downstream of commercial or industrial development (M. Chen et al., 2006; Metcalfe et al., 2010; Padhye et al., 2014). As well, biosolids, manure, and pesticides applied to agricultural land can be a source of EDCs, which can create a potential exposure pathway for humans through food consumption (Ebele et al., 2017). Importantly, wildlife and humans are not exposed to one contaminant at one particular point in time; rather they are exposed to a low-dose "cocktail" of many EDCs over an extended period of time (Kabir et al., 2015). In addition, the effects of climate change can impact the levels of contaminants in rivers. For example, if water

is scarce, there could be an increased loading of contaminants into surface waters (e.g. less dilution; higher concentration of contaminants in the water) (Padhye et al., 2014).

Therefore, it is important to understand the origins, sources and exposure pathways of EDCs. Appropriate mitigation strategies are needed to prevent the (often) unintended negative impacts of EDCs on the aquatic environment (Schug et al., 2016). The removal of EDCs from wastewater effluent is an important step to ensure that aquatic organisms and humans are not negatively impacted by EDCs.

WWTPs were not originally designed to remove EDCs, and as a result, the removal efficiencies of EDCs are low (Behera, Kim, Oh, & Park, 2011). In addition, concerns have been raised about the potential toxic by-products from EDCs that are created during the wastewater treatment process and then subsequently released into surface waters (Boxall et al., 2012). Removing EDCs from wastewater effluent "is a paramount sustainability challenge" (Schug et al., 2016; p. 843). In fact, wastewater effluent has been identified as a primary source of PPCPs into the aquatic environment (Focazio et al., 2008; Yang et al., 2017).

1.1 Terminology

EDCs can be classified as those that occur naturally, or those that are synthesized (Kabir et al., 2015). In addition, EDCs can also be classified by how often they occur and remain in the environment (Kabir et al., 2015). It is common for journal articles to list products where EDCs are found (Ebele et al., 2017; Frye et al., 2012; Montes-Grajales et al., 2017; Raghav et al., 2013; WHO/UNEP, 2013). For example, EDCs can be found in active ingredients in human and animal pharmaceuticals (Ebele et al., 2017; Montes-Grajales et al., 2017) (also known as pharmaceutically active compounds (PhACs) (M. Chen et al., 2006)), personal care products, plastics, plasticizers and surfactants, flameretardants, and pesticides (Roig et al., 2013; WHO/UNEP, 2013). Often both the origin and the occurrence of the EDC are used to classify an EDC.

In many journal articles, the term pharmaceuticals and personal care products (PPCPs) are combined. This is likely because WWTPs have been identified as a primary source of PPCPs into aquatic environments from wastewater effluent (Ebele et al.,

2017; Montes- Grajales et al., 2017). Lastly, EDCs may be referred to as emerging substances of concern (ESOC) or micro-contaminants (Canadian Water Network, 2018b; Alberta Water Portal Society, 2018) or contaminants of emerging concern (CEC) or emerging contaminants (CWN, 2018b; Raghav et al., 2013).

This paper will use the terms EDCs and PPCPs, acknowledging that not all PPCPs are endocrine disrupting (FIG. 1). However, many PPCPs have been identified as being endocrine disrupting, and overlap exists between these contaminants.

FIGURE 1.
OVERLAP
BETWEEN
EDCs AND
PPCPs
Adapted from:
Ferrey, 2011



2. PROJECT OBJECTIVES

The objective of this paper is to assess the concerns, sources, and major pathways of EDCs entering surface water, specifically freshwater. In addition, to provide recommendations regarding wastewater treatment processes to mitigate the release of EDCs from wastewater effluent, while not contributing to the formation of toxic byproducts into surface waters.

The following questions will be answered:

- 1. What are the major documented sources of EDCs?
- 2. What evidence exists about EDCs and their adverse effects on aquatic organisms and people?
- 3. What wastewater treatment processes can successfully remove EDCs, while not contributing to the formation of toxic by-products?

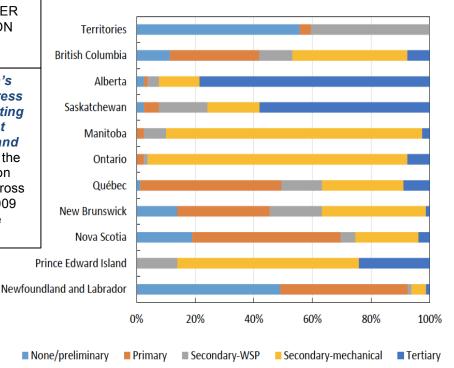
2.1 Research Justification

The Canadian Water Network (CWN) received \$400,000 in financial support from Environment and Climate Change Canada in October 2017 (CWN, 2018a). As a result, the CWN conducted a national of contaminants found review in municipal wastewater, and potential solutions to reduce the negative effects of these contaminants by using appropriate wastewater treatment processes (CWN, 2018a). During the review process, the CWN also conducted a national questionnaire, part of which identified emerging contaminants as a challenge that is not met by current WWTPs. The reasons attributed to this are: (1) lack of regulations regarding emerging contaminants, and (2) WWTPs lacking secondary treatment or lacking necessary upgrades (outdated wastewater facilities) (CWN, 2018c). In addition, this national questionnaire revealed that the participants thought PPCPs and EDCs were the top emerging contaminants, which could be addressed through wastewater treatment (CWN, 2018c). These contaminants were chosen by the survey participants because of the known (and unknown) adverse effects on human health, wildlife, and the environment (CWN, 2018c). EDCs and other emerging contaminants are highly unregulated with the exception of Switzerland (CWN, 2018d). There is sufficient science that indicates endocrine disruptors can pose a risk to the environment, and that appropriate wastewater treatment can decrease this risk (CWN, 2018a).

In 2012 the Wastewater Systems Effluent Regulation (WSER; SOR/2012-139) was introduced in Canada, and as of January 2015 these standards were implemented (CWN, 2018d). These standards are for suspended carbonaceous solids, biochemical oxygen-demanding material, total residual chlorine, and unionized ammonia. Further, the wastewater effluent must not be acutely toxic at the point it is discharged, which is based on a 96-hour test for rainbow trout (CWN, 2018d; Government of Canada, 2019b). If wastewater facilities did not meet the standards set by the WSER in 2012, they were required to apply for transitional authorizations, which allowed them to continue to discharge effluent (CWN, 2018d). The systems that received authorizations were required to upgrade their wastewater facilities by 2020, 2030, or 2040 depending on the quality of effluent, and the characteristics of the receiving water body (CWN, 2018d). WSER standards state that secondary treatment of wastewater, or an equivalent to this is required (CWN, 2018d). There are some exemptions, such as the WSER does not apply to wastewater systems that have an average daily volume of less than 100 cubic meters (CWN, 2018d). As well, it does not apply to wastewater systems north of the 54th parallel in Québec, Newfoundland and Labrador, nor in the Northwest Territories and Nunavut (CWN, 2018d), Bilateral equivalency agreements can be established if provincial or territorial wastewater regulations are equivalent to the WSER.

FIGURE 2. LEVELS OF WASTEWATER TREATMENT BASED ON POPULATION SERVICED BY SEWER SYSTEMS (Canadian Water Network, 2018d)

This figure was obtained from: Canada's Challenges and Opportunities to Address Contaminants in Wastewater - Supporting Document 2: Wastewater Treatment Practice and Regulations in Canada and Other Jurisdictions, and demonstrates the levels of wastewater treatment based on population serviced by sewer systems across Canadian provinces and territories in 2009 (CWN, 2018d). *WSP: secondary waste stabilization pond.



Many wastewater facilities are required to undergo upgrades to secondary treatment to meet the WSER standards (FIG. 2). Municipalities are investing in wastewater systems that will be used for decades (CWN, 2018d). The Canadian provinces are in a unique position as it allows them to be proactive about the concerns of today, but also the emerging concerns of the future. Municipalities that choose to implement more advanced treatment options can achieve results above current minimum requirements. Further, it is likely that in the future, as research progresses, wastewater effluent regulations will become more stringent.

Given this, it is important to understand which wastewater treatment processes can successfully remove EDCs, while not contributing to other negative environmental effects. Practical recommendations for municipalities about advanced wastewater treatments could help streamline this process. These recommendations can then be provided to other municipalities to adopt more advanced wastewater treatments. Effective management of Canada's wastewater is considered to be a critical issue (CWN, 2018a). It is important to recognize that the list of contaminants will increase, and there is a great deal of uncertainty surrounding the long-term effects of EDCs on people, and the environment (CWN, 2018a).

3. OUTLINE OF APPROACH

To answer objective 1 and 2 of this paper, a literature review was conducted between March and August 2019 using the Summon search engine on the University of British Columbia's Library, and additional searches were conducted using Google Scholar. A sample of the key words that were used are: endocrine disrupting chemicals, EDCs, endocrine disruptors, pharmaceuticals, personal care products, PPCPs, emerging contaminants, human health effects, environment, aquatic, surface water, and contaminants of emerging concern. Journal articles would often provide useful references, which were also included. In summary, journal articles, government websites, and books were used to gain a comprehensive understanding of what information and evidence was available about the field of endocrine disruption.

Objective 3 was identified from a list of top 20 questions regarding the concerns of emerging contaminants in the aquatic environment (Boxall et al., 2012). To answer objective 3, a literature review was also conducted between May and August 2019. The Summon search engine on the University of British Columbia's Library was used. It is important to note that not all wastewater treatment types were reviewed. This paper focuses on wastewater treatment types used at the Advancing Canadian Wastewater Assets (ACWA), which is a research plant located at the Pine Creek WWTP in Calgary, Alberta (AB).

Four EDCs were selected for this paper. Specifically, the four EDCs that were chosen were detected in the wastewater effluent in Calgary, AB (Chen et al., 2006). Chen et al. analyzed 14 EDCs and eight were detected in Calgary's wastewater effluent (Chen et

al., 2006). The four EDCs that were present in the highest concentrations were selected. These compounds are established as endocrine disrupting (Sosiak & Hebben, 2005); belong to priority lists provided by the European Union (DIRECTIVE 2008/ 105/EC, 2008); and guidelines exist to protect aquatic life through the Canadian Council of Ministers of the Environment (CCME, 2002). In addition, during 2002 and 2003, Alberta Environment conducted a preliminary study of emerging contaminants found in treated wastewater effluent from WWTPs in Calgary, Edmonton, Red Deer, Lethbridge, and Medicine Hat (Sosiak & Hebben, 2005). The list of target EDCs used in the Alberta Environment study was originally developed by the Institute of Ocean Sciences, Federal Department of Fisheries and Oceans, Sidney, British Columbia (Sosiak & Hebben, 2005). The EDCs used in this study are found on this target list.

As previously mentioned, this paper provides recommendations for decision makers about wastewater treatment processes, which help limit or prevent the release of EDCs into the aquatic environment. These recommendations were obtained through the literature review, and by touring the Pine Creek wastewater treatment facility and the ACWA research plant. It is intended that other metropolitan areas that treat their domestic wastewater with a centralized treatment facility can use the information provided in this white paper. In addition, this paper will provide the public with objective information to allow them to analyze the issues raised about EDCs. Further, the intent is to educate the public about the effects of EDCs, so they can form an opinion whether regulation of EDCs is required.

3.1 Scope of Project

There are many sources that transfer EDCs into the aquatic environment (5. SOURCES AND PATHWAYS OF EDCs), and these contaminants can be found in the soil, biota, groundwater and surface water (Kabir et al., 2015). However, this paper will focus on wastewater effluent as a source of EDCs into surface waters. This is not to say that wastewater effluent is the most important source of EDCs entering the environment, but rather wastewater has been identified as a primary source of micro-contaminants found in the aquatic environment. Focusing on wastewater effluent creates an opportunity to eliminate the introduction of EDCs via this route.

In addition, this paper focuses on surface waters because this is where treated (and untreated) wastewater is discharged. There is an everincreasing dependence on rivers, lakes, and coastal waters for the disposal of domestic wastewater (Holeton et al., 2011). Innovative solutions for wastewater treatment are required.

This paper will use the terms EDCs and PPCPs (1.1 Terminology). Again, acknowledging that not all PPCPs have been identified as endocrine disrupting, and the long-term effects of mixtures of PPCPs and EDCs on people and the aquatic environment are largely unknown. For example, there are considerable research gaps regarding the long-term impacts of human exposure to PPCPs through drinking water (World Health Organization, 2012; Yang et al., 2017).

4. OVERVIEW: THE ENDOCRINE SYSTEM AND EDCs

The endocrine system is responsible for critical biological functions in all vertebrates such as, metabolism, development, behavior, reproduction, and this system functions and communicates using hormones (Kabir et al., 2015; Schug et al., 2016). For example, the endocrine system is: "a system consisting of many interacting tissues that talk to each other and the rest of the body using signals mediated by molecules called hormones." (Kabir et al., 2015; p. 249). EDCs interact and display characteristics similar to hormones (Kabir et al., 2015; Schug et al., 2016), and because of this EDCs can have adverse health effects on animals and people (Kabir et al., 2015; Roig et al., 2013; Schug et al., 2016; Thomas Zoeller et al., 2012). Adverse effects in humans and animals caused by EDCs occur because they can "interfere with the effects of hormones in tissues", resulting in "developmental or physiological effects", or a change in the way the endocrine system would respond to normal events (Zoeller et al., 2014; p. 3).

Under normal conditions hormones circulate and operate in the body at a part-per-billion or part-per-trillion concentrations (Zoeller et al., 2014). EDCs are typically detected in surface waters and groundwater (including drinking water) at concentrations of part-per-billion (µg/L) to part-per-trillion (ng/L) (M. Chen et al., 2006; de Andrade, Oliveira, da Silva, & Vieira,

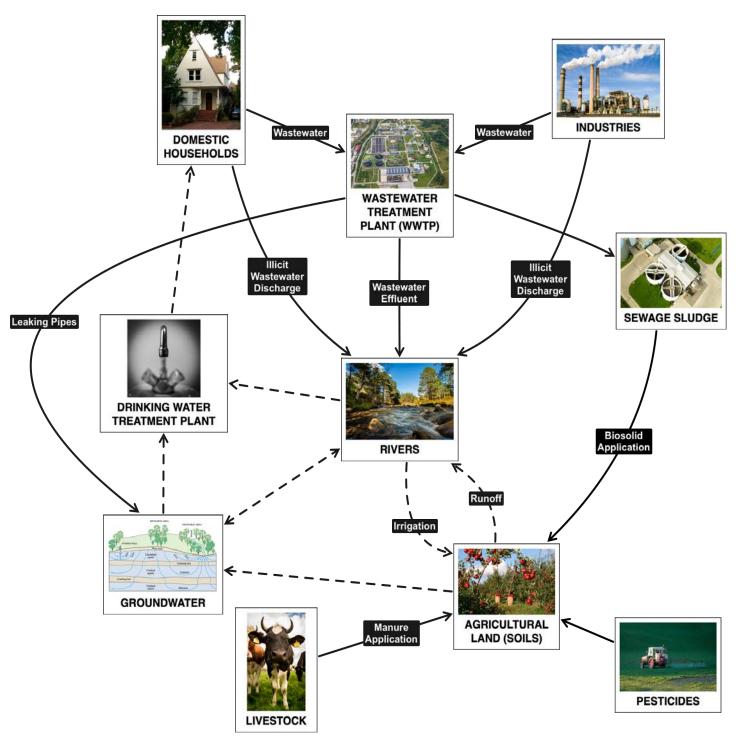
2018; Montes-Grajales et al., 2017; Sosiak & Hebben, 2005; World Health Organization, 2012; Yang et al., 2017). Arguably, this is a concern since EDCs mimic hormones, and hormones naturally operate in low concentrations. Further, pharmaceuticals were specifically designed to induce a response in people and animals at very low doses (Ebele et al., 2017). In addition, EDCs display nonmonotonic dose response (NMDR) curves, which means the effects observed at high doses and low doses differ (Frye et al., 2012; Schug et al., 2016). To provide an example, van Saal FS et al. (1997) established that low doses of dichlorodiphenyltrichloroethane (DES) (a well studied EDC) in mice stimulated prostate growth, whereas the opposite effect was observed with high doses (Schug et al., 2016).

For the last thirty years EDCs have been detected in aquatic environments partly due to the development of new sensitive analytical technologies (M. Chen et al., 2006; Yang et al., 2017). It is likely that these chemicals have been entering the aquatic environment as long as people have been using them (Sosiak & Hebben, 2005). The review article *Minireview: Endocrine Disruptors: Past Lessons and Future Directions* provides a thorough overview of the history, timeline, and evidence (and pushback) that led to the study of endocrine disruption (Schug et al., 2016).

5. SOURCES AND PATHWAYS OF EDCs

FIGURE 3. MAJOR SOURCES AND PATHWAYS OF EDCs ENTERING THE AQUATIC ENVIRONMENT

NOTE: Solid arrows are sources of EDCs released into the environment, whereas, dashed arrows are potential pathways for EDCs once they have entered the environment.



Adapted from: Ebele et al., 2017; Montes-Grajales et al., 2017

There are approximately 80,000 known chemicals in the environment, and currently 1000 chemicals have been classified as EDCs (Schug et al., 2016). As well, there are thousands of new chemicals released into the environment every year with limited and sometimes no testing, and a lack of understanding about the future impacts (Schug et al., 2016; Thomas Zoeller et al., 2012). Often products that contain EDCs provide a benefit to society (e.g. female oral contraceptives, chemotherapy drugs, antidepressants, etc.) and are released into the environment as a consequence of use, and as a result, harm on wildlife and the environment is not intentional (Schug et al., 2016). In fact, Halling-Sørenson et al. (1998) estimated that anywhere from 30% to 90% of antibiotics used by people or animals can be excreted from the body as active substances (M. Chen et al., 2006).

As research in this field continues, the number of chemicals classified as EDCs will likely grow. In multiple articles, EDCs are described as being "ubiquitous" in the aquatic environment (water, soil, and biota) (Ebele et al., 2017; Frye et al., 2012; Lv et al., 2019; Montes-Grajales et al., 2017; Roig et al., 2013; Schug et al., 2016). For example, Kolpin et al. measured the concentrations of 95 pharmaceuticals, hormones, and other organic wastewater micro-

contaminants across 30 states for a total of 139 streams, and these contaminants were detected in 80% of the streams (Kolpin et al., 2002).

There is limited biological evidence establishing that endocrine disruption is the result of a single contaminant, instead evidence supports that the effects are from many sources of EDCs (Lambert & Skelly. 2016). Perhaps, a single EDC alone would not cause harm; however, the cumulative effects of multiple EDCs can cause adverse effects on aquatic organisms and people (M. Chen et al., 2006; Evans, Jackson, Habibi, & Ikonomou, 2012; Yang et al., 2017). Wastewater effluent, runoff from fields, biosolids and manure application, and aquaculture facilities are often recognized as sources of PPCPs into the aquatic environment, but still other exposure pathways exist (FIG. 3) (Boxall et al., 2012). For example, improper disposal of medications into landfills, irrigation using wastewater effluent, and emissions from manufacturing sites can all be sources of PPCPs (Boxall et al., 2012). It is important to note: management, regulations and use of PPCPs can differ globally (Boxall et al., 2012). In some regions, a specific exposure pathway may be more important than another, but this may not be true in another region (Boxall et al., 2012).

6.THE EFFECTS OF EDCs ON AQUATIC ORGANISMS AND PEOPLE

6.1 EDCs and Aquatic Organisms

It is well known that the aquatic environment is exposed to EDCs through a variety of rural (e.g. agriculture), urban (e.g. WWTPs), and industrial sources (M. Chen et al., 2006; Sumpter, 2005). A substantial amount of literature demonstrates that EDCs can have detrimental impacts on aquatic life (Ebele et al., 2017; Kabir et al., 2015; Lambert & Skelly, 2016; Roig et al., 2013; Yang et al., 2017). This is partly because aquatic organisms are continuously exposed to EDCs, as their life (or part of it) occurs in the water. Many of the EDCs that are introduced into the aquatic environment are persistent, and not easily removed when using conventional water treatment methods (Ebele et al., 2017). In addition, chemicals that are not persistent (dissipate naturally) are often continually released into the environment due to their universal usage (Boxall et al., 2012), which results in these chemicals being "pseudo-persistent" (Ebele et al., 2017; Yang et al., 2017). For example, although Bisphenol A (BPA) degrades quickly, there are continuous inputs into the aquatic environment, thus, making it

"pseudo-persistent" (Flint, Markle, Thompson, & Wallace, 2012). As well, aquatic life is exposed to a "cocktail" of contaminants in the environment, and the additive or synergistic effects can be harmful (M. Chen et al., 2006; Ebele et al., 2017; Yang et al., 2017).

Kidd et al. (2012) found the following EDCs in wild-life: (1) Triclosan in algae, invertebrates, fish and dolphins; (2) The anticonvulsant carbamazepine, and several antidepressants were found in the tissues of wild fish, and fish caged downstream of wastewater outfalls; and (3) Human contraceptives were found in fish muscle (Kabir et al., 2015). In particular, endocrine disruption in fish is one of the more highly researched areas (Evans et al., 2012; Fernandez, Ikonomou, & Buchanan, 2007; Jeffries, Nelson, Jackson, & Habibi, 2008; Lv et al., 2019; Sumpter, 2005). Yang et al. also indicates that some biologically active chemicals can bioaccumulate in fish (Yang et al., 2017). Studies have also reported other effects; such as Gunnarsson et al. (2009) found

that fish had enlarged livers from long-term exposure to estrogenic pollutants (Yang et al., 2017). Evans et al. studied Longnose dace (Rhinichthys cataractae) in the Oldman River, AB (Evans et al., 2012). In this study, 28 EDCs were analyzed, and it was determined that multiple land uses (e.g. municipal wastewater effluent and livestock production) contributed to altered gene regulation and the

feminization of Longnose dace (Evans et al., 2012). EDCs can have a variety of impacts on fish from gene regulation to morphological development (Sumpter, 2005). In addition, Brooks et al. and Ramirez et al. detected anti-depressants and metabolites in fish tissues in part-per-billion concentrations in effluent dominated streams (Brooks et al., 2005; Ramirez et al., 2009).

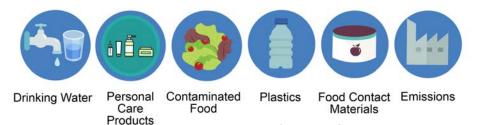
6.2 EDCs and Human Health

There are a variety of human exposure pathways to EDCs (FIG. 4). However, many studies note the lack of understanding about the long-term effects of low dose mixtures of EDCs on human health from the environment (Ebele et al., 2017; Roig et al., 2013; Schug et al., 2016). It has been stated: "An increasingly growing body of research has voiced further concerns that human populations are not immune from the dangers of EDCs." (Roig et al., 2013; p. 2297). There are periods of time where exposure to EDCs is considered critical, which means there are groups of people or populations that are more sensitive to the effects of EDCs (Frye et al., 2012; WHO/UNEP, 2013). Exposure to EDCs during fetal development, infancy, or early childhood can result in permanent effects, but the effects become visible after many years (sometimes decades) have passed (Frye et al., 2012; WHO/UNEP, 2013; Zoeller et al., 2014). As a result, long periods of time exist between exposure to EDCs and the appearance of diseases in people (Frye et al., 2012; WHO/UNEP, 2013; Zoeller et al., 2014). The field of epigenetics has also demonstrated that some EDCs can cause negative health impacts in the offspring of the exposed individual (Schug et al., 2016). Zoeller et al.

states that with respect to endocrinology, "the timing of exposure is one of the most important influences" regarding the health effects of EDCs (Zoeller et al., 2014; p. 5). Nevertheless, exposure to EDCs can still change physiology in adults (Frye et al., 2012; Zoeller et al., 2014), but usually when the EDC exposure ends the effect is reversible (WHO/UNEP, 2013).

Low concentrations of PPCPs have been detected in drinking water in various studies, but the long-term effects on people and domestic animals are largely unknown (M. Chen et al., 2006; Padhye et al., 2014; World Health Organization, 2012; Yang et al., 2017). The World Health Organization generated the report, Pharmaceuticals in Drinking-Water, and concluded: "Although current risk assessments indicate that very low concentrations of pharmaceuticals in drinking-water are very unlikely to pose any risks to human health, there are knowledge gaps in terms of assessing the risks associated with long-term. lowlevel exposures to pharmaceuticals and possible combined effects of chemical mixtures, including pharmaceuticals." (World Health Organization, 2012; p.xii).

FIGURE 4. HUMAN EXPOSURE PATHWAYS TO EDCs



Adapted from: WHO/UNEP, 2013; Zoeller, Gore, et al., 2014

6.3 Concerns: Toxicological Methods and Knowledge Gaps

Concerns have been raised about the toxicological methods that are used for determining the harmful effects of EDCs (Schug et al., 2016; Zoeller, Gore, et al., 2014). It is worth noting that part of this concern

stems from the fact that EDCs have unique characteristics (explained below), and as a result, current use toxicology methods may not be well suited for determining the harmful effects of EDCs.

Certain characteristics of EDCs (e.g. long latency from exposure to development of disease; low-dose effects; the contribution of multiple contaminants in the environment) make it very difficult to test and to determine the negative health effects on people. Further, there are likely many chemicals in the environment that are endocrine disrupting, but have not been tested (Thomas Zoeller et al., 2012). As well, current toxicological methods do not account for mixtures of EDCs (Zoeller et al., 2012). According to Schug et al., "Toxicological research focusing on high doses, such as occupational exposures, is not particularly relevant to typical (low) EDC exposure levels." (Schug et al., 2016; p. 838). Further, Schug et al. argue that there is a need for new methods to examine the additive and synergistic effects of EDCS on the environment and people (Schug et al., 2016).

EDCs will also have a different potency (activity) depending on the endpoint selected (Zoeller et al., 2014). To further explain this statement, Zoeller et al. point to heavy metal lead as an example – lead is more potent at disrupting brain development (endpoint) rather than causing death (endpoint) in people. Therefore, in order to determine the effects of a chemical the appropriate endpoint must be identified (Zoeller et al., 2014). Depending upon the endpoint chosen different information may be obtained.

As mentioned previously, EDCs can display non-monotonic dose response (NMDR) curves, which mean these chemicals cause health effects at high doses and low doses (Frye et al., 2012; Schug et al.,

2016). Further, the effects observed at high doses cannot be used to predict the effects at low doses (Schug et al., 2016). This makes it very difficult to determine a threshold (below this threshold no effects from a chemical will be observed), and it has been argued that perhaps, a threshold does not exist (Zoeller, Bergman, et al., 2014). It may be impossible to indicate a threshold because some people and populations are more sensitive to the effects of EDCs (Zoeller et al., 2014).

To further complicate the issue, exposure to EDCs is usually uncontrolled, and there are other environmental factors involved. This is very different from a controlled, randomized clinical trial (Zoeller et al., 2014). It is difficult to determine causation, and to develop methods to determine causation regarding EDCs (Zoeller et al., 2014). In addition, there is a lack of research on metabolites and by products of EDCs and their effects on the environment (Yang et al., 2017). As well, uncertainty exists about the byproducts of EDCs created during drinking water and wastewater treatment processes (Yang et al., 2017). In order to move forward, the knowledge of the effects of EDCs from the field of endocrinology and academia must be translated into other frameworks. such as toxicology, wastewater management, policy, etc. (Schug et al., 2016). At times it appears that a bridge does not connect the fields of endocrinology and toxicology, nor academia and policy with respect to EDCs. This is quite the juxtaposition, as in order to understand endocrine disruption a multidisciplinary approach must be utilized (Schug et al., 2016).

7. DOMESTIC WASTEWATER AND TREATMENT PROCESSES

The term domestic wastewater is used to describe liquids and waterborne solids from domestic and commercial/businesses, which is discharged into a wastewater treatment plant (WWTP) (e.g. water flushed down the toilet, water drained from sinks, bathtubs, laundry machines, dishwashers, etc.) (Muralikrishna & Manickam, 2017). Note: "down-the-drain" applications or personal care products are also washed down drains/ toilets and will be present in the wastewater (plus pharmaceutically active ingredients and other contaminants). In some cases, storm water is also present in wastewater depending on the structure of the WWTP (CWN, 2018d; Muralikrishna & Manickam, 2017). The term 'wastewater effluent' refers to the treated wastewater that is then released into a body of water (river, lakes, oceans, estuaries, etc.).

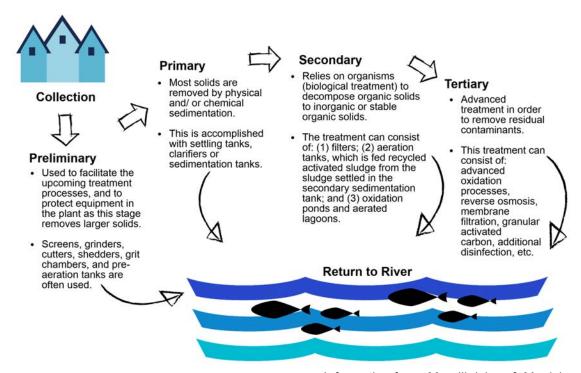
7.1 Wastewater Treatment Processes

Physical, chemical, or biological treatment varies considerably between different WWTPs (Muralikrishna & Manickam, 2017). Typically degrees of treatment are indicated by "primary", "secondary", or "tertiary" (Muralikrishna & Manickam, 2017). Note: the primary stage often includes the preliminary treatment stage. Each level of treatment plays an important role in the treatment of wastewater (FIG. 5). For example, primary treatment is where the majority of solids are removed through physical and/or chemical sedimentation (Muralikrishna & Manickam, 2017). Secondary treatment processes, such as the activated sludge process (ASP) were originally designed to remove organic matter (e.g. biological oxygen demand) and suspended solids (Yang et al., 2017).

Specifically, the ASP uses microorganisms to oxidize and remove oxygen-demanding substances to protect the aquatic environment from oxygen depletion, which could be detrimental to fish and other aquatic life (CWN, 2018b). Tertiary treatment is important in removing many residual micro-contaminants (Yang et al., 2017).

FIGURE 5. GENERAL OVERVIEW OF WASTEWATER TREATMENT PROCESSES

Wastewater effluent can be discharged into the river at any point depending on what level of treatment the wastewater facility is using. In addition, this figure provides an overview of the treatment process, but geographically processes may be different from what is presented here.



Information from: Muralikrishna & Manickam, 2017

Throughout various steps chlorination is often used for the disinfection/ destruction of pathogens (Muralikrishna & Manickam, 2017). Some WWTPs are no longer using chlorination due to the toxic effects on fish, and instead are using ozonation or ultraviolet light (CWN, 2018b; Muralikrishna & Manickam, 2017). However, the formation of toxic by-products from ozonation is also a concern (de Andrade et al., 2018).

8. OVERVIEW: WASTEWATER EFFLUENT AS A SOURCE OF PPCPs and EDCs IN SURFACE WATERS

Historically, WWTPs were not designed to remove EDCs, and as a result, a major source of EDCs in surface waters is from PPCPs found in wastewater effluent (Ebele et al., 2017; Evans et al., 2012; Luo, 2014; Montes-Grajales et al., 2017). For example, a survey of 14 Canadian cities detected several analgesic, anti-inflammatory drugs and the anti-convulsant carbamazepine in concentrations of µg/L in the treated wastewater effluent (Metcalfe, Koenig, et al., 2003). PPCPs are commonly detected in WWTPs because these products are universally

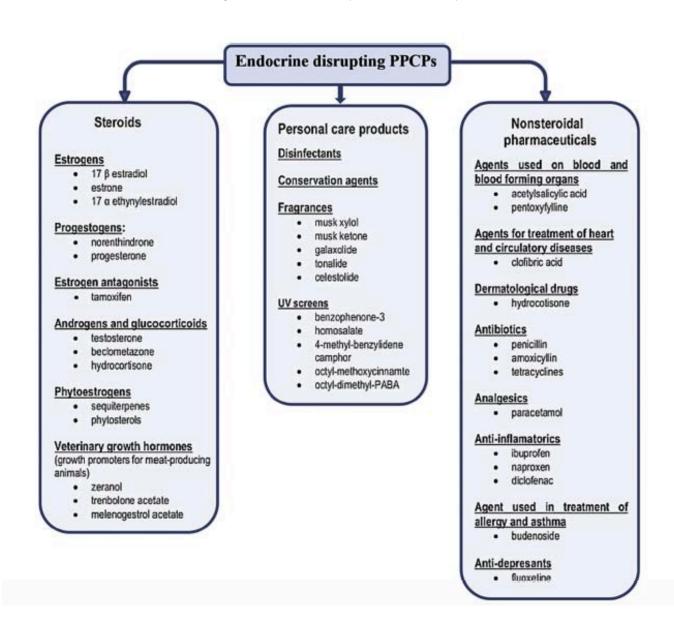
used (FIG. 6), biologically active, and often these products are disposed of improperly (e.g. flushed directly down the toilet) (Yang et al., 2017). WWTPs are inefficient at removing micro-contaminants because wastewater treatment facilities were designed to remove macro-pollutants, which are present in high concentrations and behave similarly (e.g. nutrients and organic matter) (de Andrade et al., 2018). In contrast, PPCPs are present in extremely low concentrations and have unique behaviors (de Andrade et al., 2018). In addition, certain treatments

(e.g. the activated sludge process in secondary treatment) move contaminants from one environmental compartment (the wastewater) to another (wastewater sludge) rather than eliminate the contaminant (discussed below in **8.1 Wastewater Sludge**) (Boxall et al., 2012). This results in the EDCs being released into the terrestrial environment when the sludge is applied to agricultural land (Boxall et al., 2012).

The presence of PPCPs in wastewater effluent is particularly concerning for communities that draw their drinking water from a short distance downstream of a WWTP (Padhye et al., 2014). In addition, drinking water plants do not have the capability to routinely test drinking water for the presence of PPCPs (Padhye et al., 2014). Further, the risks for humans and domestic animals from long-term exposure to concentrations of PPCPs found in drinking water are unknown (Padhye et al., 2014).

FIGURE 6. ENDOCRINE DISRUPTING PPCPs

This figure was obtained from *Pharmaceuticals and personal care products (PPCPs) in the freshwater aquatic environment* (Ebele et al., 2017).



8.1 Wastewater Sludge

Solids and water with the solids that are removed from primary and secondary treatments are classified as wastewater sludge. The sludge (once treated it is commonly referred to as biosolids) is often applied to land as fertilizer for agricultural purposes (Boxall et al., 2012; Muralikrishna & Manickam, 2017; Yang et al., 2017). The application of biosolids has many benefits, such as improving soil health (e.g. structure and fertility) due to the addition of essential nutrients and organic matter (Clarke & Cummins, 2015; Wu, Spongberg, Witter, & Sridhar, 2012).

Potential negative consequences also exist with the application of biosolids onto agricultural land. During the wastewater treatment process some PPCPs are removed from the wastewater, but then subsequently transferred to the sludge, which is then applied to agricultural lands (Yang et al., 2017). Once PPCPs are in the soil they can translocate to crop plants that are grown in the contaminated soil (Wu et al., 2012). In fact, PPCP residues have been found in biosolids and edible tissues of plants (Yang et al., 2017). This is a concern as the PPCPs can then bioaccumulate in the food chain (Wu et al., 2012; Yang et al., 2017).

M. Chen et al. also found that biosolids become enriched with EDCs from the wastewater treatment process (M. Chen et al., 2006). Further, in a field experiment Wu et al. examined the uptake of carbamazepine (anticonvulsant), diphenhydramine (antihistamine), and triclocarban (antimicrobial compound) in five vegetables (peppers, collards, lettuce, radishes, and tomatoes) grown in soils treated with biosolids (Wu et al., 2012). In this study, at the time of harvest these three compounds were detected in all of the plants (ranging from 4.8 to 1287 ng/g) (Wu et al., 2012).

Despite the low levels of PPCPs found in biosolids, it is believed by many risk assessment experts, toxicologists, and epidemiologists that there could be significant and widespread harmful impacts on the environment and humans (Clarke & Cummins, 2015). It is evident that there is potential for PPCPs to be translocated from contaminated soils to plants (Wu et al., 2012). Future studies are required to further understand the impact of PPCPs transferred from biosolids to plants, and subsequently the impacts on the ecosystem (Wu et al., 2012).

8.2 Marine Ecosystems and EDCs

Wastewater contains high concentrations of PPCPs, and wastewater discharged into marine environments is no exception (8. OVERVIEW: WASTE-WATER EFFLUENT AS A SOURCE OF PPCPs and EDCs IN SURFACE WATERS). A trend exists in Canada, which is that inland provinces have higher levels of wastewater treatment compared to coastal provinces, which discharge their wastewater into marine environments (CWN, 2018d). For example, approximately 90% of the population of Ontario and Manitoba has secondary treatment, whereas, less than half of the population of Quebec and the Atlantic provinces has secondary treatment (CWN, 2018d). Arguably, this is a logical trend as it is expected WWTPs that are upstream of drinking water would have higher levels of wastewater treatment.

Victoria, British Columbia does not treat its sewage (lacks primary treatment), but it does screen and remove large solids greater than 6 millimeters before the sewage is discharged into Juan da Fuca Strait through two deep-sea outfall pipes (Krogh, Lyons, & Lowe, 2017). However, due to new federal regulations (9. WASTEWATER EFFLUENT REGULATIONS IN CANADA) Victoria is required to upgrade their treatment facility by 2020. Once operational the WWTP will have three levels of treatment (Krogh et al., 2017). Krogh et al. (2017) collected samples of

water, sediment, and biota adjacent to the Victoria wastewater outfalls between 2009-2016 (Krogh et al., 2017). This study revealed that PPCP concentrations were high within the untreated sewage, and also in the sediment surrounding the outfalls (Krogh et al., 2017). However, 800 meters from the outfall the PPCPs in the sediments were below detection limits (Krogh et al., 2017). This study also found Northern Horse mussels (Modiolus modiolus) collected near one of the two wastewater outfalls contained high concentrations of triclosan (antimicrobial), ciprofloxacin (antibiotic), and sertraline (antidepressant) (Krogh et al., 2017). To provide another example, BPA a commonly studied EDC that has known toxic effects on people and wildlife, has been detected in seawater and marine species (Gore et al., 2014). Arguably, the detection of EDCs and PPCPs in biota is a concern for ecosystem health and resiliency.

It is worth noting that there are opposing views about the effects of dumping untreated sewage into marine environments. For example, Chapman et al. argued that the new sewage treatment facility in Victoria is "wasted", and the Minister's decision to proceed with this decision was based on the possibility of future risks rather than current scientific evidence (Chapman et al., 2008).

9. WASTEWATER EFFLUENT REGULATIONS IN CANADA

Wastewater management is regulated by municipal, provincial and the federal government (CWN, 2018d). As an overview, the federal government implements minimum standards for wastewater effluent; the provincial or territorial governments will issue permits or licenses to construct and operate wastewater facilities under their regulatory framework: and municipalities are responsible for wastewater operations and management (CCME, 2006; CWN, 2018d). Although the federal government has set regulations for wastewater, provinces also have the power to implement more stringent environmental regulations regarding wastewater effluent. Approximately 87% of Canada's population has access to some type of wastewater treatment (CWN, 2018d). Of this number, 3% receives no or preliminary treatment only, 18% has primary treatment, and 79% receives secondary treatment or higher (CWN, 2018d). Specifically, of this 79%, approximately 17% of the population receives tertiary wastewater treatment (CWN, 2018d). Provinces that have a limited water supply and high water demands tend to have the highest level of treatment (CWN, 2018d). For example, the majority of the population of Saskatchewan and Alberta has tertiary treatment (CWN, 2018d). Based on population serviced by sewer systems, Alberta has the highest percentage of tertiary wastewater treatment (CWN, 2018d).

In June 2012 the Wastewater Systems Effluent Regulations (WSER; SOR/2012-139) set national standards for municipal effluent quality (specifically, suspended solids, carbonaceous biochemical

oxygen-demanding material, total residual chlorine, and unionized ammonia), and these standards are meant to be attainable through secondary treatment (CWN, 2018d). These regulations also state that at the point of discharge the wastewater effluent must not be acutely toxic to rainbow trout (Government of Canada, 2019b). Based on federal regulations WWTPs are not required to apply more advanced (tertiary) treatment technologies (CWN, 2018b; Raghav et al., 2013). The WSER is in effect when the average daily volume of the effluent is greater than 100 cubic meters (CWN, 2018d).

The release of deleterious substances in water frequented by fish is prohibited under the Fisheries Act (R.S.C., 1985, c. F-14) (Government of Canada, 2019a). Deleterious substances under the Fisheries Act are defined as: "any substance that, if added to any water, would degrade or alter or form part of a process of degradation or alteration of the quality of that water so that it is rendered or is likely to be rendered deleterious to fish or fish habitat or to the use by man of fish that frequent that water" (Government of Canada, 2019a; p. 15). Fish under the Fisheries Act includes all life stages of fish, shellfish, crustaceans, and marine animals (Government of Canada, 2019a). Despite this, emerging contaminants, such as EDCs from wastewater effluent are highly unregulated in Canada (CWN, 2018d). Further, in Canada no drinking water or freshwater quidelines exist for the majority of pharmaceutically active compounds and EDCs (M. Chen et al., 2006).

9.1 Regulations in Alberta

Under the authority of the Environmental Protection and Enhancement Act (EPEA), Alberta Environmental and Parks (AEP) regulate the construction and operation of municipal wastewater systems (Government of Alberta, 2010). Approximately 80% of the population is serviced by AEP (Government of Alberta, 2019). Municipal Affairs and the federal government regulate the other 20% (Government of Alberta, 2019). In Alberta, as a minimum, secondary treatment is required for wastewater facilities serving populations less than 20,000 and for populations greater than 20,000 tertiary treatment is required (Alberta Government, 2013; CWN, 2018d).

10. PINE CREEK WWTP LOCATED IN CALGARY, ALBERTA

10.1 The Bow River

The City of Calgary is situated in the middle of the Bow River Watershed (BRW) located in Alberta, Canada (MAP 1) (Bow River Basin Council, 2005). The BRW originates in the Rocky Mountains along the east side of the continental divide. The Bow River begins in Bow Lake, then flows southeast to Banff

National Park and once the river exits Banff National park, it flows through the foothills onto the prairies, and at this point the river gradually widens and the gradient decreases (Bow River Basin Council, 2010). The Bow River will eventually reach the Oldman River, which creates the South Saskatchewan River

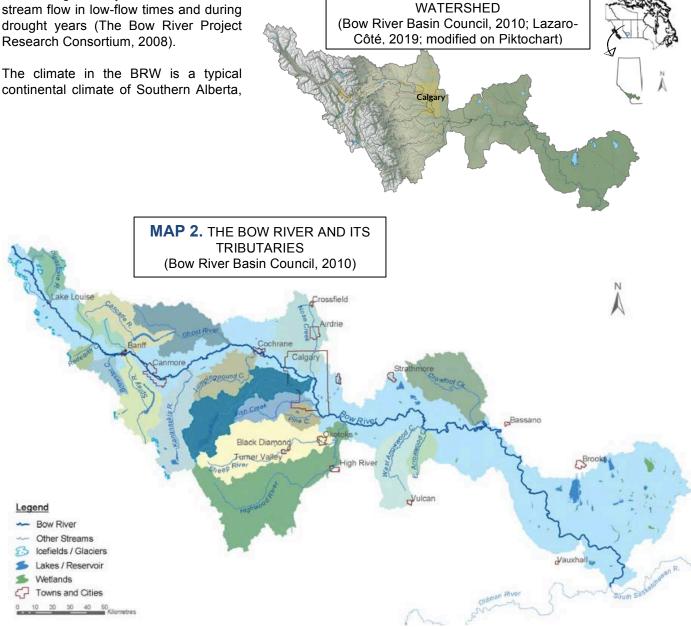
(Bow River Basin Council, 2010). To provide context, the Bow River is a 5th order stream, with 10 tributaries (MAP 2) (Bow River Basin Council, 2005).

The Bow River receives approximately 80% of its total annual flow from snowmelt from the mountains (The Bow River Project Research Consortium, 2008), and glacial melt contributes approximately 2.5% to the total annual flow in late summer/ early fall (Bow River Basin Council, 2010). Although the glacial melt

may seem insignificant it is crucial in maintaining ecosystem health stream flow in low-flow times and during drought years (The Bow River Project Research Consortium, 2008).

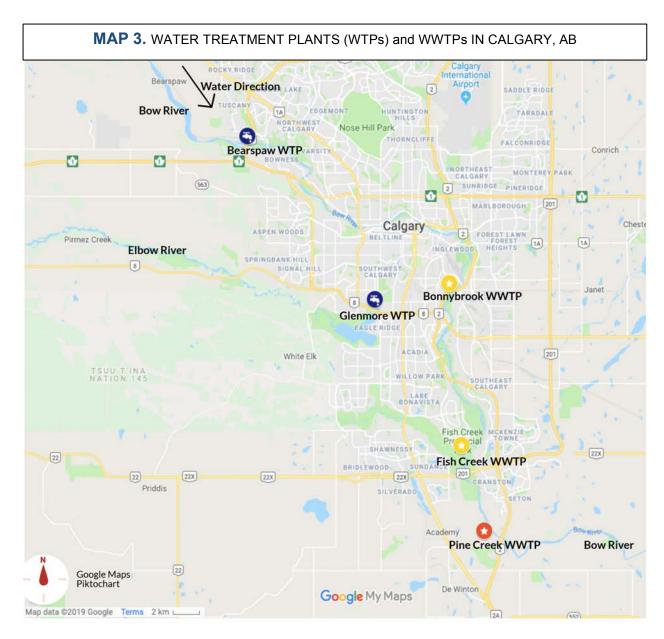
which consists of long, cold winters and short, warm summers (Bow River Basin Council, 2010). However, chinook winds can significantly change winter temperatures. Annual precipitation ranges from 500-700 millimeters in the upper portion of the Bow River with approximately half of this falling as snow (Bow River Basin Council, 2010). In Calgary the annual precipitation is about 412 millimeters, and almost 80% of this is in the form of rain (Bow River Basin Council, 2010).

MAP 1. THE BOW RIVER



10.2 The Pine Creek WWTP

Calgary has two WTPs and three WWTPs. The Bearspaw WTP receives its drinking water from the Bow River, whereas, the Glenmore WTP receives its water from the Elbow River. The three WWTPs (Bonnybrook, Fish Creek, and Pine Creek) discharge wastewater effluent into the Bow River.



The City of Calgary has three tertiary level WWTPs with ultraviolet (UV) disinfection: Bonnybrook, Fish Creek, and Pine Creek (FIG. 7) (City of Calgary, 2018) (MAP 3). This paper uses the Pine Creek WWTP for a case study (MAP 3 the orange star), which officially opened in 2010. The Pine Creek WWTP receives approximately one third of Calgary's wastewater with a relatively small portion from industries (Guertin, personal communication, 29 June 2019). As well, approximately 50% of Fish Creek's wastewater is now diverted to Pine Creek

(Guertin, personal communication, 29 June 2019). The Pine Creek facility's main building (operations, maintenance and administrative) is LEED (Leadership in Energy and Environmental Design) Gold Certified (IMAGE 1) (City of Calgary, 2018). The current capacity of Pine Creek is 100 megaliters per day (ML/d), but it will eventually have a capacity of 700 ML/d (Guertin, personal communication, 29 June 2019).

In addition, the Pine Creek WWTP is unique as it contains a fully integrated research plant called Advancing Canadian Wastewater Assets (ACWA), which is embedded in the municipal infrastructure (ACWA, 2019). The ACWA plant is a partnership between the City of Calgary and the University of Calgary, as part of the Urban Alliance with the main

objective of advancing wastewater treatment technologies in order to address current and emerging environmental, and human health concerns (University of Calgary, 2019b). It has been stated that the Pine Creek facility is one of the most technologically advanced WWTPs in Canada (Stantec, 2019).

IMAGE 1. THE MAIN BUILDING OF PINE CREEK WWTP



FIGURE 7. TERTIARY TREATMENT AT PINE CREEK WWTP: FILTRATION AND UV DISINFECTION A and B: The tertiary treatment building; C: Filtration process; D and E: The cloth-media disk filters that are used for filtration in photo C; and F: UV light disinfection



10.3 ACWA Research Plant

The ACWA plant has the following tertiary treatments: ultrafiltration, reverse osmosis, ultraviolet (UV) or UV dosed with hydrogen peroxide (H₂O₂), and ozonation (O'grady, personal communication, 27 June 2019). The ACWA plant also has an aquatic, microbiology, and an isotope science laboratory (University of Calgary 2019c). Note: The Pine Creek WWTP also contains an analytical laboratory. The ACWA plant has 12 naturalized streams (each 320 meters long), which allows for the investigation of wastewater effluent on the environment in controlled conditions (IMAGE 2) (O'grady, personal communication, 27 June 2019). These naturalized streams allow for the determination of the true effect of wastewater effluent on the ecosystem (O'grady, personal communication, 27 June 2019). For example, disinfection by-products are a concern since they can be created during wastewater treatment processes (Boxall et al., 2012; de Andrade et al., 2018; Lajeunesse, Smyth, Barclay, Sauvé, & Gagnon, 2012). These processes can be studied at ACWA. Further, these streams were designed to have similar hydrological features as natural prairie

streams; specifically, the streams were modeled after Jumping Pound Creek west of Calgary (O'grady, personal communication, 27 June 2019). In addition, the experimental set up of the streams can be changed (e.g. treatment type, flow, etc.). For example, the flow can be altered to mimic high flows that occur during spring melt in Calgary (O'grady, personal communication, 27 June 2019).

There are many research projects underway at ACWA, and they fall under a variety of research themes. These themes are as follows: wastewater research, public health protection, fate and removal of biologically active compounds, linkages between ecology and biologically active compounds, and lastly, the effects of effluent on biota and the environment (ACWA, 2019a). The ACWA research plant has an open access policy, and national and international researchers are encouraged to participate in the ACWA research program (ACWA, 2019b).

The ACWA plant receives secondary effluent from the Pine Creek WWTP, and the effluent flows through an ultrafiltration membrane system located at the ACWA plant (O'grady, personal communication, 27 June 2019; University of Calgary, 2019a). The flow is then diverted to an advanced treatment module (either RO, advanced oxidation or ozonation) (FIG. 8) (O'grady, personal communication, 27 June 2019). Water from the Bow River is stored in a small reservoir (see 'head pond' on **FIG. 8**) that fills the 12 naturalized streams, and approximately 3% of the treated effluent from the ACWA research plant is diverted to the streams (O'grady, personal communication, 27 June 2019).

FIGURE 8. ACWA INTEGRATION INTO PINE CREEK WWTP

Typically, secondary effluent is sent from the Pine Creek WWTP to the ACWA research plant. However, the ACWA streams can also receive final effluent from the Pine Creek WWTP. ACWA effluents from the naturalized streams have two pathways: (1) the effluent is returned to the Pine Creek WWTP or (2) the ACWA effluent is discharged to the Bow River.

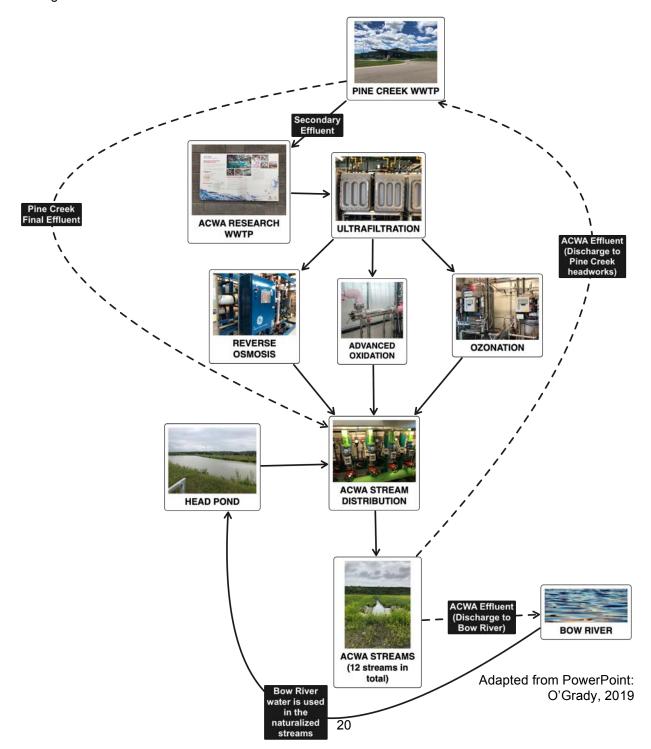


IMAGE 2. THE 12 NATURALIZED ACWA RESEARCH STREAMS (REPLICAS) EMBEDDED IN THE NATURAL ENVIRONMENT



Image from: https://www.ucalgary.ca/acwa/facilities/research-streams
Modified on: Piktochart

11. EFFICACY OF WASTEWATER TREATMENT

Since WWTPs were not designed to remove microcontaminants the removal rate can vary from negligible to 99% (M. Chen et al., 2006). WWTPs equipped with primary or secondary treatment processes only partially remove PPCPs (Yang et al., 2017). Wang et al. (2014) noted poor removal efficiency (<20%) of PPCPs (e.g. carbamazepine, caffeine, DEET, metoprolol, trimethoprim, sulpiride) in primary sedimentation tanks in a WWTP in Shanghai, China (Yang et al., 2017). A reason for low removal of certain PPCPs in primary sedimentation tanks is due to the compound's hydrophilic nature (discussed below) (Yang et al., 2017). Behera et al. found that the secondary WWTP in Ulsan, Korea had low removal efficiencies of mefenamic acid, carbamazepine, and metoprolol (Behera et al., 2011). Lajeunesse et al. also found limitations with primary and secondary treatment to remove antidepressants from wastewater effluent in Canadian WWTPs (Lajeunesse et al., 2012). Additional removal of contaminants is possible with advanced tertiary treatments, such as advanced oxidation processes (Yang et al., 2017). It is evident that the type of treatment used in WWTPs is a clear factor

that determines the removal efficiency of EDCs (Behera et al., 2011).

The chemical, physical, and biological factors also determine the fate of PPCPs and EDCs during wastewater treatment (Miao, Yang, & Metcalfe, 2005). For example, the chemical and physical characteristics of the contaminant and the associated by-products (e.g. solubility, biodegradability, volatility, etc.), pH, and microbial decomposition rates impact removal efficiencies (Yang et al., 2017). Certain contaminants may remain in the wastewater if they are resistant and hydrophilic. Whereas, hydrophobic compounds may bind to the sewage sludge during treatment (Boxall et al., 2012; Miao et al., 2005). However, the adsorption capability of the activated sludge will also influence removal efficiency rates (Yang et al., 2017). Factors such as the sludge age, time, and the design of the equipment will impact adsorption capability (Yang et al., 2017). As well, some pharmaceuticals can cause inhibitory or toxic effects on the activated sludge bacteria, resulting in a

decreased removal efficiency, which was demonstrated in WWTPs with secondary treatment in Hong Kong, China, and Europe (Yang et al., 2017).

The overall effectiveness of removal efficiencies for contaminants in wastewater can also vary depending on the time of day (M. Chen et al., 2006). This is because the composition and volume of the wastewater influent will vary from population activity and the

season (M. Chen et al., 2006; Jeffries et al., 2010). For example, DEET (insect repellent) concentrations are higher in the summer months or in climates that are warmer than in winter months or cold climates (Padhye et al., 2014). Seasonality not only impacts human activity (changes in contaminant composition), but also the temperature of the water and nutrient loads, and other physiochemical conditions (Jeffries et al., 2010).

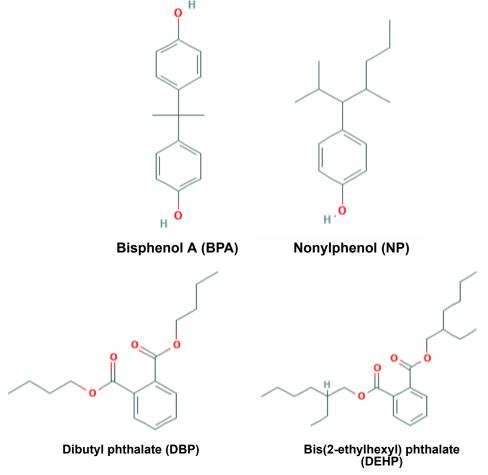
11.1 Target EDCs

This paper focuses on removal efficiencies for the following four EDCs (FIG. 9):

- Bisphenol A (BPA): A potent EDC from polyvinyl chloride (PVC) plastics
- Nonylphenol (NP): A potent EDC from surfactants and detergents; also in pesticides, a lubricating oil additive, curing of epoxy resins
- Dibutyl phthalate (DBP): An EDC from plasticizers; also found in carpets, paints, insect repellents, hair spray
- Bis(2-ethylhexyl) phthalate (DEHP): An EDC from plasticizers; also, commonly used in wide variety of consumer products

- Descriptions about EDCs are from: Sosiak & Hebben, 2005

FIGURE 9. CHEMICAL STRUCTURES OF TARGET EDCs



Images: PubChem2019

BPA has gained high recognition as an EDC, likely because exposure to BPA can occur from leaching plastic containers, including baby bottles. Some companies no longer use BPA, and advertise their products as "BPA-free". As mentioned in 6.2 EDCs and Human Health, the timing of EDC exposure is critical, and infants are susceptible to the effects of EDCs. As a result, under the Canada Consumer Product Safety Act (S.C 2010, c. 21) it is illegal to manufacture, import, advertise, or sell baby bottles containing BPA (Government of Canada, 2010). In addition, many organizations, such as the World Health Organization and the National Toxicology Program have shared concerns about the effects of BPA on fetal brain development and behavior (Gore et al., 2014). The banning of BPA in baby products does help to reduce infant/ toddler exposure to BPA. However, it is still one of the most produced industrial chemicals in the world (e.g. global production in 2003 was 2,214,000 metric tons) (R. ping Huang et al., 2017). Consequently, BPA is frequently detected in the aquatic environment around the world (Bertanza et al., 2011; P. J. Chen et al., 2006; R. ping Huang et al., 2017; Y. Huang, 2010). Butters (2008) noted that in North America it is in the top 31 EDCs detected in drinking water (Y. Huang, 2010). Liu et al. (2017) also notes the adverse effects on fish and wildlife, such as intersex induction, infertility, disruption in mating, and increased mortality (R. ping Huang et al., 2017). Gore et al. notes that in 2014 almost 100 epidemiological studies were published, which state the human health effects of BPA exposure, such as a variety of reproductive disorders, behavior, and energy balance disorders (Gore et al., 2014).

NP can be found be found in surfactants and detergents, and since these typically have "down-thedrain" application, they are commonly introduced into the aquatic environment through the discharge of wastewater effluent (Bertanza et al., 2011; EPA, 2018). NP also has many industrial applications, and is found in several consumer products (EPA, 2018). Environment Canada has stated that several researchers have observed bioaccumulation of NP in aquatic organisms. Specifically, NP has been detected in common blue mussels when exposed to wastewater effluent under laboratory conditions (Environment Canada, 2002). As well, NP exposure is associated with reproductive and developmental effects as demonstrated in rodents (EPA, 2018). According to the Canadian Council of Ministers of the Environment (CCME): "numerous acute and chronic toxicity data for NP are available for freshwater fish" (CCME, 2002; p. 3). NP is also toxic to other aquatic organisms, including aquatic invertebrates and aguatic plants (U.S. Environmental Protection Agency, 2010).

Phthalate Esters have been stated to be one of the most frequently detected organic contaminants in the environment (Gao & Wen, 2016). DEHP and DBP being the most commonly reported (Peijnenburg & Struijs, 2006). The global production of phthalate esters is approximately 4.3 million tons, and astonishingly DEHP accounts for approximately half of this (Peijnenburg & Struijs, 2006). According to Chen et al. (2007) exposure to DEHP can cause a variety of negative health effects in experimental animals such as cancer, liver damage, and reproductive disorders (Y. Huang, 2010). In addition, several studies advise that children exposed to low levels of DEHP can cause an increased risk of allergic diseases, such as asthma and eczema (Braun, Sathyanarayana, & Hauser, 2013). Gestational exposure to DEHP or DBP may prevent the normal development in infants and children (Braun et al., 2013). The potential health risks for children when exposed to phthalate esters has resulted in the banning of DEHP and DBP in children's toys in the United States (Consumer Product Safety Improvement Act - CPSIA) (Braun et al., 2013).

BPA, NP, and DEHP are included in the European Union's priority list for substances and pollutants (DIRECTIVE2008/105/EC, 2008). In addition, the CCME has set guidelines for the phthalate esters for the protection of aquatic life, which are 19 µg/L and 16 µg/L for DBP and DEHP, respectively (CCME, 1999). The CCME has also set a guideline of 1.0 μg/L for NP to protect aquatic life (CCME, 2002). A Canadian federal water quality quideline also exists for BPA of 3.5 µg/L in order to protect aquatic life. and mammalian consumers of aquatic life exposed to BPA (Environment and Climate Change Canada, 2018). It is important to note, guidelines do not mean that these values are "never-to-be-exceeded", as they are not regulations, but rather they provide a benchmark or an idea of where water quality parameters should be, and they are based on toxicological data (Environment and Climate Change Canada, 2018; p. 2).

These four EDCs (**FIG. 9**) have been detected in wastewater effluent in Calgary, AB (M. Chen et al., 2006) and other WWTPs in Alberta ranging from $0.002-5.505~\mu g/L$ (Sosiak & Hebben, 2005), even though they received tertiary treatment in the form of UV disinfection. However, this concern is not unique to Alberta, as globally these four EDCs are frequently detected in wastewater effluent and the aquatic environment (Bertanza et al., 2011; Esplugas et al., 2007; Y. Huang, 2010; Luo, 2014; Yang et al., 2017). Although tertiary treatment achieves higher removal efficiencies of micro-contaminants than primary and

secondary treatment (Luo, 2014; Yang et al., 2017), tertiary treated effluent is still considered to be a

source of micro-contaminants in the aquatic environment (Altmann et al., 2012).

11.2 Advanced Oxidation Processes

Advanced treatment technologies achieve higher removal efficiencies for emerging contaminants when compared to conventional treatment (Luo, 2014; Yang et al., 2017). However, there is no current treatment (including advanced) that is available to ensure the removal of all micro-contaminants due to their diverse and unique properties. Nevertheless, conventional treatment processes have been deemed inadequate at removing many EDCs and PPCPs (Luo, 2014; Yang et al., 2017). In fact, Luo et al. states that overall highly resistant micro-pollutants are poorly removed during biological secondary treatment regardless of the wastewater operating parameters, and tertiary treatment options should be considered (Luo, 2014).

Advanced oxidation processes (AOPs) have been identified as potential successful methods to remove

EDCs from wastewater (Ameta, 2014; Esplugas et al., 2007; Fast, 2015). This is because AOPs oxidize and mineralize many organic contaminants (e.g. EDCs and PPCPs) into carbon dioxide and inorganic ions, which results in the degradation of these unwanted pollutants (Esplugas et al., 2007; Fast, 2015). Note: it is the hydroxyl radicals (HO•) that are formed during the AOP that degrades the emerging contaminants in wastewater (Fast, 2015). This is because the hydroxyl radical has an unpaired electron, which makes it highly reactive with organic contaminants (i.e. the EDCs and PPCPs) (Fast, 2015). Oxidizing agents that are commonly used in AOPs to produce a strong oxidant $(HO\bullet)$ include, but are not limited to: ultraviolet (UV), ozone (O₃) and hydrogen peroxide (H₂O₂) (Fast, 2015).

To provide an overview, AOPs involve three basic steps:

- 1) The formation of a strong oxidant (e. g. HO^{\bullet}) (as mentioned above, often UV, O_3 or H_2O_2 is used);
- 2) The oxidant will react with the emerging contaminant and convert it to a biodegradable compound; and
- 3) Subsequent oxidation of the biodegradable compound (formed in step 2) will mineralize/ decompose ("break down"), in which H₂O, CO₂ and inorganic salts are the end result (Ameta, 2014).

11.3 Efficacy of UV, UV/H₂O₂ and Ozonation

TABLE 2. SUMMARY: REMOVAL EFFICIENCES OF BPA, NP, DBP, AND DEHP

NOTE: It is very important that the removal efficiencies provided below are not interpreted as the only factor involved in determining if a treatment process is effective or suitable. The generation of toxic by-products, synergistic effects, and the impacts on human health and aquatic organisms are also of concern. As well, some of these studies occurred in laboratory conditions, and others at WWTPs, which can contribute to different results. The primary purpose of this table is to demonstrate the wide range of removal efficiencies that can be obtained with different AOPs and EDCs. Details about type of water and methods were included when available.

EDC	Description and Use	Type of Water	Treatment	Removal efficiency and comments	Reference
Bisphenol A (BPA)	A potent EDC from PVC plastics	Milli Q deionized water	UV	Ineffective at removing BPA; low pressure lamp used; pH = 4.3-5.3	(P. J. Chen et al., 2006)
		Deionized water, model natural drinking water and	UV/H ₂ O ₂	Greater removal efficiencies were achieved when using H ₂ O ₂ ; medium and low pressure	(Rosenfeldt & Linden, 2004)

		river water		lamps used; $200 \text{mgH}_2 \text{O}_2 / \text{L}$; pH = 6-8	
		Distilled water	Ozonation	>99% removal achieved and a reduction in estrogenic activity was obtained after 10 minutes	(Alum, Yoon, Westerhoff, & Abbaszadegan, 2004)
				90% removal achieved after 80 min at 8 mgO ₃ /L, or 27 min at 11 mgO ₃ /L; also, the need for chemical and biological approaches was demonstrated	(Bertanza et al., 2011)
		Domestic wastewater	Ozonation	~ 70% removal of BPA with ozonation alone, but ~100% removal when combined with ultrafiltration (UF); lower estrogenic activity also detected with the combination of O ₃ /UF	(Si, Hu, & Huang, 2018)
Nonylphenol (NP)	A potent EDC from surfactants and detergents, formulant found in pesticides, lubricating oil additive, curing of epoxy resins	Twice distilled water	UV/H ₂ O ₂	Addition of H ₂ O ₂ to UV treatment substantially improved removal efficiency of NP; pH dependent; the most optimal conditions were 250 µmol/L at a pH of 11	(Dulov, Dulova, & Trapido, 2013)
		Domestic wastewater	Ozonation	90% removal achieved after 80 min at 8 mgO ₃ /L, or 27 min at 11 mgO ₃ /L; biological approaches are also needed in addition to chemical	(Bertanza et al., 2011)

Continued on next page: Phthalate Esters

Di- <i>n</i> -butyl phthalate (DBP)	An EDC from plasticizers, also found in carpets, paints, insect repellents, hair spray	Deionized still water	UV	>90% can be degraded with UV in 60 minutes with pH > 7 (Lau, Chu, & Graham, 2005); low pressure lamps used (254 nm wavelength)	(Lau et al., 2005)
			Ozonation	After 60 minutes >20% of DBP remained; O ₃ combined with UV improved the degradation rate	(Li, Zhu, Chen, Zhang, & Chen, 2005; Ning, Graham, Zhang, Nakonechny, & Gamal El-Din, 2007)
Bis(2- ethylhexyl) phthalate (DEHP)	An EDC from plasticizers; commonly used in wide variety of consumer products	Milli Q deionized water	UV	43% removal efficiency achieved; low pressure lamps used	(Zarean, Bina, Ebrahimi, H, & Esteki, 2015)
			UV/H ₂ O ₂	73.5% removal with UV alone, and 100% with the addition of H_2O_2 after 180 minutes; optimal conditions 40mg H_2O_2/L , 5 µg DEHP/mL, pH =7	(C. Y. Chen, 2010)
		Milli Q deionized water	Ozonation	50% removal efficiency achieved; degradation rate of 93% possible with UV/O ₃	(Zarean et al., 2015)

Adapted from: Esplugas et al., 2007

A common problem emerges as seen in **TABLE 2**, which is: one treatment process may be successful at removing a particular contaminant, but not others. Ozonation can remove approximately 90% of BPA and NP (Bertanza et al., 2011), but only 50% of DEHP (Zarean et al., 2015). UV was able to remove greater than 90% of DBP (Lau et al., 2005), but only 43% of DEHP (Zarean et al., 2015), and was ineffective at removing BPA (P. J. Chen et al., 2006). However, the removal efficiency of DEHP increased to approximately 90% when ozonation was combined with UV (Zarean et al., 2015). Si et al. found the combination of O_3 and ultrafiltration obtained almost 100% removal for estrone, 17β-estradiol, estriol, 17α-ethynyl estradiol, and BPA from wastewater effluent

(Si et al., 2018). As well, when H_2O_2 was added to the UV treatment, greater removal efficiencies were achieved for BPA (Rosenfeldt & Linden, 2004), NP (Dulov et al., 2013), and DEHP (C. Y. Chen, 2010). Thus, a combination of AOPs may be more appropriate when treating wastewater for microcontaminants (Fast, 2015; Liu et al., 2018).

The formation of toxic by-products during AOPs is also a significant concern (Boxall et al., 2012; de Andrade et al., 2018). Although there has been an increasing concern about the presence of emerging contaminants, there has been much less research regarding the creation of their by-products and their effects on the aquatic environment (Hernández,

Ibáñez, GraciaLor, & Sancho, 2011). Fast states: "A technology that effectively removes emerging contaminants, but also releases other damaging or toxic materials is not a practical technology" (Fast, 2015; p. 42).

Vogna et al. (2004) determined that approximately 100% removal rates were achieved for carbamazepine when using UV and H_2O_2 , but the intermediate products formed during the oxidation process were more toxic than the original compound (Esplugas et al., 2007). Huang et al. (2015) studied ozone oxidation products of ibuprofen (which are commonly detected in wastewater) and discovered that they pose a greater risk for acute toxicity than the original compound (Yang et al., 2017). Therefore, the formation of toxic by-products of the selected/ target contaminant is a concern, in addition to the other contaminants present in the wastewater.

Stalter et al. found adverse effects on fish from ozonated wastewater and stated "ozonation should not be applied without subsequent post treatment appropriate for oxidation by-products removal (e.g. sand filtration)" (Stalter, Magdeburg, Weil, Knacker, & Oehlmann, 2010; p. 439). Specifically, this study (Stalter et al., 2009) occurred in a WWTP in Switzerland and conducted an ecotoxicological assessment with the 'fish early life stage toxicity test' (FELST), which exposed fish to conventional treated wastewater. wastewater post ozonation, wastewater post ozonation with subsequent sand filtration. The fish exposed to ozonated wastewater suffered severe brain damage and had a significant decrease in body weight and length (Stalter et al., 2009). The fish exposed to conventional treated wastewater, or to the ozonated wastewater that was subject to sand filtration did not (Stalter et al., 2010). The adverse effects from ozonation were likely from the creation of toxic by-products (Stalter et al., 2010). Importantly, sand filtration was able to prevent the adverse effects on fish from ozonation (Stalter et al., 2010).

Treatment types have different strengths and weaknesses (Fast, 2015), and they will perform differently depending on the characteristics of the contaminant and the study conditions as demonstrated (**TABLE 2**). Treatments that have been used longer and that provide a proven track record in producing an effluent that meets current water quality standards should be considered, as they are more reliable (Fast, 2015). Consequently, Fast ranked the following combination of AOPs as reliable systems: H_2O_2/O_3 , O_3/UV and UV/H_2O_2 (Fast, 2015). Esplugas et al. argues that ozonation is one of the most

studied processes, which increases its chance of success (Esplugas et al., 2007). The assumption that ozonation is more understood in comparison to recently developed treatments is likely due to the scrutiny the process has undergone. For example, an Austrian municipal WWTP installed a pilot scale ozonation plant for the additional treatment of wastewater and found that the plant had high removal efficiencies for the majority of contaminants (Schaar, Clara, Gans, & Kreuzinger, 2010). The importance of combining ozonation with post treatment (e.g. sand filtration) to remove toxic by-products was also discovered (Stalter et al., 2010). Similarly, Synder et al. (2003) found that the effluent from AOPs should receive subsequent treatment in order to remove by-products (Fast, 2015).

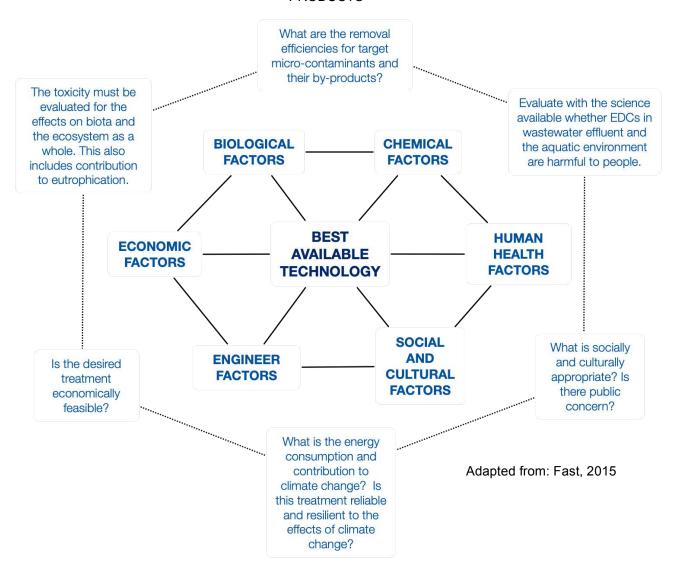
It is crucial that other factors are also considered when analyzing the efficacy of advanced wastewater treatment processes (FIG. 10). As well, the "best available technology" will likely be a combination of treatment methods. Numerous articles discuss the removal efficiencies of only the original parent compound. Future research should also consider the formation of by-products and metabolites formed during the treatment process. This means, the creation of by-products should be identified, quantified, and evaluated for their biological activity (Lajeunesse et al., 2012). Studying contaminants in isolation has many purposes (e.g. gain a thorough understanding of the chemical and physical characteristics of a contaminant or group of contaminants, and the treatment process, etc.). However, micro-contaminants do not exist in isolation, but instead wastewater is a "cocktail" of a wide range of contaminants. It is of utmost importance that subsequent studies are conducted to determine whether these treatments truly reduce toxicity for aquatic organism (Lazaro-Côté, Personal Communication, 10 July 2019). Chemical analysis alone is not sufficient to determine the synergistic effects of mixtures of contaminants (Bertanza et al., 2011).

Fast conducted a holistic analysis of some AOPs $(H_2O_2/O_3,\ O_3/UV,\ H_2O_2/UV,\ titanium\ dioxide\ photocatalysis,\ and\ Fenton's\ reaction)\ in\ which\ these AOPs\ were\ assumed\ to\ be\ equally\ capable\ of\ producing\ a\ high\ degradation\ rate\ of\ microcontaminants\ (Fast,\ 2015).\ Importantly,\ the\ analysis\ included\ factors,\ such\ as\ impacts\ on\ human\ health,\ economic\ feasibility,\ energy\ consumption\ and\ contribution\ to\ climate\ change.\ It\ was\ these\ additional\ factors\ that\ determined\ which\ treatment\ was\ the\ most\ suitable\ (Fast,\ 2015).\ Further,\ often\ public\ concern\ drives\ whether\ advanced\ treatment\ is\ implemented\ or\ not\ (Luo,\ 2014).\ Therefore,\ it\ is\ important\ to\ include\ parameters\ such\ as\ public\ and\ contribution\ and\ conclude\ parameters\ such\ as\ public\ concern\ drives\ parameters\ parameter\ param$

acceptance, ease of use and economic feasibility, as demonstrated by Fast (2015). Perhaps, a similar approach is needed where a variety of factors are considered in order to truly analyze which treatment methods successfully remove EDCs from wastewater, while not contributing to the formation of toxic

by-products (**FIG. 10**). Unfortunately, a lack of regulations may hinder the application of these processes (Barceló, 2003), as well as the high operation costs incurred with these advanced treatments (Luo, 2014).

FIGURE 10. A HOLISTIC APPROACH TO DETERMINE WHICH WASTEWATER TREATMENT METHOD IS ABLE TO SUCCESSFULLY REMOVE EDCs, WHILE NOT CONTRIBUTING TO TOXIC BY-PRODUCTS



12. DISCUSSION

The objective of this paper is to assess the concerns, sources and major pathways of EDCs into surface water. This paper identified and evaluated: (1) major documented sources of EDCs (2) evidence regarding EDCs and their adverse effects on people and the aquatic environment, and (3) wastewater treatment

processes capable of removing EDCs, while not contributing to the formation of toxic by-products.

EDCs are introduced into the environment through a variety of urban, rural, and industrial sources. For example, wastewater effluent, runoff from urban

centers (storm water), agricultural runoff (biosolids, manure, and pesticide application), aquaculture, emissions from manufacturing sites, and improper disposal of PPCPs (e.g. littering, or incorrect disposal of pharmaceuticals). A major documented source of EDCs entering the aquatic environment is from wastewater effluent, due to the inefficient removal of micro-contaminants during the wastewater treatment process. EDCs are frequently detected in treated wastewater, surface waters, groundwater and drinking water at concentrations of part-per-billion to part-per-trillion (M. Chen et al., 2006; de Andrade et al., 2018; Montes-Grajales et al., 2017; Sosiak & Hebben, 2005; World Health Organization, 2012; Yang et al., 2017).

This literature review indicates that the risk of endocrine disruption in humans and wildlife from the environment is from multiple contaminants and not from a single contaminant. At this point, the longterm effects of low concentrations of EDCs and PPCPs in drinking water on people and domestic animals are largely unknown (M. Chen et al., 2006; Padhye et al., 2014; World Health Organization, 2012; Yang et al., 2017). In addition, the effects of low levels of PPCPs detected in biosolids applied to agricultural land are also unknown (it has been shown that PPCPs can be transferred from contaminated soils to plants). Many risk assessment experts, toxicologists, and epidemiologists express their concerns about EDCs in biosolids and indicate that there could be significant and widespread harmful impacts on the environment and human health (Clarke & Cummins, 2015).

A substantial amount of literature indicates that EDCs have detrimental impacts on aquatic life (Ebele et al., 2017; Kabir et al., 2015; Lambert & Skelly, 2016; Roig et al., 2013; Yang et al., 2017). The following has been observed in fish: (a) EDCs and PPCPs have been detected in fish tissues (Brooks et al., 2005; EPA, 2018; Gore et al., 2014; Kabir et al., 2005; Kidd et al., 2012; Ramirez et al., 2009; Yang et al., 2017); (b) Enlarged livers (Gunnarsson et al. 2009); (c) Feminization of fish (Evans et al., 2012); (d) Abnormal morphological and developmental effects (Stalter et al., 2010; Sumpter, 2005), such as a decrease in size and length of body (Stalter et al., 2010); (e) Brain damage (Stalter et al., 2010); and (f) Altered gene regulation (Sumpter, 2005). Perhaps, a single EDC alone would not cause harm; however, the cumulative effect of multiple EDCs in the aquatic environment has proven to have adverse effects on aquatic organisms.

The presence of EDCs in wastewater effluent is highly unregulated in Canada. Recently new federal regulations were implemented in Canada stating that a minimum of secondary treatment, or an equivalent treatment is required (WSER; SOR/2012-139). As a result, municipalities are investing in wastewater systems that will be used for decades. Researchers have found that WWTPs equipped with secondary treatment are only partially able to remove microcontaminants. Advanced treatment is necessary in order to further enhance the removal of these contaminants (Altmann et al., 2012). Thus, Canada is in a unique position where municipalities can choose to be proactive about emerging contaminants and exceed minimum requirements. It is also likely that in the future as research progresses, wastewater effluent regulations will become more stringent.

There are challenges with the implementation of AOPs, such as high operational costs, and the formation of toxic by-products (Luo, Importantly, the selection of an AOP in isolation is not the most effective choice to eliminate microcontaminants or to avoid the formation of toxic byproducts. A combination of AOPs serves as a more appropriate choice for the removal of EDCs (Li et al., 2005; Liu et al., 2018). The combination of UV/H₂O₂ has higher removal efficiencies than UV alone. Similarly, ozonation yields higher removal efficiencies when combined with other AOPs. For ozonation to be a successful candidate it must be combined with a post treatment to avoid the toxic effects of byproducts on the aquatic environment (Stalter et al., 2010).

There are likely other successful wastewater treatment methods, however this paper focuses on AOPs. Nevertheless, the literature demonstrates that a holistic approach is needed to successfully determine which advanced wastewater treatment can successfully remove EDCs, while not contributing to other negative environmental effects (FIG. 10). The best available technology for wastewater treatment will continue to develop as new scientific findings emerge. Perhaps it is not surprising that a holistic approach is needed, as it is the contribution of a wide range of people, such as endocrinologists, toxicologists, the public, environmental scientists, chemists, engineers, various specialists, government bodies, non-profit organizations, academics, and many researchers that has made this field of study as informed as it is now. As a result, to determine the "best" advanced wastewater treatment it should also encompass multiple viewpoints (FIG. 12).

FIGURE 12. THE BEST AVAILABLE TECHNOLOGY/ TECHNOLOGIES WILL CONSIST OF MULTIPLE VIEWPOINTS



The City of Calgary is an example of a municipality that is leading edge, and it exceeds regulatory requirements in Canada. Importantly, UV disinfection obtains higher removal efficiencies for EDCs than secondary treatment. However, UV disinfection still cannot remove all EDCs present in Calgary's wastewater. This is indicated by the presence of BPA, NP, DEHP and DBP in Calgary's wastewater effluent that received UV disinfection treatment (Chen et al., 2006). Facilities such as the ACWA research plant located at the Pine Creek WWTP in Calgary, Alberta offer a unique opportunity to help improve wastewater technologies and identify which wastewater treatment methods may be more appropriate in the future. The naturalized streams at the ACWA research plant allow for the determination of the true effect of various types of wastewater effluent on an ecosystem.

It is important to recognize that scientific research is dynamic, and over time the best available technology will change as science advances. The wellbeing of humankind and the environment should be central components in this scientific endeavor. The presence of EDCs and PPCPs in the environment is a complex land and water issue and as a result, there are still knowledge gaps regarding the long-term effects of EDCs in the environment and on human health. Scientific research will continue to fill these knowledge gaps (Martuzzi & Tickner, 2004). While this continues, decisions can be made based on the best available evidence, while accepting that some uncertainties exist (Martuzzi & Tickner, 2004). This paper provides evidence that secondary treatment only partially removes EDCs and PPCPs from wastewater effluent. As a result, the PPCPs and EDCs that are not removed are then subsequently released into the aquatic environment. Adverse effects on aquatic life are well documented, and there is a growing concern about the long-term effects of low dose mixtures of EDCs on human health and the environment. A combination of AOPs, or an AOP with other subsequent treatment provides an opportunity to mitigate the effects of EDCs and their by-products on humans, wildlife, and the environment.

13. CONCLUDING REMARKS

Adaptive wastewater management is required to successfully tackle the complex problem regarding the effects of EDCs being released into the aquatic environment. Continuous improvement must be made as new scientific information becomes available. A feedback loop should exist, which measures, analyzes, and incorporates scientific changes and advancements (Canadian Water Network, 2018). When possible, environmental monitoring

of EDCs and PPCPs should occur to determine if the wastewater treatment is achieving the desired effect, and to prevent unintended consequences.

It is important for decision makers to adapt as science progresses, and not to wait until the harm is so great that it has caused detrimental effects to people and the environment (Martuzzi & Tickner, 2004). The wellbeing of people and the environment should be key factors during the decision-making process. As said by Kriebel et al. "scientific studies can tell us something about the costs, risks, and benefits of a proposed action, but there will always be value judgments that require political decisions" (Kriebel et al., 2001; p. 875). Although data gaps remain, significant data exists regarding the effects of EDCs on aquatic life. With this in mind, policy decisions should be made that errs on the side of caution when it involves human health and the environment (Kriebel et al., 2001).

13.1 Recommendations

- Advanced wastewater options should be considered to mitigate the effects of EDCs on the aquatic environment, and the unknown long-term effects to human health.
- Ozonation should not be adopted unless it is combined with additional processes to prevent the release of toxic by-products (Stalter et al., 2010).
- A combination of AOPs has proven to be more effective, rather than a single AOP when removing EDCs and their by-products.
- Removal efficiencies of parent compounds (the target EDCs) provide valuable information. However, without considering the formation of byproducts and biological activity (the effects on biota) the evidence indicates that unintended negative consequences are likely to occur, such as toxic effects on aquatic life.
- Monitoring a wide range of EDCs is very costly and time consuming (Padhye et al., 2014). Studies have used specific substances common in

- municipal wastewater as indicators in tracking wastewater contamination in surface waters (Padhye et al., 2014). For example, Burse et al. (2008) used cotinine and caffeine as indicators in order to track wastewater contamination (Padhye et al., 2014). Perhaps, certain EDCs or PPCPs could potentially act as "indicators" for a rapid screening for the presence of EDCs in drinking water facilities (Padhye et al., 2014).
- Education, raising consumer awareness, and source control are important components to reduce PPCPs in wastewater (World Health Organization, 2012). For example, ensuring the proper disposal of PPCPs, or sharing knowledge and information with peers about EDCs and PPCPs in the aquatic environment.
- It is important to recognize that how the issue of EDCs is framed, different conclusions can be reached. It is challenging, but important to include the frameworks from a variety of disciplines. This can help eliminate a disciplinary bias, while recognizing the interconnectedness of land and water.

NOTE: This paper addresses EDCs and PPCPs entering the aquatic environment from wastewater effluent, and the associated environmental and human health concerns. This does not negate other important water quality and quantity concerns. Rather, this information can be viewed as a component of a much larger system or as a "piece of the puzzle", which can be used to help build a sustainable future.

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